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Femtosecond response of J aggregates adsorbed onto silver colloid surfaces

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We have performed femtosecond pump-probe spectroscopy measurements in 1,1'-diethyl-3,3'-bis(4-sulfobutyl)-5,5',6,6'-tetrachlorobenz imidazolocarbocyanine (also known as TDBC) J aggregates adsorbed onto silver colloidal surfaces. We show that the dependence on probe power and wavelength of the induced emission band dynamics, intensity, and position can only be explained by assuming stimulated emission from the one-exciton state. The stimulated emission originates from the amplification of the one-exciton state emission by an induced transition from the two-exciton state to the one-exciton state. One of the key causes of the stimulated emission is the formation of coherently coupled TDBC molecules on colloidal silver surfaces. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1597941]

I. INTRODUCTION

Molecular aggregates are formed by self-assembly of molecules, which are bound to each other by noncovalent interactions. Optical materials derived from molecular aggregates are widely used as spectral sensitizers in photography,[1] and as optical probes measuring mitochondrial membrane potential and detecting apoptosis (controlled cell death) in living cells.[2,3] Moreover, molecular aggregates play a crucial role in nature: light harvesting and the primary charge-separation steps in photosynthesis are facilitated by aggregated species.[4] Current consensus is that all of these features arise from the formation of excitons. In J aggregates a few molecules are coherently coupled, thus resulting in quantum confinement of the states, and form a coherent size. However, the physical size of the J aggregates may consist of thousands of coherent sizes. The physical structure is in the micrometer scale while the coherent size is anticipated to be in nanometers. The coherent size—the number of molecules coherently responding to the external optical field—is responsible for the linear and nonlinear optical properties.

J aggregates exhibit intriguing optical and spectral properties such as super radiant emission,[5–9] ultrafast optical switching,[10] electroluminescence,[11] strong exciton-photon coupling,[12] superquenching of fluorescence for biosensing applications,[13] and mirrorless optical bistability.[14] These attractive features make J aggregates very promising nanoscale materials for future technological applications.

Understanding excited-state dynamics is very important for any device application utilizing J aggregates as optical material. Our aim is to study the excited-state mechanisms which govern the photon emission process. The resolution of this issue should eventually help in the engineering and fabrication of optical devices such as J-aggregate based light emitting diodes covering the whole visible region. We report the observation of stimulated emission from J aggregates adsorbed onto silver colloid surfaces using femtosecond excitation. The stimulated emission is inferred from the excitation intensity and wavelength dependence of the emission band.

II. EXPERIMENT

Sodium salt of 1,1'-diethyl-3,3'-bis(4-sulfobutyl)-5,5',6,6'-tetrachlorobenzimidazolocarbocyanine (TDBC, see bottom of Fig. 1 for the structure) was purchased from Molecular Probes Inc., Eugene, OR, and used without further purification. Colloidal silver suspensions were prepared by reduction of $AgNO_3$ with $NaBH_4$. Then 0.3 ml of 5 mM of $AgNO_3$ was drop wise added into 10 mM of 49.7 ml of $NaBH_4$ under vigorous stirring in an ice bath. The resulting silver solution had an absorption peak at 384 nm, and was stable for several weeks. J aggregates are prepared by mixing 6 ml of 1 mM TDBC in methanol with 25 ml of aqueous silver colloid solution.

The output of a Spectra-Physics optical parametric amplifier at 587 nm was used as the pump beam. A white light continuum generated by focusing an amplified femtosecond pulse into a 2-mm-thick sapphire plate was used as the probe beam.[15] A fiber optic spectrometer with two channels is used to detect optical signals. The pump and probe beams were spatially overlapped onto a 2-mm-thick flowing cell. Transient transmission signal $T(\lambda,t) = \{[I_T(\lambda,t) - I_{TB}(\lambda)]/[I_R(\lambda,t) - I_{RB}(\lambda)]\}$ and reference signal $R(\lambda,t) = \{[I_R(\lambda,t) - I_{TB}(\lambda)]/[I_R(\lambda,t) - I_{RB}(\lambda)]\}$ without the pump pulse were recorded in appropriate chan-

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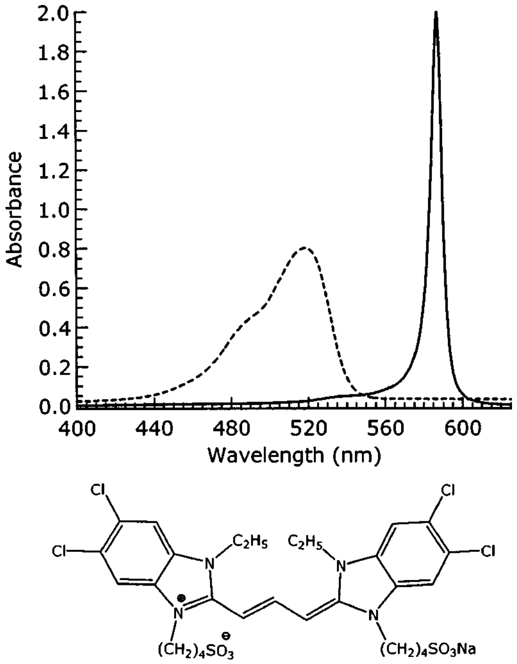

FIG. 1. Absorption spectra of TDBC monomer in methanol and J aggregates adsorbed onto silver colloid surfaces. The spectral bandwidth of J aggregates is approximately 200 cm^{-1} at room temperature. Chemical structure below the spectra is that of TDBC.

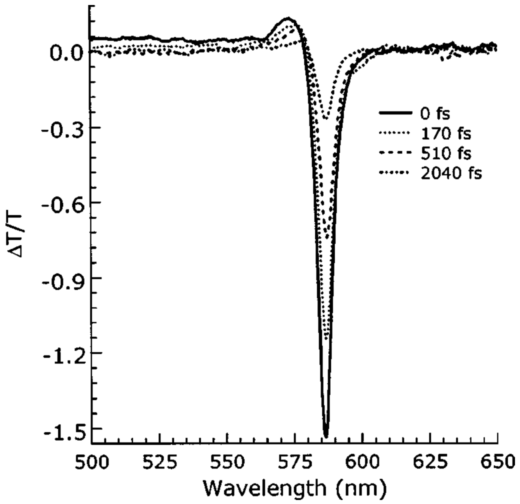

FIG. 2. Representative time-resolved differential transmission spectra at various delay times. The excitation wavelength was 587 nm with a spectral bandwidth of 12 nm (290 cm^{-1}), which completely covers the linear absorption band of the J aggregates. The pump and probe intensities were 1.4×10^{15} and 8×10^{11} photons/cm^2, respectively. The pulse width was 150 fs.

nels of the spectrometer. Here, $I_T(\lambda,t)$, $I_R(\lambda,t)$, $I_{TB}(\lambda)$, $I_{RB}(\lambda)$ are, respectively, the transient transmission, the transient reference, the reference transmission, and the reference background spectra. The differential transmission spectra were measured as $\Delta T/T=[T(\lambda,t)-R(\lambda,t)]/R(\lambda,t)$. The contribution of the steady-state fluorescence and very strong linear absorption of the J aggregate to the normalized differential absorption spectra were minimized. These two effects are independent of the time overlap of the pump and the probe pulses. A reference spectrum was taken when both pump and probe pulses were present and when the probe pulse preceded the pump pulse by approximately 2 ns. No signal was observed when the probe pulses preceded the pump pulses. A transient absorption signal appeared when both pulses overlapped in time. This procedure ensured that the linear absorption and steady-state fluorescence emission caused by the pump and the probe pulses did not affect the differential absorption spectrum. It also enabled us to detect only the time-delay dependent absorption or emission caused by the sample. In addition, after every change of the probe intensity a new reference spectrum was stored. Therefore, an increase in the probe power did not change the signal in the absence of the delay-dependent emission.

III. RESULTS AND ANALYSIS

Figure 1 shows the absorption spectrum of the TDBC J aggregate adsorbed on silver colloid surfaces together with the absorption spectrum of the monomer in methanol. The monomer peak position is located at $\sim$520 nm. The absorption peak of the J aggregate is shifted to 587 nm with a bandwith of 6.8 nm (200 cm^{-1} or 24 meV) at room temperature. The redshift of the J-aggregate absorption is due to the delocalization of the electronic excitation caused by dipole–dipole interactions between TDBC molecules. The very narrow bandwidth at room temperature is an indication of a well ordered structure of the aggregate on the colloid surface. The silver colloid surfaces provide a suitable environment for the nucleation and growth of TDBC molecules to form J aggregates. The absence of the monomer absorption band suggests that almost all of TDBC molecules are part of the J aggregates.

Figure 2 represents a series of differential pump-probe transmission spectra for various femtosecond time delays. Near zero delay, a typical pump-probe spectrum for the TDBC J aggregate shows a negative signal centered about 587 nm, and a blueshifted positive signal at 573 nm. The blueshifted signal, an induced absorption (an excited-state absorption), is assigned to a transition from the one-exciton state to the two-exciton state.[16–22] The blueshift is the result of Pauli exclusion of double excitation of a single molecule on the aggregate and exciton–exciton interactions.[20–22] The origin of the shift was also proposed to be the relocation of the counter ion of the chromophore following the optical excitation.[23] The strong negative signal at 587 nm (indicating strong transmission and/or induced emission) has been previously observed[16–20] and can be attributed to strong bleaching due to the depletion of the ground state and the stimulated emission caused by optical pumping at 587 nm. However, we will show that the dynamics and power dependence of this band suggest that it partly originates from the stimulated emission of the one-exciton state.

Figure 3 shows the femtosecond response of the induced emission and induced absorption signals as a function of delay time delay between the pump and probe pulses. Both signals exhibit a bi-exponential decay with time constants of 430 fs and 2.50 ps for the induced emission signal at 587 nm, and 670 fs and 4.75 ps for the induced absorption signal at 573 nm. The femtosecond decay is, in general, ascribed to

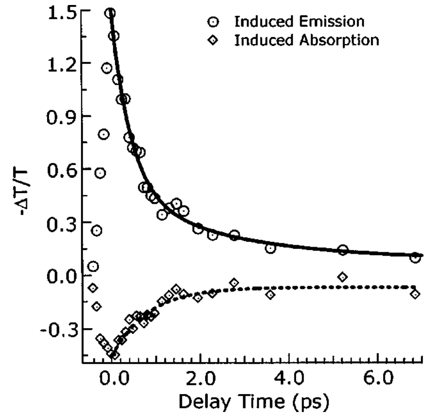

FIG. 3. Femtosecond optical response of the induced emission and absorption signals as a function of delay time. The pump and probe intensities were 1.4×10^{15} and 8×10^{11} photons/cm^2, respectively. The pulse width was 150 fs.

the relaxation of the two-exciton state; while the picosecond decay is attributed to the exciton–exciton annihilation.[16–19] The bi-exponential decay times firmly indicate exciton–exciton interactions resulting in annihilation/amplification processes. These processes compete with each other to determine the outcome of emission from the J aggregates. In this scenario, the dynamics of each process is critical: since the relaxation of the two-exciton state (1/430 fs) to the one-exciton state is much faster than the annihilation rate (1/2.50 ps), the outcome could be the amplification of the photons.

The mechanism for the stimulated emission from J aggregates could be the following: a photon arising from an excitonic transition from the two-exciton state to the one-exciton state stimulates the emission of the one-exciton band. The pump pulse at 587 nm populates the one-exciton state and part of the white light continuum at 573 nm causes a transition from the one-exciton state to the two-exciton state. If the two- to one-exciton transition stimulates the one-exciton state emission, any increase of the two-exciton state population should result in an amplification of the one-exciton emission, i.e., the stimulated emission. The two-exciton state can be populated by increasing the probe or pump pulse power. When the probe power is increased, one does not expect to observe an increase in the induced emission band around 587 nm unless the mechanism described above is correct. This observation could be an unambiguous indication of the stimulated emission from J aggregates. To demonstrate that the optical signal at 587 nm includes a contribution from the stimulated emission we have performed pump-probe experiments at different probe power while keeping the pump power constant.

Figure 4(a) shows the excitation intensity dependence of the induced emission signal for different probe (white light continuum) powers at zero time delay. The negative signal around 587 nm as a function of probe power is shown to increase about ninefold without saturation. It is important to recall the data acquisition procedure: after changing the probe intensity, a new reference spectrum was stored, which eliminates the amplification of the steady-state fluorescence contribution due to an increase in probe power. Therefore, an increase in the probe power solely represents the time-dependent emission. This strong stimulated emission is observed in TDBC J aggregates adsorbed onto colloidal surfaces at room temperature but not in aqueous solutions under the same conditions. This implies that colloidal surfaces are one of the key factors to observe the stimulated emission.[16–19,24] It is also possible to populate the two-exciton state by direct excitation by increasing pump power. For this experiment the pump power was varied while the probe power was maintained unchanged. As seen in Fig. 4(b), the intensity of the induced emission band around 587 nm rapidly reaches saturation. This is expected for a high pump power since the one-exciton band is rapidly fully populated because of the long lifetime of the one-exciton state (several picoseconds).[18,24] On the other hand, an increase in the probe power does not saturate the two-exciton state due to very short lifetime of the two-exciton state compared to the one-exciton state. These experiments strongly confirm that the stimulated emission from J aggregates involves the interactions of the multi-exciton states.

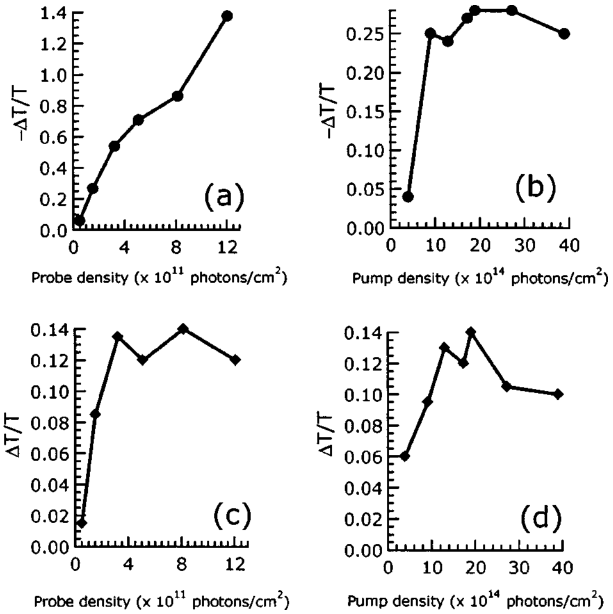

FIG. 4. The excitation-intensity dependence of the induced emission signal (a) and (b) and the induced absorption signal (c) and (d) at zero femtosecond delay time. The excitation intensity for the curves in (a) and (c) was 1.2×10^{15} photons/cm^2. The excitation intensity for the curves in (b) and (d) was 1.0×10^{12} photons/cm^2.

The excitation intensity dependence of the induced absorption is quite different from the induced emission. The two-exciton state lifetime is expected to be in subpicoseconds while the one-exciton state is in picoseconds. As a result, the population of the one-exciton state is always large resulting in a relatively steady exciton density for the induced absorption process. The induced absorption should not increase when either the pump or probe power is increased. Therefore, one should not expect any enhancement of the induced absorption signal when the pump or the probe is increased. Figures 4(c) and 4(d) strongly confirm this expectation.

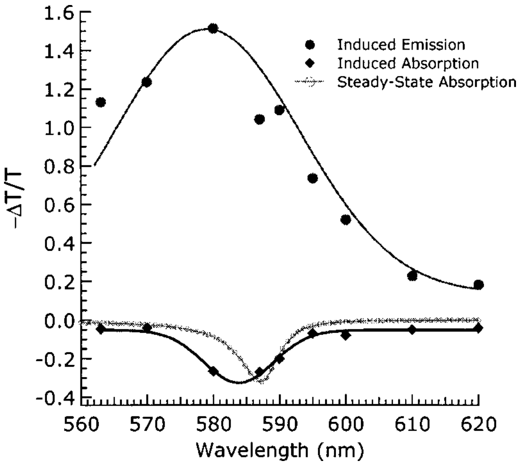

FIG. 5. The pump-wavelength dependence of the induced absorption and emission signals. The pump and probe intensities were 8×10^{14} and 6×10^{11} photons/cm^2, respectively. The spectral bandwidth of the pump beam was 12 nm. Steady-state absorption (rescaled) is included for comparison. The lines are Gaussian functions for fitting the experimental measurements.

The wavelength dependence of the induced emission and induced absorption bands is plotted in Fig. 5. The spectra were measured at the time-delay position corresponding to maximum in intensity of the induced emission. Interestingly, the maximum of the induced emission band appears at 580 nm instead of 587 nm, which is the maximum of the linear absorption. When the excitation wavelength is shifted blue the pump beam not only populates the one-exciton band, but also populates the two-exciton band by a transition originating from the one-exciton state. This is because the energy difference between the two- and the one-exciton states (at 17 241 cm^{-1}) is slightly higher than that of the one-exciton state and the ground state (at 17 035 cm^{-1}). Thus, the pump wavelength at 580 nm provides an increase in the transmitted signal. This finding strongly confirms our conclusion that the transmitted signal is due to the stimulated emission that arises from the amplification of the emission of the one-exciton state by the transition from the two-exciton state to the one-exciton state. It also explains the appearance of very asymmetric intensities of the bands, as seen in Fig. 2.

IV. CONCLUSION

We have reported the results of femtosecond pump-probe spectroscopy of TDBC J aggregates adsorbed onto silver colloidal surfaces. We have shown that the induced emission band about 587 nm is likely due to stimulated emission of the one-exciton state. The stimulated emission originates from the amplification of the one-exciton state emission by the transition arising from the two-exciton state to the one-exciton state. These results confirm earlier observations suggesting the possibility of an optical material composed of J aggregates emitting mirrorless laser-like emission with extremely low optical excitation threshold.[6,7]

ACKNOWLEDGMENTS

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[1] P. B. Gilman and W. West, in *Theory of the Photographic Process*, edited by T. H. James (Macmillan, New York, 1977), p. 277.
[2] S. Smiley, M. Reers, C. Mottola-Hartshorn, M. Lin, A. Chen, T. W. Smith, G. D. Steele, Jr., and L. B. Chen, Proc. Natl. Acad. Sci. U.S.A. **88**, 3671 (1991).
[3] S. Salvioli, A. Ardizzoni, C. Franchesci, and A. Cossarizza, FEBS Lett. **411**, 77 (1997).
[4] R. M. Pearlstein, in *Photosynthesis* (Elsevier, Amsterdam, 1987), p. 299.
[5] S. Özçelik and D. L. Akins, J. Phys. Chem. B **103**, 8926 (1999).
[6] S. Özçelik, I. Özçelik, and D. L. Akins, Appl. Phys. Lett. **73**, 1946 (1998).
[7] S. Özçelik and D. L. Akins, Appl. Phys. Lett. **71**, 3057 (1997).
[8] H. Fidder, J. Knoester, and D. A. Wiersma, Chem. Phys. Lett. **171**, 529 (1990).
[9] F. C. Spano and S. Mukamel, J. Chem. Phys. **91**, 7988 (1989).
[10] Y. Sato, M. Furuki, M. Tian, I. Iwasa, L. S. Pu, and S. Tatsuura, Appl. Phys. Lett. **80**, 2254 (2002).
[11] E. I. Mal'tsev, D. A. Lypenko, B. I. Shapiro, M. A. Brusentsave, G. H. W. Milburn, J. Wright, A. Hendriksen, V. I. Berendtaev, B. V. Kotov, and A. V. Vannikov, Appl. Phys. Lett. **75**, 1896 (1999).
[12] D. G. Lidzey, D. D. C. Bradley, A. Armitage, S. Walker, and M. S. Skolnick, Science **288**, 1620 (2000).
[13] R. M. Jones, L. Lu, R. Helgeson, T. S. Bergstedt, D. W. McBranch, and D. G. Whitten, Proc. Natl. Acad. Sci. U.S.A. **98**, 14769 (2001).
[14] H. Glaeske, V. A. Malyshev, and K.-H. Feller, J. Chem. Phys. **114**, 1966 (2001).
[15] G. Yağlioğlu, Ph. D. thesis, City University of New York, 2000, pp. 44–46.
[16] A. Johnson, S. Kumazaki, and K. Yoshihara, Chem. Phys. Lett. **211**, 511 (1993).
[17] K. Misawa, K. Minoshima, H. Ono, and T. Kobayashi, Chem. Phys. Lett. **218**, 67 (1994).
[18] M. Van Burgel, D. A. Wiersma, and K. Duppen, J. Chem. Phys. **102**, 20 (1995).
[19] H. Kano and T. Kobayashi, J. Chem. Phys. **116**, 184 (2002).
[20] F. C. Spano, Chem. Phys. Lett. **220**, 365 (1994).
[21] F. C. Spano, Chem. Phys. Lett. **234**, 29 (1995).
[22] H. Fidder, J. Knoster, and D. A. Wiersma, J. Chem. Phys. **98**, 6564 (1993).
[23] K. Misawa, K. Minoshima, H. Ono, and T. Kobayashi, Chem. Phys. Lett. **220**, 251 (1994).
[24] S. Özçelik and D. L. Akins, unpublished study based on excitation intensity dependent measurements of fluorescence lifetimes of TDBC and BIC J aggregates in aqueous solutions.