

Electronic Energy Transfer in CdSe Quantum Dot Solids

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(Received 10 July 1995)

We demonstrate electronic energy transfer between close packed quantum dots using cw and time resolved photoluminescence. Optically clear and thin, close packed quantum dot solids were prepared from mixtures of small and large CdSe quantum dots (38.5 and 62 Å, $\sigma < 4.5\%$). Quenching of the luminescence (lifetime) of the small dots accompanied by enhancement of the luminescence (lifetime) of the large dots is consistent with long-range resonance transfer of electronic excitations from the more electronically confined states of the small dots to the higher excited states of the large dots.

PACS numbers: 73.20.Dx, 78.55.Et

Close packed quantum dot (QD) solids present opportunities to explore both the collective physical phenomena that develop as proximal QDs interact and the electronic and optical properties of QD solid state materials with potential device applications. Advances in the fabrication of well-defined QD structures by, for example, lithographic [1], molecular beam epitaxy [2], and wet chemical [3] methods now allow the fundamental interactions in these structures to be uncovered. The QD is the 0D analog of the 2D quantum well (QW), having discrete electronic transitions that shift to higher energy with decreasing dot diameter [4]. Interwell couplings in QW heterostructures continue to be studied for both their fundamental physics and their importance in devices [5]. QD solids provide a convenient medium for potential novel optical and electronic devices that exploit both the unique properties of the individual dots and the cooperative effects in the solid. For example, layers of densely packed CdSe QDs incorporated between polymeric electron and hole transport materials electroluminescence with colors characteristic of the QDs [6]. Semiconductor QDs have generated interest as nonlinear optical materials because their oscillator strengths are concentrated in discrete highly polarizable excitonic states [7]. Optical nonlinearity should be further enhanced in a QD array as coupling of electronic excitations between dots expands the exciton coherence length, enabling it to collect oscillator strength from dots within that larger volume [8].

In this Letter we present observations and analysis of electronic energy transfer in QD solids, arising from dipole-dipole interdot interactions. We spectroscopically probe electronic energy transfer between proximal dots in a close packed solid designed from a mixture of two sizes of CdSe QDs. cw and time resolved photoluminescence (PL) and photoluminescence excitation (PLE) give us independent measures of energy transfer in the mixed QD solid.

Samples of CdSe QDs 38.5 (small) and 62 Å (large) in diameter ($\sigma < 4.5\%$) were synthesized according to the method of Murray, Norris, and Bawendi [9]. This synthetic route enabled us to control the dot size and

optical properties and to separate the spectral features of the dots in the mixed system. The individual CdSe QDs have been extensively characterized both structurally and optically [9,10]. Organic capping groups coordinating the QD surface sterically stabilize the dots in solution. Optically clear (nonscattering), thin solid films were deposited from solutions of small and large dots [11]. All measurements were collected for films $\sim 0.1\text{--}0.4\ \mu\text{m}$ thick to minimize reabsorption of emitted photons. The outer diameter of the large dots in the mixed film was < 0.05 at the emission peak of the small dots, making direct reabsorption of the luminescence from the small dots by the large dots negligible.

Small-angle x-ray scattering (SAXS) was used to characterize the average local structure of the QD solids [11]. We collect SAXS patterns [Figs. 1(a) and 1(b)] for dots dispersed in poly(vinyl butyral) (PVB) to obtain form factors for the individual dots [12]. We fit each SAXS pattern (solid lines) to determine dot size and sample size distribution using the form factor for a sphere and allowing

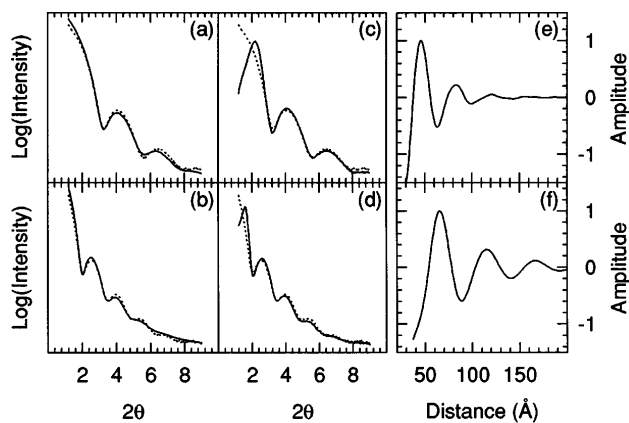


FIG. 1. SAXS patterns for CdSe QDs dispersed in PVB (dotted lines) fit by form factors for spheres (solid lines) (a) 38.5 Å and (b) 62 Å in diameter each with $\sigma \sim 4.5\%$. Scattered intensities for (c) 38.5 Å and (d) 62 Å dots densely packed in films (solid lines) vs that for dots dispersed in PVB (dotted lines). Radial distribution functions generated for the (e) 38.5 Å and (f) 62 Å CdSe QD solids.

for a Gaussian distribution in diameter. The ringing of the scattered intensity, previously unresolved, demonstrates the monodispersity of our samples. Our fits yield dot diameters of 38.5 [Fig. 1(a)] and 62 Å [Fig. 1(b)] with standard deviations of 4.5%. Figures 1(c) and 1(d) compare scattered intensities for the 38.5 and 62 Å dots dispersed in PVB (dotted lines) and in densely packed films (solid lines). The diffracted intensities from the QD solids contain interferences arising from local ordering of close packed dots in the glassy solids [12]. We use the experimental form factors for the dots in PVB to extract radial distribution functions for the QD solids [Figs. 1(e) and 1(f)] [12]. The first peak defines the nearest neighbor distance and the higher oscillations are replicas of this distance. The QDs are close packed with an ~ 11 Å spacing from the organic cap. The monodispersity of our QD samples makes it possible to establish a well-defined structural model for the QD solids.

Figures 2(a) and 2(b) show room temperature (RT) and 10 K optical absorption and emission spectra for films prepared from the small and large QDs. The discrete absorption resonances and sharp band-edge emission are characteristic of the size dependent, quantized electronic excitations for these QDs. We study electronic energy transfer between close packed QDs in a mixed system consisting of 18% large dots and 82% small dots.

Optical studies of QDs dispersed in solution probe the photophysics of individual dots. The spectral response of the QD solid is a convolution of the individual properties of the dots and the collective properties of the solid [1]. RT and 10 K PL spectra for the mixed system of dots in solution [Figs. 2(c) and 2(d)] and in the solid [Figs. 2(e) and 2(f)] are shown by solid lines. PL measurements

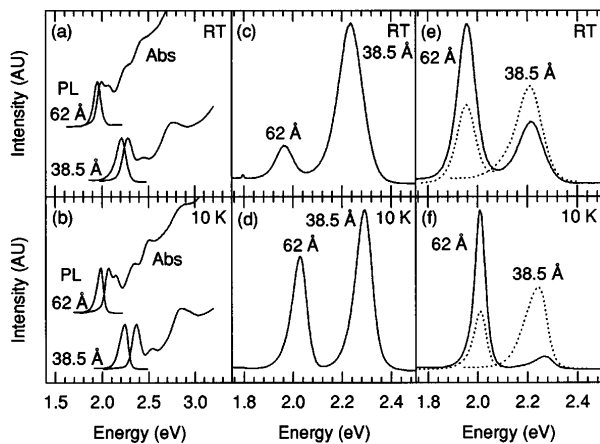


FIG. 2. Absorption and emission spectra for 38.5 and 62 Å CdSe QD solids at (a) room temperature (RT) and (b) 10 K. PL spectra for 2.762 eV excitation of the mixed system of 18% 62 Å dots in 82% 38.5 Å dots (solid lines) dispersed in solution at (c) RT and (d) 10 K and close packed in the solid at (e) RT and (f) 10 K. Dotted lines plot the relative quantum yields for 38.5 Å dots in a pure film and for 62 Å dots in the mixed film when excited to the red (2.143 eV) of the 38.5 Å dots absorption edge at (e) RT and (f) 10 K.

reveal an increase in the ratio of large to small dot luminescence quantum yields (QY) in the film vs in solution. Dotted lines in Figs. 2(e) and 2(f) plot the relative QYs for small dots in a pure film and for large dots in the mixed film when excited to the red of the small dot absorption edge [13]. Excitation to the red of the small dot absorption edge measures the response of the system to photoexcitation of only the large dots. Comparison of QYs reveals quenching of the emission of the small dots accompanied by enhancement of the emission of the large dots in the mixed film when both the small and large dots are excited.

PLE monitoring the fluorescence peak of the large dots resolves the ground state absorptions from which their fluorescence originates. Figure 3 shows PLE spectra for a mixed film and solution. Comparison with PLE for a dispersion of pure large dots [Fig. 3(c)] confirms that fluorescence from large dots in the mixed solution [Fig. 3(b)] arises only from large dot absorptions. Comparison of the PLE for the mixed solid [Fig. 3(a)] with the absorption spectrum for the small dots [Fig. 2(b)] reveals that fluorescence from large dots in the mixed solid originates from photoexcitations in both small and large dots.

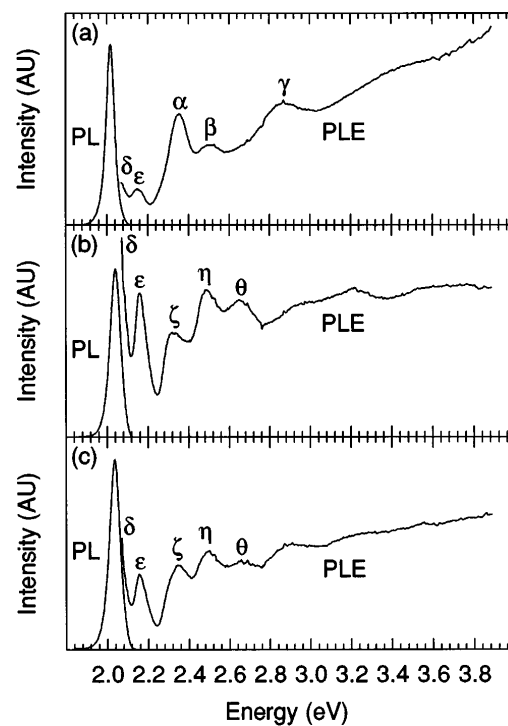


FIG. 3. PL spectra (10 K) were collected using 2.762 eV excitation. PLE spectra monitoring the peak in the 62 Å dots PL (~ 1.6 meV bandpass) for the mixed (a) film and (b) solution. (c) PLE of 62 Å dots in solution. The resonances in PLE for the mixed solid are assigned to absorptions of both the 38.5 Å dots, where $\alpha = 1S_{3/2}1S_e$, $\beta = 2S_{3/2}1S_e$, and $\gamma = 1P_{3/2}1P_e/2S_{1/2}1S_e$ transitions, and the 62 Å dots, where $\delta = 1S_{3/2}1S_e$, $\epsilon = 2S_{3/2}1S_e$, $\zeta = 1P_{3/2}1P_e$, $\eta = 2S_{1/2}1S_e$, and $\theta = 3S_{1/2}1S_e$ transitions [20].

Time resolved PL was used to measure RT luminescence dynamics for dots in pure and mixed films. Dotted lines in Fig. 4 show PL decays monitoring the fluorescence peak for small dots in (a) a pure and in (b) the mixed film and for large dots when exciting the mixed film to the (c) blue and (d) red of the small dot absorption edge. The PL lifetime of the small dots is decreased while that of the large dots is increased in the mixed film when both the small and large dots are excited. The observations in Figs. 2–4 are consistent with electron energy transfer from the small to the large dots.

Measurements of enhanced luminescence have been used to study electronic energy transfer in mixed molecular solids and between dye molecules, chromophores, and phosphors [14]. Transfer of an excitation requires coupling between the emitting molecule (the donor) and a ground state molecule (the acceptor). At intermolecular separations ≤ 100 Å, long-range resonance transfer (LRRT) of electronic excitation arises from coupling the transition dipoles of the excited donor and a ground state acceptor [14–16]. Enhanced fluorescence requires the acceptor to have both a transition resonant with the donor and a lower energy state in which to trap the excitation [14–16]. In our mixed solid the small dots are the donors and the large dots are the acceptors. We calculate the rate and efficiency of energy transfer from small to large dots in terms of spectroscopic quantities. The time evolution of the PL decays for the small and large dots confirms the LRRT model and the energy transfer characteristics.

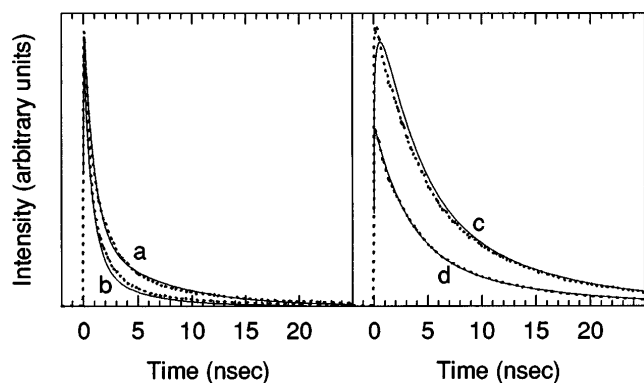


FIG. 4. PL decays (dotted lines) monitoring the fluorescence peaks for 38.5 Å dots in (a) a pure and in (b) the mixed film and for 62 Å dots in the mixed film when excited to the (c) blue and (d) red of the 38.5 Å dot absorption edge. Decays for the 38.5 Å dots in the pure film (a) and for the 62 Å dots in the mixed film when excited to the red of the 38.5 Å dots absorption edge (d) are fit by biexponentials (solid lines). The decrease in the PL lifetime for the 38.5 Å dots in the mixed film fits Förster's decay law for LRRT [solid line (b)]. The increase in the PL lifetime for the 62 Å dots when exciting the mixed film to the blue of the 38.5 Å dots absorption edge is calculated including LRRT of electronic excitations [solid line (c)]. PL decays were measured using time correlated single photon counting (~ 80 psec resolution) and exciting samples with 2.143 and 2.302 eV pulses. The instrumental response was convoluted in all our fits and calculations.

Förster theory relates the interaction between transition dipoles of a donor and an acceptor to the spectral overlap of donor emission and acceptor absorption [14]. We use this theory to calculate the rate (k_{DA}) and critical distance (R_0) for LRRT. R_0 defines the distance at which k_{DA} equals the rate of donor deexcitation by competing mechanisms. R_0 is then a measure of transfer efficiency where, for randomly oriented dipoles [14–16],

$$R_0 \propto \left(\frac{\varphi_D}{n^4} \int_0^\infty F_D(\tilde{\nu}) \varepsilon_A(\tilde{\nu}) \frac{d\tilde{\nu}}{\tilde{\nu}^4} \right)^{1/6}, \quad (1)$$

φ_D is the QY of the donor, n is the film refractive index, $F_D(\tilde{\nu})$ is the normalized spectrum for donor emission, and $\varepsilon_A(\tilde{\nu})$ is the molar extinction coefficient for acceptor absorption. We assume random orientation of transition dipoles as the transition dipole is defined by the CdSe unit cell [4] and each dot is randomly oriented in the glassy solid. We take n as the volume weighted average of that for the QDs and the organic cap. Equation (1) yields $R_0 = 47$ Å at RT and 67 Å at 10 K. The temperature dependence of R_0 arises from the increase in QY for the small dots with decreasing temperature.

PL decays for the small and large dots (Fig. 4) confirm that energy transfer arises from long-range resonant interactions and not from exciton diffusion. LRRT has a rate $\propto t^{-1/2}$ while exciton diffusion has a time independent transfer rate [17]. We fit the nonexponential PL decays (solid lines) for the small (a) and large (d) dots in the absence of energy transfer with biexponentials, representing the distributions of lifetimes. We assume the transfer rate is the same for all the small dots in the mixed solid. The decrease in the PL lifetime for the small dots fits Förster's decay law for LRRT [17] [solid line (b)]

$$n_{D,\text{mixed}}(t) = n_{D,\text{pure}}(t) \exp \left[-\gamma \left(\frac{\pi t}{\bar{\tau}_D} \right)^{1/2} \right], \quad (2)$$

where $\gamma = C \left(\frac{4}{3} \pi R_0^3 \right)$. $n_{D,\text{pure}}(t)$ and $\bar{\tau}_D$ are the biexponential fit (curve a) and the weighted average PL lifetime for the small dots in the pure solid. C is the concentration of large dots in the mixed solid (calculated from their absorbance). The fit yields $R_0 = 48$ Å, consistent with that obtained above using spectral overlap. Exciting the mixed solid to the blue of the small dot absorption edge increases the PL lifetime of the large dots as excitations are generated both directly by the source and indirectly by resonant transfer from the small dots. The PL decay for the large dots is computed [solid line (c)] combining the decay of photoexcitations, described by the biexponential fit [curve (d)], with the decay of excitations resonantly transferred from the small dots, described by Förster's decay law [curve (b)]. The excellent agreement between calculated and experimental curves establishes that LRRT leads to electronic energy transfer from the small to the large dots in the mixed QD solid.

Since we have established the LRRT mechanism from the time dependence, we can also calculate R_0 from the quenching of the QY for the small dots in the mixed film

relative to that in a pure film [Figs. 2(e) and 2(f)]. R_0 is expressed in terms of this quenching by integrating Eq. (2) and $n_{D,pure}(t)$ over time, assuming a weighted average lifetime for the dots, yielding [17]

$$\frac{\phi_{D,mixed}}{\phi_{D,pure}} = 1 - \frac{\pi}{2} \gamma \exp\left(\frac{\pi\gamma^2}{4}\right) \operatorname{erfc}\left(\frac{\pi^{1/2}\gamma}{2}\right). \quad (3)$$

We obtain $R_0 = 47 \text{ \AA}$ at RT and 81 \AA at 10 K.

In summary, the spectral overlap of donor emission and acceptor absorption and the quenching of the donor luminescence independently give us $R_0 = 47$ at RT and $R_0 = 67$ and 81 \AA , respectively, at 10 K. RT quenching of the donor PL lifetime confirms the time dependence for LRRT with $R_0 = 48 \text{ \AA}$. Comparison of R_0 with the distance between donor and acceptor centers ($R_{DA} = 61.25 \text{ \AA}$) suggests that coupling between QDs is a nearest neighbor interaction. The rate of electronic energy transfer is $k_{DA} = \tau_D^{-1}(R_0/R_{DA})^6$ where τ_D is the lifetime of the small dots in the pure film [18]. We obtain $k_{DA} = 1 \times 10^8 \text{ sec}^{-1}$ at RT and $k_{DA} = 0.6 \times 10^8 \text{ sec}^{-1}$ at 10 K, consistent with characteristic values for LRRT [15,19].

Förster's relationship between dipolar coupling and spectroscopic quantities is valid for donors and acceptors separated by $\geq 20 \text{ \AA}$ [16]. Coupling between CdSe QDs is expressed as the sum of dipole-dipole interactions between unit cells in donor and acceptor dots. Since the separation between dot surfaces is $\sim 11 \text{ \AA}$, the interaction between unit cell transition moments near neighboring dot surfaces may have contributions from higher multipoles. The $1/(R^{n+m+1})^2$ spatial dependence of the energy transfer rate, where n and m are the orders of the interacting poles, suggests, however, that higher multipoles are important for only a small number of unit cells near neighboring dot surfaces. Contributions from higher multipoles should be further decreased since interactions are weighted by the spatial overlap of electron and hole wave functions which are maximized at the dot centers.

This Letter presents spectroscopic measurements of electronic energy transfer in QD solids arising from dipolar coupling between proximal QDs. We measured quenching of the luminescence (lifetime) of small dots accompanied by enhancement of the luminescence (lifetime) of large dots in a mixed CdSe QD solid. Our observations are consistent with long-range resonance transfer of electronic excitations from the small to the large dots. The spectral overlap of donor emission and acceptor absorption, the quenching of the donor luminescence, and the decrease in the donor luminescence lifetime give us three independent and consistent measures of the energy transfer efficiency. The $t^{-1/2}$ energy transfer rate reproduces the time evolution of the small and large dot luminescence decays confirming that LRRT leads to electronic energy transfer between close packed dots.

M. G. B. thanks the David and Lucille Packard Foundation and the Sloan Foundation for fellowships. This research was funded in part by NSF Grants No. DMR-

91-57491 and No. ECS-91-1907 and by the NSF-MRSEC program Grant No. DMR-94-00034.

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