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Predicting the linear optical response of *J*-aggregate microcavity exciton-polariton devices

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We demonstrate that linear dispersion theory accurately predicts the linear optical response of strongly coupled microcavity exciton-polariton devices containing thin films of *J* aggregates of the cyanine dye [5,6-dichloro-2-[3-[5,6-dichloro-1-ethyl-3-(3-sulfopropyl)-2(3H)-benzimidazolidene]-1-propenyl]-1-ethyl-3-(3-sulfopropyl) benzimidazolium hydroxide, inner salt, sodium salt] (TDBC) when a spectrally resolved complex index of refraction derived by model-free quasi-Kramers-Kronig regression is used for the *J*-aggregate thin film. We show that the Rabi splitting can be finely tuned through the *J*-aggregate film thickness, and we estimate that the minimum linewidth of lower branch exciton polaritons at room temperature in TDBC *J*-aggregate-based structures is 8.4 meV.

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In the past two decades, research in the strong QED coupling of light and matter in solid-state systems introduced microcavity exciton-polariton devices as potential low-threshold sources of coherent light.[1,2] It was shown that the matter component of these strongly coupled devices can consist of inorganic semiconductor quantum wells, quantum dots, or organic semiconductors.[1,3–6] Organic semiconductors, such as *J* aggregates of cyanine dyes, are particularly attractive candidate materials in strongly coupled structures due to the large binding energy of their Frenkel exciton and the large oscillator strength of their optical transitions,[7] which enabled the first observation of room-temperature exciton-polariton phenomena and the first demonstration of exciton-polariton electroluminescence.[6,8–10] In modeling the linear optical response of such strongly coupled structures, linear dispersion theory (LDT) has emerged as a powerful tool capable of accurately predicting the exciton-polariton spectra of inorganic microcavity devices.[3,11–13] In this study, we demonstrate that LDT can accurately predict the linear optical response of microcavity exciton polaritons in organic systems as well when a detailed spectrally resolved optical response of the *J*-aggregate resonance is utilized in the model. Using a model-free Kramers-Kronig regression we derive the spectrally resolved index of refraction of the *J*-aggregate thin film and use it in an LDT model (i.e., in propagation and matching matrices or *T* matrices) together with published values for the dielectric functions of microcavity spacer and mirror materials. We show agreement of the predicted and measured linear optical response for various thicknesses of *J*-aggregate thin films matching the exciton-polariton dispersion as a function of the in-plane wave vector (i.e., corresponding to external probe angle). By numerically simulating cavities with high quality-factors and multiple *J*-aggregate layers, we show that Rabi splitting can be made large enough such that the lower branch (LB) exciton-polariton peak is in the Lorentzian tail of the dielectric function, allowing for an estimate of the minimum linewidth achievable for the LB exciton polariton in [5,6-dichloro-2-[3-[5,6-dichloro-1-ethyl-3-(3-sulfopropyl)-2(3H)-benzimidazolidene]-1-propenyl]-1-ethyl-3-(3-sulfopropyl) benzimidazolium hydroxide, inner salt, sodium salt] (TDBC) *J*-aggregate systems.[14]

Previous efforts in modeling exciton-polariton systems with LDT have included using an exact dielectric function for an inorganic quantum well system in order to accurately model the effects of structural disorder on the linear optical response.[15,16] Similarly, prior modeling of the linear optical response of *J*-aggregate microcavity exciton-polariton devices has largely followed the same LDT methods but never using an exact spectrally resolved complex dielectric function.[9,10,17,18] An approximate *J*-aggregate dielectric function was used in fitting the optical spectra of complete devices necessitating that one or multiple artificial "shoulder states" be added to approximate the significant asymmetry of the observed upper branch (UB) and LB exciton-polariton linewidths.[19] In the present study, however, the index of refraction of the *J*-aggregate layer need not be inferred from the complete microcavity device, but rather the Kramers-Kronig derivation is performed on (intensity) reflectance measurements from separate neat thin films. The microcavity exciton-polariton device structures tested in this study are shown in Fig. 1 together with optical probe geometry.

The structures are grown on 14.5-pair distributed Bragg reflectors (DBRs) on SiO_2 (silica) substrates obtained from Visimax Technologies. The DBRs consist of pairs of plasma-enhanced-evaporated TiO_2 (titania) and SiO_2, starting and ending in TiO_2. The bottom microcavity spacer consists of an rf-sputter-deposited layer of SiO_2 of quarter-wavelength thickness $\lambda/4n_{SiO_2}$, at the free-space wavelength $\lambda = 595$ nm, which corresponds to the main exciton resonance of the TDBC *J*-aggregate thin film. Using the ellipsometry-measured index of refraction $n_{SiO_2}(\lambda = 633 \text{ nm}) = 1.456$, the SiO_2 spacer is grown to 102.1 nm thick. The *J*-aggregate thin film is layer by layer (LBL) deposited with the substrate undergoing sequential immersions in cationic and anionic solutions (SICAS). The cationic solution is a 30-mM solution of poly(diallyldimethylammonium chloride) [(PDAC) CAS 26062-79-3 obtained from Sigma Aldrich] in deionized water. The anionic solution is a 50 μM solution of the *J*-aggregating cyanine dye TDBC (CAS 28272-54-0 obtained from Nippon Kankoh Shikiso Kenkyusho Co., Ltd.). The *J*-aggregate thin-film deposition process and the thin-film morphology are detailed in a previous study.[20] For different substrates, the number of SICAS is varied from 4.5 (ending with an immersion in PDAC) to

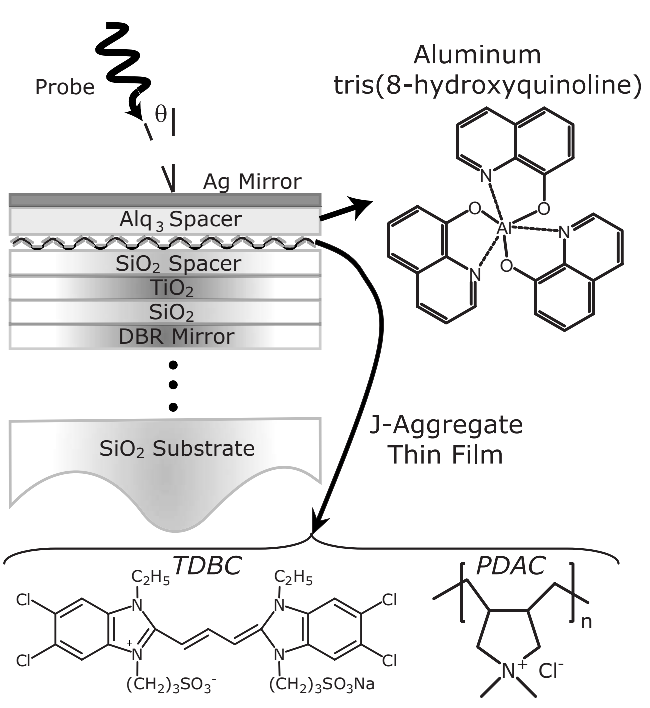

FIG. 1. Device structure and materials. The microcavity mirrors are comprised of a thin silver mirror on the top of the device through which the optical response is probed and a 14.5 pair TiO_2/SiO_2 (titania/silica) DBR. The active layer is a thin (5–12 nm) LBL film of cationic PDAC and anionic *J*-aggregated TDBC. The bottom microcavity spacer is a sputtered SiO_2 film, and the top cavity spacer is an evaporated Alq_3 film.

8.5. The top spacer consists of a thermally evaporated film of Alq_3 [aluminum tris(8-hydroxyquinoline)], a common molecular thin film used in organic light emitting devices. The thickness of Alq_3 depends on the corresponding number of SICAS of *J*-aggregate film, with 61.5, 59, and 56.5 nm used for 4.5, 6.5, and 8.5 SICAS, respectively. Finally, the top semitransparent mirror consists of a 42.5 nm thermally evaporated film of silver.

The optical constants of the TDBC *J*-aggregate thin films used in the exciton-polariton devices are measured on glass microscope slides that underwent the same numbers of SICAS concurrently with the microcavity device DBR/SiO_2 substrates. The reflectivity of these *J*-aggregate films is measured using a Cary 5E UV-Vis-NIR spectrometer and spectral reflectance accessory with film thicknesses based on a previous study of LBL *J*-aggregate thin films.[20] The complex spectrally resolved index of refraction ($\tilde{n}=n+i\kappa$) is then determined using a quasi-Kramers-Kronig regression.[20] The thin-film reflectivity measurements and derived indices of refraction for 4.5, 6.5, and 8.5 SICAS films are shown in Fig. 2(a), where the thicknesses used for the three films are 5.1, 8.5, and 11.9 nm, respectively.

Using the derived indices of refraction for the *J*-aggregate thin films with varying numbers of SICAS, the linear optical response of the complete microcavity exciton-polariton device can be engineered. We use $n_{SiO_2}=1.462$ for the SiO_2 layers, both in the DBR and bottom spacer; $n_{glass}=1.5$ for the substrate; and for the Alq_3 top spacer and TiO_2 layers, we use published indices of refraction.[21,22] The index of refraction for the silver mirror is obtained by interpolating published reference values.[23] The results of our LDT T-matrix simulations and the corresponding reflectivity measurements are shown in Fig. 2(b) in the region of the UB and LB exciton polaritons at an angle of $\theta=7°$.

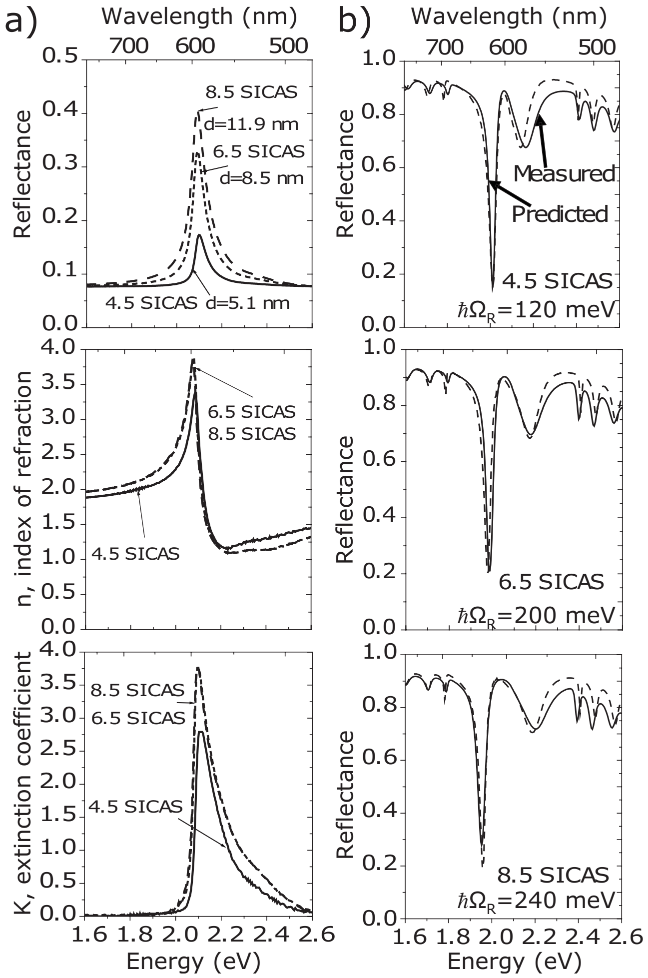

FIG. 2. (a) Thin-film reflectance and real and imaginary (extinction coefficient) parts of index of refraction of *J*-aggregate thin films derived using Kramers-Kronig regression. The film thickness estimates based on a previous study are indicated (Ref. 20). The change in the index of refraction indicates that the dye concentration changes in the film as substrates undergo more SICAS. (b) Comparison of measured and predicted reflectance spectra for complete devices. The predicted reflectance spectra are calculated using the complex indices of refraction and estimated thicknesses along with published dielectric functions for TiO_2 and Alq_3 and n_{SiO_2} $=1.462$ (Refs. 21 and 22).

For the best match between the numerical analysis and the experimental measurements in the T-matrix simulations in Fig. 2, the Alq_3 thicknesses used are 65, 62.5, and 60 nm for the 4.5, 6.5, and 8.5 SICAS samples, respectively. Additionally, a thickness of 32 nm is used for the top silver mirror. The discrepancies of 4.5 nm in the Alq_3 thicknesses and 10.5 nm in the silver thickness are likely due to penetration of the evaporated silver into the Alq_3 layer during growth. Accounting for these discrepancies results in a very good fit of the predicted linear optical response to the measured spectra.

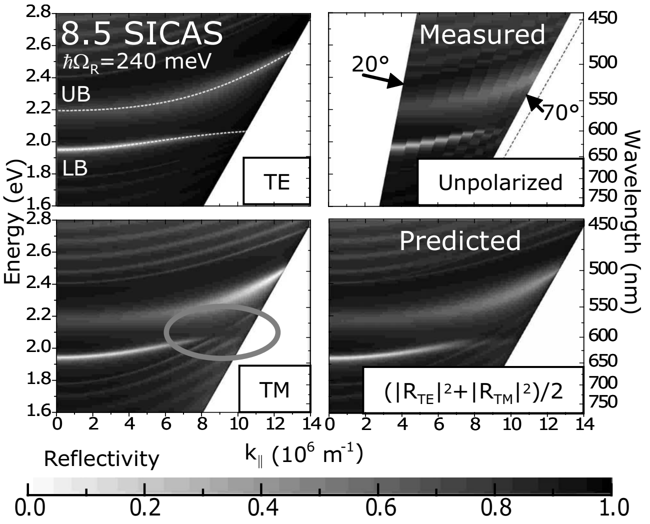

FIG. 3. Predicted reflectivity of 8.5 SICAS device versus in-plane wave vector (i.e., external probe angle) for TE and TM polarization and comparison of measured and predicted unpolarized reflectivity for 8.5 SICAS sample (50% TE and 50% TM). The predictions are calculated using Kramers-Kronig-derived optical constants of the 8.5 SICAS *J*-aggregate active layer shown in Fig. 2(a). The TE-polarized spectrum is shown with a fit to the general two-level-system eigenenergies. In TM polarization, due to the narrowing of the DBR stop band and the large Rabi splitting, the first few Bragg modes of the DBR cross the exciton resonance at large angles (Refs. 24 and 25).

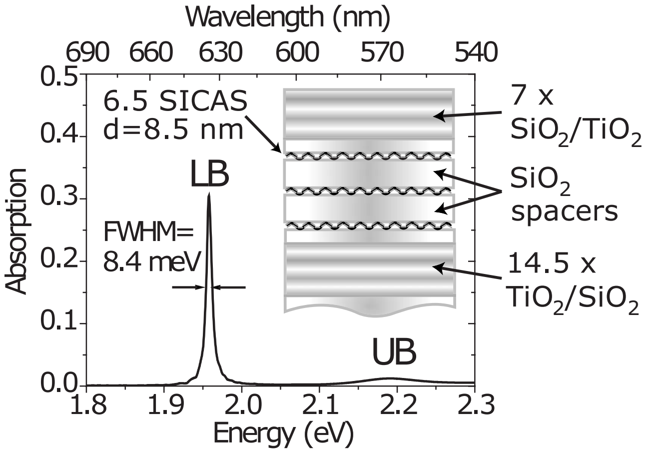

FIG. 4. Simulated absorption spectrum of LB and UB exciton polaritons for device structure in the inset, using dispersion-free SiO_2 spacer layers and the 6.5 SICAS layer properties from Fig. 2(a). With a high-quality microcavity ($Q > 3000$) and large Rabi splitting ($\hbar\Omega_R = 220$ meV) from multiple *J*-aggregate layers at cavity antinodes, a theoretical linewidth of 8.4 meV for the lower branch can be achieved.

With the derived index of refraction for the *J*-aggregate thin film and the quality of the linear optical response fit indicated in Fig. 2, we calculate detailed microcavity exciton-polariton reflectivity dispersion relations for the TE and TM modes of the Fig. 1 devices. The results of these calculations are plotted in Fig. 3 for the 8.5 SICAS sample; the 4.5 and 6.5 SICAS samples show similar results and have been left out for brevity. By comparing the numerically derived TE plot to the eigenenergies of the strongly coupled exciton-microcavity system [given by

$$E_{\pm} = \frac{E_{\text{cav}} + E_{\text{ex}}}{2} \pm \frac{1}{2}\sqrt{(\hbar\Omega_R)^2 + (E_{\text{cav}} - E_{\text{ex}})^2}, \tag{1}$$

where E_+ and E_- are the UB and LB exciton-polariton energies, respectively, E_{cav} and E_{ex} are the cavity and exciton energies, respectively, and Ω_R is the Rabi splitting], we derive the value for the Rabi splitting in each system.[3] The cavity energy versus external angle θ is given by

$$E_{\text{cav}} = \frac{E_{\text{cav}}(\theta = 0)}{\sqrt{1 - \frac{\sin^2\theta}{n^2}}}, \tag{2}$$

where n is the effective cavity index of refraction. For the TE fitting in Fig. 3, $n = 1.7$.

Notably, in the TM dispersion, narrowing of the DBR stop band at large angles results in the first few Bragg modes crossing through the exciton resonance, as previously described by Savona *et al.*[24] and showed in CdTe inorganic microcavities by Richard *et al.*[25]

We measure the unpolarized reflectivity versus angle for the microcavity samples using a Cary variable-angle spectral reflectance accessory to verify the accuracy of our T-matrix-calculated exciton-polariton dispersion relation (see Fig. 3 for the 8.5 SICAS sample data). The predicted reflectivity dispersion relation (for unpolarized light given by assuming 50% TE and 50% TM incident light) shows good agreement with the measured reflectivity, including the splitting of the TE and TM modes at large angle and the crossing of the first few Bragg modes in TM with the *J*-aggregate exciton resonance at $\lambda = 595$ nm.

Finally, by numerically simulating a high-quality factor cavity utilizing multiple *J*-aggregate layers, we can extract a theoretical limit for the lower branch linewidth of devices utilizing the TDBC LBL *J*-aggregate thin films. As demonstrated by Houdre *et al.*,[14] for large values of Rabi splitting, the exciton-polariton resonances are spectrally separated from the inhomogeneously broadened exciton resonance, such that the linewidths of the polariton resonances are determined by the homogeneously broadened tails of the exciton dielectric function. By using dispersion-free spacer layers, three 6.5 SICAS *J*-aggregate layers, and two high-quality DBR mirrors in a simulated cavity shown in the inset of Fig. 4, we calculate the absorption of the structure (plotted in Fig. 4) and find a theoretical LB exciton-polariton linewidth of 8.4 meV (cavity $Q > 3000$ determined by simulating without the *J*-aggregate layers). This linewidth value is two to three times smaller than those used in recent theoretical papers on *J*-aggregate exciton polaritons.[26–29]

We demonstrated that LDT can accurately model the linear optical properties of strongly coupled *J*-aggregate microcavity exciton-polariton devices when the spectrally resolved complex index of refraction is utilized. Using a model-free Kramers-Kronig regression, we accurately determined the *J*-aggregate thin-film index of refraction and combined it with published dielectric functions for the other microcavity device constituents to accurately predict the linear optical response of *J*-aggregate microcavity exciton-polariton devices. Our work demonstrates that the LDT method is a valuable theoretical tool for deriving the minimum exciton-polariton linewidth in *J*-aggregate-based devices, a key parameter for modeling dynamics, and can assist us in the design of the next generation of strongly coupled *J*-aggregate structures that exhibit giant Rabi splitting.

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