

## Narrow-Band Absorption-Enhanced Quantum Dot/J-Aggregate Conjugates

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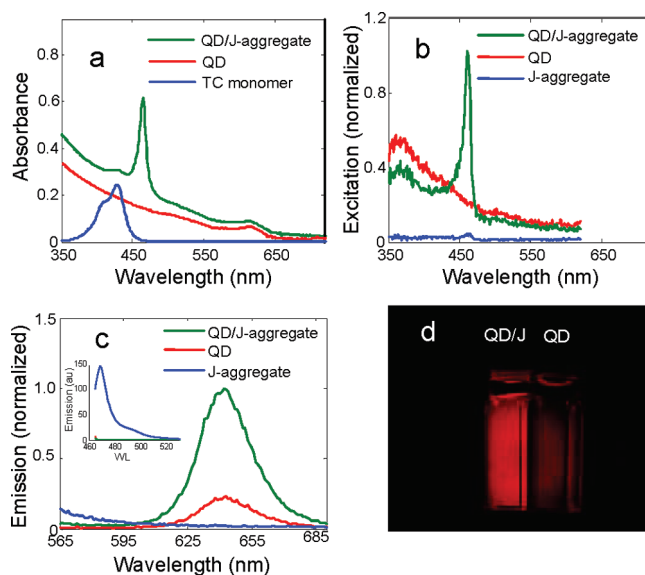
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We report narrow-band absorption enhancement of colloidal quantum dots (QDs) through efficient Förster resonance energy transfer (FRET) from J-aggregated cyanine dyes. These J-aggregate donors are electrostatically associated to the QDs in solution via surface ligands.

J-aggregates are used as light sensitizers for silver halide photographic films,<sup>1</sup> and their properties have long attracted interest.<sup>2–10</sup> Coherent coupling of molecules in the aggregate leads to an intense, narrow absorption feature,<sup>11</sup> so a thin film of J-aggregates can attenuate the same fraction of incident light at the absorption maximum as a far thicker film of unaggregated dye. Efficient energy transfer from a J-aggregate donor to a QD acceptor would enhance the absorption cross section of the QD in the J-aggregate absorption band while retaining tunable emission. Such narrow-band-sensitized QDs may have applications in down-conversion LEDs or in engineering hybrid optical structures in thin films.<sup>9,12,13</sup> Others have studied energy transfer between films of J-aggregates and QDs<sup>14</sup> and between films of different J-aggregates.<sup>15,16</sup> Here we report the fabrication of a QD/J-aggregate conjugate in solution that exhibits energy transfer from the J-aggregates to a QD with a transfer efficiency approaching unity.

Previously we reported energy transfer from QDs to associated J-aggregates in solution.<sup>17</sup> The QD emission spectrum had a large spectral overlap with the dye absorption, and the energy transfer rate was increased through the presence of many acceptors. Thus, efficient FRET occurred even though the QDs and J-aggregates were separated by long ligands or amphiphilic polymers. In this work, we use a negatively charged, 472 nm-emitting thiocyanine J-aggregate (TCJ) and CdSe/ZnCdS QDs (635 nm emission). While larger QDs have a greater absorption cross section than smaller QDs, they also lead to a larger donor/acceptor separation. To compensate for this separation and to promote electrostatic attraction, we synthesized the short ligand 2-mercaptoethyl-*N,N,N*-trimethylammonium chloride (mta). Ligand exchange with mta confers a pH-insensitive positive charge while avoiding spurious reactivity with the QD surface. Dynamic light scattering (DLS) gave a hydrodynamic radius of  $4.3 \pm 0.4$  nm [Figure S4 in the Supporting Information (SI)], a small increase over the nanocrystal radius [3.6 nm by TEM (Figure S3)].

The absorption spectrum of the QD/dye sample showed that both constituents were present (Figure 1a). Because the dye requires electrolytes in order to aggregate in aqueous solution and because unbound electrolytes were removed, the J-aggregate feature at 465 nm indicates that the mta–QD surface acts as a template for J-aggregation. The excitation spectrum collected while monitoring emission at 635 nm (Figure 1b) has features similar to those of the absorption spectrum. Both the absorption and excitation of the QD/J-aggregate conjugates are 5 times greater at the J-band than the



**Figure 1.** Steady-state optical characterization of QD/J-aggregates. (a) Absorption spectra in deionized H<sub>2</sub>O. The spectral features of both QDs and TC monomers are discernible. (b) Excitation spectra taken at 635 nm emission. The J-aggregates contribute only when conjugated to QDs. (c) Emission spectra taken at 460 nm excitation. The integrated emission of the QD/J-aggregate conjugates is 5 times greater than that for QDs alone. The inset shows emission spectra renormalized to J-aggregate emission. For the QD/J-aggregate conjugates, the 472 nm emission is indistinguishable from the baseline. (d) Photograph of QD/J-aggregate conjugates and QDs alone at identical QD concentration, using 457 nm illumination and a band-pass filter ( $630 \pm 15$  nm) to remove excitation light.

corresponding QD spectra, demonstrating narrow-band absorption enhancement (fwhm = 13 nm). TCJ emission is negligible at 635 nm, so excitation from J-aggregate absorption enhances QD emission, as expected for FRET.

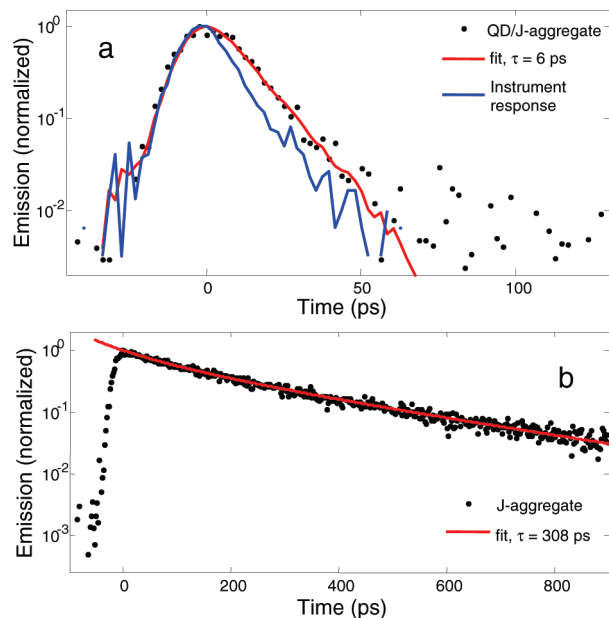
The integrated emission of QD/J-aggregate conjugates near 635 nm was 5 times greater than that for QDs alone, consistent with the excitation spectrum and enhanced QD emission (Figure 1c). Furthermore, the emission at 472 nm for the QD/J-aggregate conjugates was attenuated by >99% relative to that for the J-aggregates alone (Figure 1c, inset). The photograph of QD and QD/J-aggregate samples illuminated near the J-band qualitatively confirms the narrow-band enhancement (Figure 1d).

Absorption and re-emission cannot account for the increase in QD emission, as we observed the same J-aggregate emission quenching and QD emission enhancement using a cell with a 90% shorter path length. In this short cell, the QD optical density was 0.02 at 465 nm, so the quenched donor emission and enhanced acceptor emission point to near-field energy transfer and are consistent with FRET at >99% efficiency.

We verified the transfer efficiency via transient photoluminescence measurements at the TCJ emission (472 nm). For the

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**Figure 2.** Time-resolved emission decays taken at 472 nm. (a) QD/J-aggregate data, fit with a convolution of the instrument response (blue) with an exponential decay function. This fit accounts for 97% of the exciton depopulation (see the SI for more details). (b) TCJ data, fit using an exciton–exciton annihilation model.

J-aggregates alone, a two-parameter fit<sup>18</sup> indicated that the dominant decay pathway has a lifetime of  $308 \pm 13$  ps (Figure 2b).<sup>19</sup> The 472 nm emission of the QD/J-aggregate conjugates had a lifetime of about 6 ps (Figure 2a), a 48-fold increase in the exciton depopulation rate over TCJ alone. Efficient energy transfer is more rapid than the donor’s radiative lifetime, and this rate corresponds to a 98% energy transfer efficiency from the J-aggregates to the QDs. Thus, the results from transient and steady-state emission spectra are consistent to within  $\sim 1\%$ .

We compared our results to the predictions of Förster theory to assess its applicability.<sup>20</sup> From the measured TCJ quantum yield, QD absorption cross section, and spectral overlap, the Förster radius for this donor–acceptor pair was 8.8 nm (see the SI). A 98% FRET efficiency would occur for donor–acceptor separations of 4.6 nm. This is identical to the hydrodynamic radius of the mta–QDs ( $4.3 \pm 0.4$  nm) within experimental error and consistent with energy transfer predominantly from the closest possible point, adjacent to the QD surface.

This short donor–acceptor distance is reasonable because of the delocalized nature of J-aggregate excitation. J-aggregates consist of segments of coherently coupled dye molecules, and these segments transfer energy among one another.<sup>1,21</sup> Even if the J-aggregates extend far beyond the QD surface in a construct (Figure S5), an exciton can transfer within the aggregate until it comes close to the QD acceptor. The short mta ligand length allows J-aggregates to approach the QD surface more closely than in previous studies.<sup>14</sup> These aggregates act like narrow-band optical antennae through rapid, efficient FRET.

To demonstrate the generality of our method, we conjugated negatively charged QDs to positively charged J-aggregates of TTBC (see the SI) that emit at 594 nm. After ligand exchange with sodium 3-mercapto-1-propanesulfonate (mps), we associated the anionic QDs with the TTBC J-aggregates in solution. DLS data for these

QD/J-aggregate conjugates showed species with a well-defined hydrodynamic radius (4.2 nm), and the TTBC J-aggregates added little to the radius of mps–QDs in solution (4.0 nm). In this pair, QD emission was enhanced and J-aggregate emission quenched by  $\sim 82\%$  relative to J-aggregates alone. The incomplete energy transfer is attributed to decreased spectral overlap of the TTBC emission with QD absorption relative to that for TC emission (Figures S6–S8).

In a control experiment, negatively charged mps–QDs were combined with a different negatively charged J-aggregating dye, BIC (see the SI).<sup>22</sup> Excitation of this sample near the J-band showed no significant enhancement of the QD emission, and it is evident that the QDs and J-aggregates were not associated (Figure S9).

In conclusion, we have used QDs as templates for J-aggregation in solution and demonstrated rapid, near-unit-efficiency FRET from cyanine J-aggregates to the associated QDs. The J-aggregates serve as narrow-band optical antennae and enhance the QD absorption 5-fold at the J-aggregate absorption band.

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**Supporting Information Available:** Synthetic and spectroscopic procedures and analysis, energy transfer calculations, sizing data, and data for oppositely charged QD/J-aggregate conjugates. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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