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Narrowband Absorption-Enhanced Quantum Dot/J-aggregate Conjugates

Brian J. Walker[†], Gautham P. Nair[†], Lisa F. Marshall[†], Vladimir Bulović[‡], and Mouni G. Bawendi[†]

Mouni G. Bawendi: mgb@mit.edu

[†]Department of Chemistry, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139

[‡]Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, MA 02139

We report the narrowband absorption enhancement of colloidal quantum dots (QDs) through efficient Förster Resonance Energy Transfer 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 photosensitizers for silver halide film¹ 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 than 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 narrowband-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 QDs¹⁴ 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 J-aggregates to a QD with 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, a small increase over the nanocrystal radius (3.6 nm by TEM, Fig. S3-4).

Correspondence to: Vladimir Bulović ; Mouni G. Bawendi, mgb@mit.edu.

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>.

The absorption spectrum of the QD/dye sample showed that both constituents were present (Fig. 1a). Because the dye requires electrolytes to aggregate in aqueous solution and because unbound electrolytes have been 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 (Fig. 1b) has similar features to the absorption spectrum. Both absorption and excitation of QD/J-aggregate conjugates are 5x greater at the J-band than the corresponding QD spectra, demonstrating narrowband absorption enhancement (FWHM = 13 nm). TCJ emission is negligible at 635 nm, so excitation from J-aggregate absorption enhances QD emission, as expected for Förster Resonance Energy Transfer (FRET).

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

Absorption/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 is 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 with >99% efficiency.

We verified the transfer efficiency via transient photoluminescence measurements at the TCJ emission (472 nm). For the J-aggregate alone, a two-parameter fit¹⁸ indicates that the dominant decay pathway has a 308 ± 13 ps lifetime (Fig. 2b).¹⁹ The 472 nm emission of the QD/J-aggregate had a lifetime of about 6 ps, (Fig. 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 J-aggregates to QDs. Thus, the results from transient and steady-state emission spectra are consistent to within about 1%.

We compared our results to the predictions of Förster theory to assess its applicability.²⁰ For the measured TCJ quantum yield, QD absorption cross section and spectral overlap, the Förster radius for this donor-acceptor pair is 8.8 nm (supporting information). A 98% FRET efficiency would occur for donor-acceptor separations of 4.6 nm. This is identical to the hydrodynamic radius of mta-QDs within error (4.3 ± 0.4 nm) and is consistent with energy transfer predominantly from the closest possible point, adjacent to the quantum dot surface.

This short donor-acceptor distance is reasonable due to the delocalized nature of J-aggregate excitation. J-aggregates consist of segments of coherently-coupled dye molecules, and these segments transfer energy between one another.^{1,21} Even if the J-aggregates extend far beyond the QD surface in a construct (Fig. S5), an exciton can transfer within the aggregate until it comes close to the quantum dot 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 that emit at 594 nm, TTBC. After ligand exchange with sodium 3-mercapto-1-propanesulfonate (mps), we associated the anionic QDs with TTBC J-aggregates in solution. DLS data of these QD/J-aggregate conjugates showed species with a well-defined hydrodynamic radius (4.2 nm), and the TTBC J-aggregates add little to the radius of mps-QDs in solution (4.0 nm). In this pair, QD emission was enhanced and J-

aggregate emission was quenched by about 82% relative to J-aggregates alone. Incomplete energy transfer is attributed to decreased spectral overlap of TTBC emission with QD absorption relative to TC emission with QD absorption (Fig. S6-S8)

In a control experiment, negatively charged mps-QDs were combined with a different negatively-charged J-aggregating dye, BIC.²² Excitation of this sample near the J-band shows no significant enhancement of QD emission, and it is evident that the QD and J-aggregate were not associated (Fig. S9).

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

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1.

Steady-state optical characterization of QD/J-aggregates. (a) Absorption spectra in DI H₂O. The spectral features of both QDs and TC monomers are discernable. (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 QD/J-aggregate is 5x greater than for QDs alone. (c, inset) Emission spectra, renormalized to J-aggregate emission. In the QD/J-aggregate the 472 nm emission is indistinguishable from baseline. (d) Photograph of QD/J-aggregate and QD alone at identical QD concentration, illuminated at 457 nm light using a band pass filter [630 ± 15 nm] to remove excitation light.

Figure 2.

Time-resolved emission decays taken at 472 nm. (A) QD/J-aggregates, fit with a convolution of the instrument response (shown) with an exponential decay function. This fit accounts for 97% of the exciton depopulation. See supporting information for more details. (B) Thiocyanine J-aggregates, fit using an exciton-exciton annihilation model.