

Twenty-Fold Enhancement of Molecular Fluorescence by Coupling to a J-Aggregate Critically Coupled Resonator

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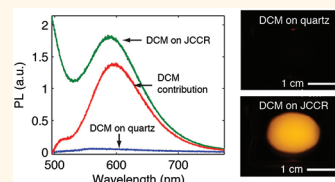
Over the past decade, work on the control of radiative properties of luminescent materials has led to the development of strategies for enhancement of fluorescence by near-field coupling of constituent lumophores to optical fields associated with metal nanostructures.^{1–4} Plasmonic metal nanostructures can increase the fluorescence of lumophores by locally enhancing the incident optical field, by modifying the lumophore radiative rate, and by increasing the outcoupling of light. For example, fluorescence enhancements of up to 1340-fold have been demonstrated in bowtie nanoantennas,³ in the vicinity of scanning probe tips,^{5–8} and even in large-area structures.^{4,9} While providing high local fields and large enhancement factors, such schemes are highly sensitive to the nanoscale geometry of the plasmonic structures, resulting in either large enhancement or effective quenching.^{2,7}

In this study, we present an alternative, purely excitonic, and large-area approach to the enhancement of lumophore emission by coupling the lumophore to a highly absorbing resonant optical structure. The enhancement structure contains a thin film of strongly absorbing molecular J-aggregates¹⁰ placed at the antinode of the electric field at a distance $\lambda_0/4$ away from a mirror, where λ_0 is the wavelength of incident light. The resulting structure, referred to as a J-aggregate critically coupled resonator (JCCR), absorbs nearly all of the incident light due to destructive interference between light reflected by the mirror and light reflected by the J-aggregate. Earlier work demonstrated 97% absorption in three molecular layers, corresponding to a 5 nm thick film of J-aggregates in a JCCR structure,¹¹ and the same principle has been used to enhance the signal in surface-enhanced Raman spectroscopy.¹² The optical energy incident and absorbed in the JCCR structure is localized

ABSTRACT We report a 20-fold enhancement in the fluorescence of the organic dye DCM when resonantly coupled to a strongly optically absorbing structure of a thin film of spin-deposited molecular J-aggregates in a critically coupled resonator (JCCR) geometry.

A submonolayer equivalent of DCM molecules is shown to absorb and re-emit 2.2% of the incident resonant photons when coupled to the JCCR enhancement structure, compared to 0.1% for the bare film of same thickness on quartz. Such a JCCR structure is a general energy focusing platform that localizes over 90% of incident light energy within a 15 nm thin film layer in the form of excitons that can subsequently be transferred to collocated lumophores. Applications of the exciton-mediated concentration of optical energy are discussed in the context of solid-state lighting, photodetection, and single photon optics.

KEYWORDS: fluorescence enhancement · J-aggregates · resonator · FRET · plasmonics · organic optoelectronics



in the form of J-aggregate excitons. Target lumophores placed on the surface of the JCCR are coupled to these localized excitons by Förster resonant energy transfer (FRET) (Figure 1a). As a result, the JCCR acts as a platform for strongly enhancing the effective optical absorption cross section of the target lumophores, increasing their emission under fixed optical excitation. The presence of the mirror in this structure increases the absorption of the J-aggregate film but does not modify the rate of FRET between J-aggregate excitons and donor lumophores, which is a near-field interaction. Likewise, the emission rate of the donor lumophores is unaffected because the target lumophore emission is not resonant with the critically coupled resonator. The presence of the mirror does, however, increase the forward outcoupling of the lumophore emission by a factor of ~ 2 .

The absorption and emission spectrum of J-aggregated films of different molecules can be tuned across the entire visible spectrum and into the near-infrared,¹⁰ thus enabling

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Received for review October 3, 2011 and accepted November 28, 2011.

Published online November 28, 2011
10.1021/nn203789t

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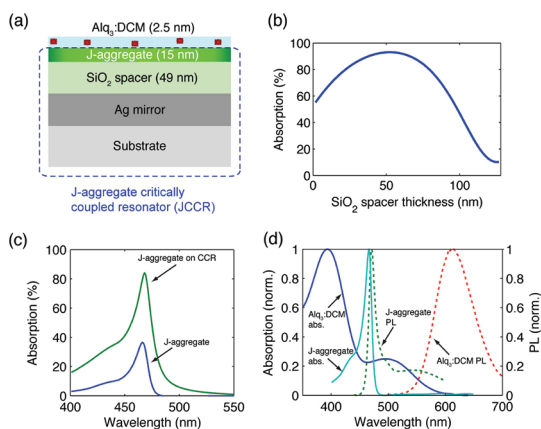


Figure 1. (a) J-aggregate critically coupled resonator (JCCR) fluorescence enhancement structure with 2.5 nm of DCM: Alq₃ (2.5% w/w) deposited on top as the exciton acceptor layer. (b) Calculated absorption of the JCCR as a function of SiO₂ spacer layer thickness, showing a maximum at 50 nm, corresponding to a resonant condition. (c) Absorption of the 15 nm thick J-aggregate thin film on quartz and increased absorption of the same film when placed on the critically coupled resonator and excited at 7° relative to normal incidence. (d) Normalized absorption (solid lines) and emission (dashed lines) spectra of the J-aggregate and DCM:Alq₃ layers.

broad tunability in the spectral response of JCCRs. With this broad spectral coverage, the fluorescence of a wide range of target lumophores, such as organic molecules or inorganic quantum dots, can be enhanced by simply choosing the appropriate J-aggregate material for the JCCR. Furthermore, due to the small Stokes shift of J-aggregates (~5 nm), the fluorescence of the target lumophores is enhanced by increasing the absorption at the spectral peak of their uncoupled absorption. The study presented in this paper demonstrates a 20-fold enhancement in the emission of the laser dye DCM (4-dicyanmethylene-2-methyl-6-(*p*-dimethylaminostyryl)-4*H*-pyran) by utilizing the JCCR excitonic enhancement structure.

The key feature of the enhancement scheme is the localization of optical energy in a thin nanocrystalline film of J-aggregates with a thickness comparable to the FRET radius for energy transfer from J-aggregates to DCM molecules. The J-aggregates used in this study are characterized by a narrow and intense absorption band centered at $\lambda = 465$ nm (Figure 1b), red-shifted relative to the monomer absorption, which is a result of coherent transition dipole coupling between molecules within the aggregate.¹⁰ The J-aggregate solution is prepared by dissolving a thiocyanine dye¹³ in 2,2,2-trifluoroethanol at a concentration of 1.5 mg/mL. The solution is then spin-deposited either on a cleaned quartz substrate or on previously prepared critically coupled resonator (CCR) substrates rotated at 2000 rpm for 60 s. The resulting J-aggregate film is 15 nm thick, as measured by atomic force microscopy step height analysis, and has a 20 nm fwhm absorption line with a peak

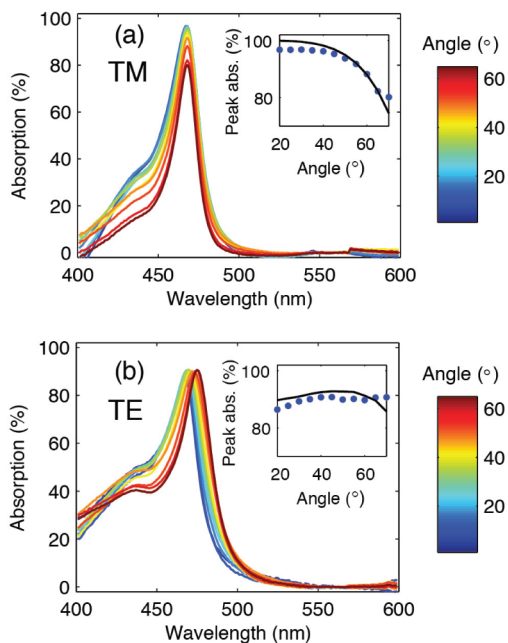


Figure 2. Absorption spectrum of the JCCR structure as a function of angle of the incident (a) TM- and (b) TE-polarized light. Insets show the measured peak absorption at each angle (blue dots) and the absorption calculated using the transfer matrix formalism (black lines).

absorption of 36%, corresponding to the absorption coefficient of $\alpha = 3 \times 10^5 \text{ cm}^{-1}$.

To form the CCRs, a 300 nm thick Ag mirror is thermally evaporated on a 1 mm thick quartz substrate at a base pressure of 3×10^{-6} Torr and a growth rate of 0.5 nm/s, producing a mirror with 97% reflectivity. The spacer layer, which separates the overlying J-aggregate film from the mirror, is formed by sputter depositing 50 nm of SiO₂ on the Ag mirror. The 15 nm J-aggregate film is subsequently spin-deposited on the SiO₂ spacer layer. The spacer layer thickness is chosen such that the sum of the optical path length in SiO₂ and the 30 nm optical penetration of the $\lambda = 465$ nm light incident onto the Ag mirror¹⁴ results in the J-aggregate film being positioned at the antinode of the electric field. Transfer matrix simulations,¹⁵ plotted in Figure 1b, show that maximum absorption of the JCCR is achieved when the SiO₂ spacer layer thickness is 50 nm, corresponding to the resonant condition.

At the resonant condition, the peak absorption of the JCCR is 86% (Figure 1c), measured by probing the reflectivity of the structure with unpolarized light at near-normal incidence (7° away from the normal). The line width of the J-aggregate film absorption in the JCCR geometry is increased from 17 to 25 nm due to the broad absorption tail to the blue of the main peak. Figure 2 shows that the absorption of the JCCR is largely independent of angle for TE-polarized excitation and falls off only slightly under TM-polarized excitation. These measurements are in agreement with the transfer

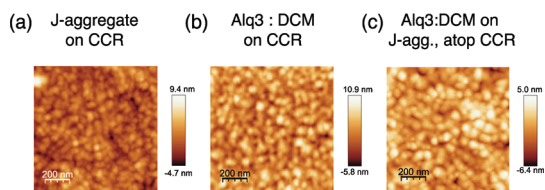


Figure 3. AFM images of (a) J-aggregate on the CCR structure (rms roughness 1.2 ± 0.2 nm), (b) DCM:Alq₃ on the CCR structure (rms roughness 1.2 ± 0.1 nm), and (c) DCM:Alq₃ on the J-aggregate layer atop the CCR (rms roughness 1.7 ± 0.4 nm).

matrix simulations of the JCCR, as plotted in the insets of Figure 2.

The JCCR structure can be used as a general platform for enhancing the absorption and fluorescence of luminescent nanostructures, such as organic molecules or quantum dots, deposited on top of the JCCR. The greatest fluorescence enhancement will occur when the overlap between the J-aggregate emission and the absorption of the overlying material is maximized, as this condition maximizes the rate of FRET. To that end, in the present work, the J-aggregate emission spectrum (centered at $\lambda = 470$ nm) overlaps with the absorption spectrum (centered at $\lambda = 495$ nm) of the overlying DCM molecules, which will act as energy acceptors (Figure 1b), resulting in a calculated FRET radius, R_F , for J-aggregate to DCM energy transfer of 2.75 nm.¹⁶ Furthermore, the DCM emission is centered at $\lambda = 610$ nm, ensuring that the J-aggregate and DCM luminescence are spectrally separated, and is hence easy to resolve in optical measurements.

DCM molecules are coated on top of the JCCR as a dilute thin film of DCM molecules doped at 2.5% w/w into Alq₃ (tris(8-hydroxyquinolinato)aluminum) molecular host material. Alq₃ molecules are optically transparent at the J-aggregate and DCM emission wavelengths. The DCM:Alq₃ film is 2.5 nm thick and is deposited on the JCCR structure by simultaneous thermal vacuum evaporation of Alq₃ and DCM at rates of 4 and 0.1 Å/s, respectively, and at a base pressure of 3×10^{-6} Torr. The resulting effective thickness of the deposited DCM molecules is 0.06 nm, which is much thinner than a single molecular layer, and implies an incomplete DCM monolayer with an average separation between DCM molecules of 4 nm (as sketched in Figure 1a). Figure 3 shows the surface morphology of the JCCR samples, characterized by atomic force microscopy (AFM) at various points in the fabrication process, with surface roughness of 1.7 ± 0.4 nm for the completed structures. The low roughness allows the JCCR to be approximated as a one-dimensional structure, making it more conducive to modeling of FRET, exciton diffusion, and other dynamics in the system. The layered geometry is advantageous because it allows for the fluorescence enhancement of a range of materials that can be deposited by vacuum or solution methods directly onto the JCCR. To prevent

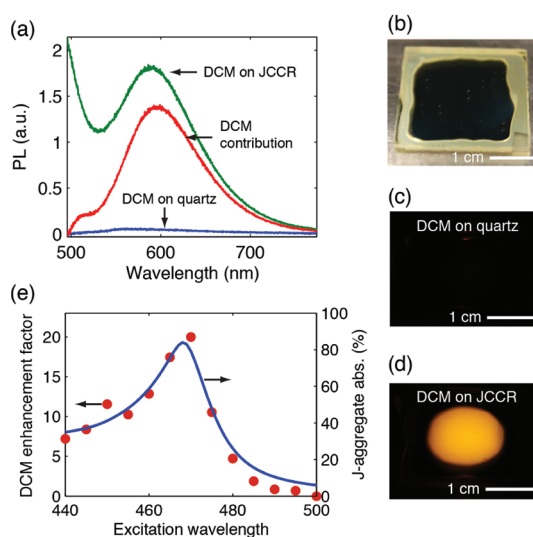


Figure 4. (a) Emission spectra of isolated DCM film, DCM film on JCCR, and the DCM contribution when atop the JCCR showing a 20-fold enhancement in the spectrally integrated DCM emission. (b) Ambient light image of the DCM film deposited on the JCCR and encapsulated with UV curing epoxy and a quartz coverslip. (c,d) Images of DCM emission on quartz substrate (c) and on JCCR (d) under $\lambda = 465$ nm excitation. Images taken with 0.1 s exposure and a $\lambda = 550$ nm long-pass filter. (e) Enhancement factor of DCM emission as a function of excitation wavelength and comparison to the absorption spectrum of the JCCR.

degradation of the organic layers under atmospheric exposure, the samples are encapsulated in a nitrogen glovebox using a ring of UV-curing air-impermeable epoxy and a quartz coverslip (Figure 4b).

The enhancement of DCM fluorescence when on top of the JCCR is characterized by measuring both the internal quantum efficiency (IQE) and external quantum efficiency (EQE) of the structures in an integrating sphere following the technique of de Mello *et al.*¹⁷ In this measurement, the samples are situated at the center of the integrating sphere and illuminated with the output of a grating monochromator and a tungsten halogen lamp at an intensity of $60 \mu\text{W}/\text{cm}^2$ at $\lambda = 465$ nm and a spectral bandwidth of 6 nm. The PL is collected with an optical fiber and imaged on a CCD spectrograph. All collected spectra are corrected by calibrating the system using a halogen light source with a known spectrum.

As a control sample, the 2.5 nm film of DCM:Alq₃ is also simultaneously deposited on a quartz substrate and encapsulated in the nitrogen glovebox. The absorption of the control film is measured to be 0.5%, with an IQE of 20%, and hence an EQE of 0.1%. Due to the low intensity of emission from the 2.5 nm film, the IQE of DCM:Alq₃ was determined by measuring the absorption and PL of a thick 140 nm film deposited on quartz. The PL spectrum of the 2.5 nm DCM:Alq₃ control film is shown in Figure 4a. An optical image of this sample under the same $60 \mu\text{W}/\text{cm}^2$ illumination taken with a digital SLR camera at 0.1 s exposure and a

$\lambda = 550$ nm long-pass filter shows almost no visible emission (Figure 4c).

Upon deposition of the same DCM:Alq₃ film on the JCCR structure, the DCM emission is dramatically enhanced. Figure 4a shows the emission spectrum from the DCM-on-JCCR structure, which is a sum of the enhanced DCM emission and the red tail of the J-aggregate emission. Subtraction of the J-aggregate tail from the total PL spectrum isolates the DCM contribution. This wavelength-integrated JCCR-enhanced DCM emission is 20 times greater than the wavelength-integrated emission from the control DCM sample. The optical image of the enhanced DCM sample (Figure 4d), taken under the same conditions as the control sample (Figure 4c), shows visual verification of the dramatic enhancement in fluorescence from a submonolayer equivalent of DCM molecules. The EQE of the DCM is enhanced to 2.2%, while the IQE remains unchanged at 20%. In other words, the effect of the FRET coupling to the JCCR is to increase the effective absorption cross section of the DCM molecules (and hence absorption coefficient of the film). The original cross section of the DCM molecules is $\sigma_D = 1.3 \times 10^{-16}$ cm² ($\alpha_D = 2 \times 10^4$ cm⁻¹) for the control DCM film. When coupled to the JCCR, the DCM cross section is effectively enhanced to $\sigma_{D,JCCR} = 2.6 \times 10^{-15}$ cm² ($\alpha_{D,JCCR} = 4 \times 10^5$ cm⁻¹).

The fluorescence enhancement factor is maximized when the excitation is resonant with the J-aggregate absorption and the CCR spacing ($\lambda = 465$ nm). Figure 4e shows the enhancement factor for a range of excitation wavelengths and is observed to follow the absorption spectrum of the JCCR. Significant enhancement (>7-fold) occurs over a 40 nm range, making this excitonic approach to fluorescence enhancement suitable for applications where the incident illumination has appreciable spectral bandwidth.

It is instructive to compare the fluorescence enhancement provided by the JCCR structure to the enhancement achieved when the DCM is excited by FRET from the Alq₃ host material. Enhancement in DCM emission is expected because a large number of Alq₃ molecules within the FRET radius can excite the DCM molecule. Such a guest–host excitation scheme has previously been used in the excitation of organic LEDs¹⁸ and organic solid-state lasers.¹⁹ A DCM:Alq₃ film (140 nm thick) was prepared on a quartz substrate and excited at two wavelengths: at $\lambda = 400$ nm, where Alq₃ absorption dominates, and at $\lambda = 490$ nm, the peak of the DCM absorption. The integrated intensity of the DCM emission when pumping the DCM indirectly by energy transfer from Alq₃ is found to be only a factor of 2 higher than when exciting the DCM directly (Figure 5)—10 times less enhancement than achieved with the JCCR structure.

The presented JCCR structure is a general platform for absorption (and hence fluorescence) enhancement

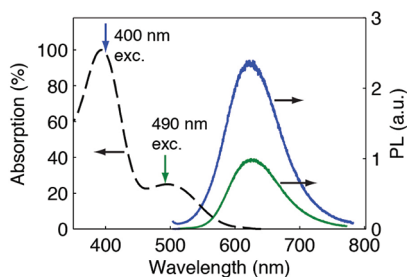


Figure 5. Factor of 2 enhancement in DCM emission is observed due to energy transfer from Alq₃ in a 140 nm thick film of DCM:Alq₃, significantly less than the 20-fold enhancement observed when using the JCCR. The DCM was excited directly at $\lambda = 490$ nm, while the Alq₃ is excited at $\lambda = 400$ nm at the same intensity.

of a wide range of nanostructured materials, including organic molecules and semiconductor quantum dots. In this paper, a model system is studied showing a 20-fold enhancement in the absorption cross section of the organic dye DCM measured through the enhancement of the molecular fluorescence. The enhancement is obtained due to FRET coupling of the DCM molecules to the strongly absorbing JCCR structure. The absorption of the JCCR is found to be over 80% for incidence angles from 7 to 70°, and the fluorescence enhancement greater than a factor of 7 was observed over a 40 nm excitation bandwidth, making this approach appropriate for applications where the incident light is spectrally broad and not directional. The fluorescence enhancement factor can be improved by optimizing the J-aggregate material for increased exciton diffusion length in the direction transverse to the plane of the film, thus transferring a larger fraction of the generated excitons to the acceptor layer.

The JCCR system shows promise as a platform for a number of applications where efficient absorption and re-emission of light is critical. For example, in LED lighting with luminescent down-conversion, the luminescent emitters can represent a significant fraction of the total cost of the luminescent optical elements. By enhancing the quantum dot emission using the JCCR design, the required amount of material could be substantially reduced. Likewise, the JCCR can be used for absorption enhancement of the photosensitive material in a photodetector. The system can also be extended to the regime of high-efficiency single photon optics by optimizing the J-aggregate to acceptor FRET and by harnessing the enhancement due to lateral diffusion of excitons in the J-aggregate film in the low density limit of acceptors. Such a system could be the building block for single molecule FRET microscopy.

Acknowledgment. The authors acknowledge support from the Department of Energy, Energy Frontiers Research Center for Excitonics, and the Institute for Soldier Nanotechnology. G.M.A. and B.J.W. acknowledge the support of the National Science Foundation Graduate Research Fellowship, and G.M.A. acknowledges support by the Hertz Foundation Fellowship.

Measurements were performed in the MIT Nanostructured Materials Metrology Laboratory on the equipment provided by the eni-MIT Solar Frontiers Center.

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