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

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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,[1] and their properties have long attracted interest.[2−10] Coherent coupling of molecules in the aggregate leads to an intense, narrow absorption feature,[11] 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.[9,12,13] Others have studied energy transfer between films of J-aggregates and QDs[14] and between films of different J-aggregates.[15,16] 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.[17] 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 thiacyanine 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 ± 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 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.

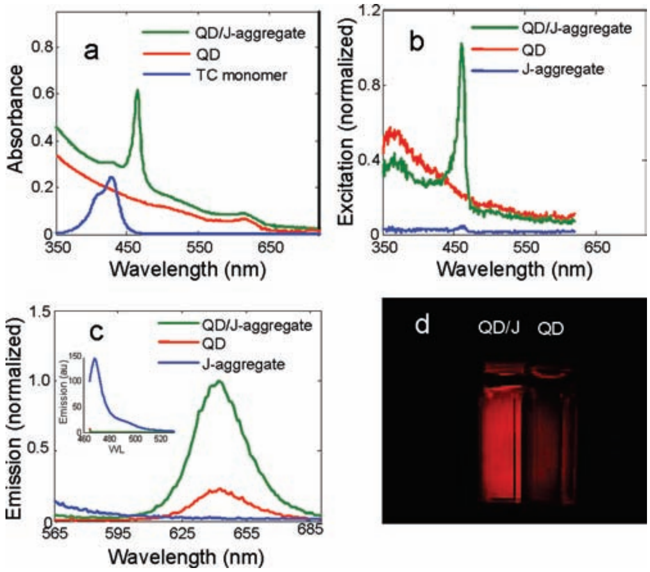

Figure 1. Steady-state optical characterization of QD/J-aggregates. (a) Absorption spectra in deionized H_2O. The spectral features of both QDs and TC monomers are discernible. (b) Excitation spectra taken at 635 nm emission. The J-aggregates contribute only when conjugated to QDs. (c) Emission spectra 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 ± 15 nm) to remove excitation light.

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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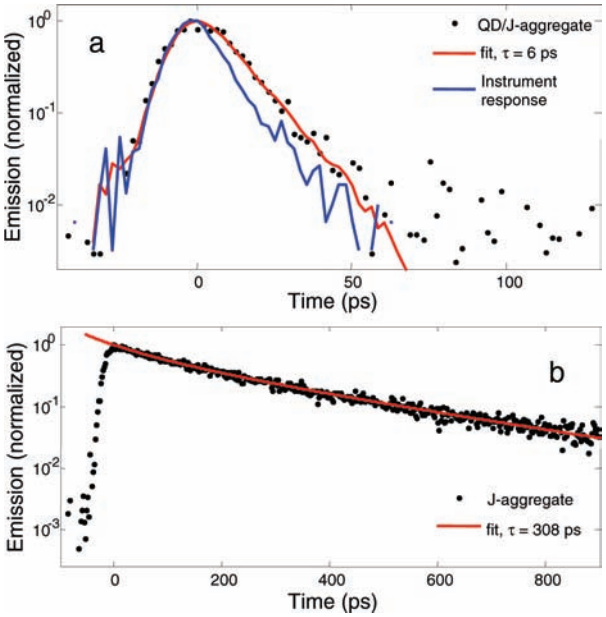

Figure 2. Time-resolved emission decays taken at 472 nm. (a) QD/J-aggregate data, fit with a convolution of the instrument response (blue) with an exponential decay function. This fit accounts for 97% of the exciton depopulation (see the SI for more details). (b) TCJ data, fit using an exciton−exciton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

J-aggregates alone, a two-parameter fit[18] indicated that the dominant decay pathway has a lifetime of 308 ± 13 ps (Figure 2b).[19] 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 ∼1%.

We compared our results to the predictions of Förster theory to assess its applicability.[20] 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 ± 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.[1,21] 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.[14] 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 ∼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).[22] 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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