is concluded that we are observing the combined contributions of increasing k_r and decreasing k_{nr} .

The wavelengths of the absorption maximum of the J-band in samples of 40 and 70 °C agitation are 645 and 652 nm, respectively, corresponding to transition energies of 1.92 and 1.90 eV. This small difference of 0.02 eV, which might potentially be translated into a size-dependent ΔE , is too small, however, to explain the observed change of k_s , as can be seen from the energy gap dependence shown in Figure 2.

The mechanism of exciton-tapping supersensitization^{41,42} as-

(41) West, W.; Caroll, B. H. J. Chem. Phys. 1947, 15, 529.

sumes that k_s decreases with increasing aggregate size. Terminal molecules of a given aggregate act as traps for the highly mobile excitons and enhance the probability of electron injection into the conduction band of silver halide (AgX) to give (AgX)⁻ and $(dye)_n^+$. It is therefore considered that the observed decrease in $k_{\rm s}$ with aggregate size supports the mechanism of the excitontrapping supersensitization.

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(42) West, W.; Caroll, B. H. J. Chem. Phys. 1951, 19, 417.

Size Dependence of Excited-State Dynamics for J-Aggregates at AgBr Interfaces

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The dependence of fluorescence lifetime and relative quantum yield on temperature and aggregate size has been investigated for the J-aggregate of pseudoisocyanine (PIC) on an AgBr surface, varying the average physical size of the aggregate in a statistical sense by diluting it with a close structural analogue. The dominant feature controlling the excited-state dynamics is found to be energy transfer to a defect state which is nonradiative at room temperature. The rate of this transfer process increases with aggregate size. At large aggregate sizes, a weak superradiant enhancement of the J-aggregate radiative rate is also observed, with a temperature dependence which suggests strong coupling of the J-aggregate exciton to a low-frequency phonon. Since both the energy transfer to the defect state and the radiative decay compete with the desired process of electron transfer from the aggregate excited state to the AgBr conduction band, the sensitizing efficiency of the J-aggregate is expected to decrease with increasing aggregate size. Measurement of this size-dependent sensitizing efficiency shows a smaller loss than expected, indicating that the electron-transfer rate from the aggregate excited state to the AgBr conduction band increases with increasing aggregate size.

Introduction

The excited-state dynamics of J-aggregated dyes are of interest for many reasons. These aggregates, originally identified in the 1930s by Scheibe¹ and Jelley,² exhibit an intense excitonic absorption band which is red-shifted and narrowed relative to the monomer absorption. In the field of photography, J-aggregates of cyanine dyes are extensively used as sensitizing dyes³ for silver halide materials. For this application, the narrow line widths of these aggregates and their tendency to adsorb strongly to the silver halide surface up to monolayer coverages make them particularly useful. In addition, much recent interest has centered on the ability of J-aggregates to exhibit coherent excitation phenomena and the possibility that such effects might give strongly enhanced nonlinear optical properties.4

Examination of the radiative dynamics of dye aggregates has led to the concept of an effective coherence size, $N_{\rm eff}$, for the aggregate.⁵⁻⁷ Molecules within the coherence size are closely coupled and respond in phase to the external optical field. As a result, the radiative decay rate is increased by a factor $N_{\rm eff}$, giving superradiance, and enhanced optical nonlinearities may result. In a perfect, rigid aggregate, the coherence size is limited only by the number of molecules contained within the dimension defined by the wavelength of the exciting light.⁸ Calculations by Spano et al.⁷ have shown that exciton-phonon coupling decreases the coherence size, resulting in a dependence of this size on the coupling strength, the phonon bandwidth, and the aggregate temperature. For small aggregates, $N_{\rm eff}$ also depends on the

aggregate physical size, N, but as N increases, a convergent, size-independent value of $N_{\rm eff}$, N^* , is reached. Spano and Mukamel⁹ also determined that static inhomogeneous broadening can limit the value of the coherence size for the rigid aggregate, an effect which has been further investigated by Wiersma and coworkers.^{10,11} In this case, the parameter controlling the extent of the limitation is σ/V , where σ is the width of the inhomogeneously broadened transition and $\hbar V$ is the intermolecular dipole-dipole coupling energy. Early measurements¹²⁻¹⁵ of the fluorescence decay kinetics of

J-aggregates formed in solution gave very short lifetimes, on the order of a few picoseconds. However, later investigations^{16,17} have

- (1) Schelbe, G. Angew. Chem. 1956, 49, 563.
 (2) Jelley, E. E. Nature 1936, 138, 1009.
 (3) West, W.; Gilman, P. B., Jr. In The Theory of the Photographic Process; 4th ed.; James, T. H., Ed.; Macmillan: New York, 1977; p 251.
 (4) Spano, F. C.; Mukamel, S. Phys. Rev. A 1989, 40, 5783.
 (5) Möbius, D.; Kuhn, H. Isr. J. Chem. 1979, 18, 375.
 (6) Möbius, D.; Kuhn, H. J. Appl. Phys. 1988, 64, 5138.
 (7) Spano, F. C.; Kuklinski, J. R.; Mukamel, S. J. Chem. Phys. 1991, 94, 7534.
- 7534.
- (8) Grad, J.; Hernandez, G.; Mukamel, S. Phys. Rev. A 1988, 37, 3838. (9) Spano, F. C.; Mukamel, S. J. Chem. Phys. 1989, 91, 683.
 (10) Fidder, H.; Terpstra, J.; Wiersma, D. A. J. Chem. Phys. 1991, 94,

[†] University of Rochester. [‡]Eastman Kodak Co.

⁽¹⁾ Scheibe, G. Angew. Chem. 1936, 49, 563.

⁶⁸⁹⁵

⁽¹¹⁾ Fidder, H.; Knoester, J.; Wiersma, D. A. J. Chem. Phys. 1991, 95, 7880.

⁽¹²⁾ Fink, F.; Klose, E.; Teuchner, K.; Dähne, S. Chem. Phys. Lett. 1977, 45, 548.

⁽¹³⁾ Rentsch, S. K.; Danielius, R. V.; Gadonas, R. A.; Piskarkas, A. Chem. Phys. Lett. 1981, 84, 446.

⁽¹⁴⁾ Kopainsky, B.; Kaiser, W. Chem. Phys. Lett. 1982, 88, 357.

⁽¹⁵⁾ Yu, Z. X.; Lu, P. Y.; Alfano, R. R. Chem. Phys. 1983, 79, 289. (16) Brumbaugh, D. V.; Muenter, A. A.; Knox, W.; Mourou, G.; Wittmershaus, B. J. Lumin. 1984, 31, 783.

[§]Temple University.

determined that exciton-exciton annihilation causes the excitedstate relaxation of these aggregates to be intensity dependent. Under appropriately low excitation intensity, aqueous solutions of pseudoisocyanine (PIC) J-aggregates have fluorescence lifetimes of several hundred picoseconds at room temperature. Convincing experimental confirmation of the superradiance of these aggregates is found in the detailed temperature-dependence studies of DeBoer and Wiersma¹⁸ on PIC J-aggregates in an ethylene glycol/water glass. Their results, which show fluorescence liftimes of 40 and 70 ps at temperatures below 50 K and linear increases in lifetime at higher temperatures, have been fit by Spano et al.¹⁹ to the exciton-phonon coupling formalism referenced above. Fluorescence decays of J-aggregates adsorbed to surfaces generally have shown shorter room-temperature lifetimes than the solution aggregates. Dorn and Müller²⁰ measured a lifetime of 8.2 ps for a Langmuir-Blodgett monolayer of PIC J-aggregate at room temperature and interpreted the decrease in this lifetime to 5.5 ps at 143 K as evidence for superradiant enhancement. Recent work by Fidder et al.¹⁰ supports a short lifetime, ~ 10 ps, for these monolayer J-aggregates at 1.5 K. However, both these studies lack the data on fluorescence yield which are required to confirm that the short lifetime is a result of superradiant enhancement. Investigations by Kemnitz et al.²¹ have also shown fluorescence lifetimes for a thiacarbocyanine J-aggregate adsorbed to AgBr or SiO₂ microcrystals to be quite short, 5-25 ps at room temperature. Data on fluorescence yield are also lacking for these studies.

While the theoretical studies predict a dependence of the Jaggregate radiative rate on aggregate physical size, particularly for small aggregates, little experimental data are available to confirm this prediction. From the differences in radiative decay rate, DeBoer and Wiersma¹⁸ inferred a difference in size between the two PIC J-aggregates observed in ethylene glycol/water glass but had no independent evidence for the size difference. By increasing the temperature of dyeing the AgBr microcrystals, Kemnitz et al.²¹ produced an increase in the thiacarbocyanine J-aggregate size and observed an intriguing decrease in fluorescence lifetime. We have recently described an approach for achieving a broad range of statistical size variation for PIC Jaggregates on AgBr by diluting the aggregates with a close structural analogue.22

In this paper we report the effect of this size variation on the excited-state dynamics of PIC J-aggregates adsorbed to AgBr. Fluorescence lifetimes and relative quantum yields are determined for the size series at room temperature and temperatures to 90 K. Evidence for superradiance is examined, and the importance of other factors controlling the excited-state dynamics is discussed. In the process of dye sensitization of silver halide, processes (such as superradiance) which increase the rate of deactivation of the dye excited state are undesirable, since these processes compete with electron transfer from the excited dye to the silver halide conduction band. Consequently, the effect of the size variation on the sensitizing efficiency of the PIC J-aggregates is also investigated.

Experimental Section

The dye 1,1'-diethyl-2,2'-cyanine p-toluenesulfonate (PIC) and its azacyanine analogue were synthesized in the Dye Research Laboratory of Eastman Kodak Company. Structures for these dyes are shown in Figure 1. The silver bromide microcrystalline dispersion was prepared by double-jet addition²³ of aqueous AgNO₃ and NaBr solutions to a gelatin solution at 68 °C with silver ion activity controlled to produce octahedral crystals of



Figure 1. Structures of the dye PIC and of its azacyanine analogue.

narrow size distribution and average grain volume of 0.026 μ m³ (octahedral edge length 0.38 μ m). After removal of soluble salts and addition of gelatin and water, portions of the dispersion were dyed with premixed dilute methanolic solutions of PIC and azacyanine at 40 °C. The temperature of the melts was raised to 60 °C and held for 20 min. After return to 40 °C, the melts received spreading agent (surfactant) and were coated on a poly(ethylene terephthalate) film base at coverages of 0.54 or 1.08 g of Ag/m^2 and 2.16 g of gelatin/m². The total dye added to each melt was constant at 60% of the amount of PIC required to form a monolayer on the crystal surfaces.

The 0.38-µm AgBr octahedral size was chosen to be large enough to allow photographic measurements to be made at reasonable exposure times (see below). However, as a result of the microcrystal size, the coatings are highly turbid in the visible region of the spectrum. For such samples, the quantity of light absorbed at any given wavelength is measured as the absorptance A = 1-T - R, where T is the total transmittance and R is the total reflectance.²⁴ To obtain the absorptance spectra, the coatings were placed in the integrating sphere of a Diano Match-Scan spectrophotometer in order to directly measure A as a function of wavelength. The spectral bandpass of the instrument was 10 nm

Fluorescence spectra were measured in a Spex Fluorolog 222 spectrofluorometer, using front surface excitation. To minimize effects from reabsorption of fluorescence emission, samples at the 0.54 g of Ag/m² laydown were used for PIC concentrations above 0.25 mole fraction, while the higher Ag laydown coatings were used for the lower PIC concentrations. Room-temperature relative fluorescence quantum yields for PIC concentrations from 0.125 to 1.0 mole fractions were determined by integrating the corrected fluorescence spectra obtained with 530-nm excitation, subtracting the integrated background emission from an undyed sample excited under the same conditions, and dividing the result by the absorptance at 530 nm. For PIC concentrations below 0.125 mole fraction, the 530-nm absorptance became difficult to measure directly. Consequently, fluorescence yields were measured using two different methods. In the first method, fluorescence was excited at 530 or 500 nm. (For the lowest concentration samples, 500-nm excitation was required to obtain the envelope of the fluorescence spectrum free of scattered light.) Yields were calculated as described above except that the values for the absorptance were extrapolated from the absorptance values for higher concentration samples. In the second method, yields were determined using 420-nm excitation. This wavelength excites the azacyanine dye, which then transfers the bulk of its excitation energy to the PIC. As a result, ϕ_f^{b} , the relative PIC fluorescence yield observed for 420-nm excitation, is given by $\phi_f^{b} = \phi_f \phi_f$, where ϕ_t is the yield of energy transfer from the azacyanine to the PIC and ϕ_f is the relative fluorescence yield for direct excitation. The relative yield $\phi_{\rm f}^{\rm b}$ of PIC emission for 420-nm excitation was calculated by the procedure used for the 530-nm excitation. The yield of energy transfer ϕ_t from the azacyanine to the PIC was

⁽¹⁷⁾ Sundstrom, V.; Gillbro, T. J. Chem. Phys. 1985, 83, 2733.
(18) DeBoer, S.; Wiersma, D. A. Chem. Phys. Lett. 1990, 165, 45.
(19) Spano, F. C.; Kuklinski, J. R.; Mukamel, S. Phys. Rev. Lett. 1990,

^{65, 211.} (20) Dorn, H.-P.; Müller, A. Appl. Phys. B 1987, 43, 167

 ⁽²¹⁾ Kemnitz, K.; Yoshihara, K.; Tani, T. J. Phys. Chem. 1990, 94, 3099.
 (22) Spano, F. C.; Kuklinski, J. R.; Mukamel, S.; Brumbaugh, D. V.;

Burberry, M.; Muenter, A. A. Mol. Cryst. Liq. Cryst. 1991, 194, 331.
 (23) Berry, C. R.; Skillman, D. C. Photogr. Sci. Eng. 1962, 6, 159

⁽²⁴⁾ Herz, A.; Danner, R.; Janusonis, G. In Adsorption from Aqueous Solution; Weber, W. J. Jr., Matijevic, E., Eds.; Advances in Chemistry 79; American Chemical Society: Washington, DC, 1968.

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then determined from the quenching of the azacyanine fluorescence and this value of $\phi_{\rm t}$ used to determine $\phi_{\rm f}$ from $\phi_{\rm f}^{\rm b}$. The results using these two methods gave relative values for $\phi_{\rm f}$ which agreed within 10%. This agreement indicates that the yields measured with 420-nm excitation were not significantly distorted by quenching of the azacyanine fluorescence from charge transfer to the PIC

Although light exposure of the samples was minimized by attenuating the excitation beam to the minimum practical intensity, small decreases in fluorescence emission occurred as the samples were illuminated. These decreases were measured by monitoring the intensity of the emission peak as a function of exposure time for freshly exposed samples. The decrease in intensity after 50 s of exposure (about half the time required for a full fluorescence scan) varied from 1-2% decreases for the lowest PIC concentrations to 20-30% decreases for the highest concentrations. A correction factor of the initial fluorescence intensity divided by the intensity at 50 s was applied to all the room-temperature fluorescence yields to compensate for this effect. After all corrections were applied, the relative yields obtained were referenced to the yield for the 0.005 mole fraction PIC sample, assigned a value of 1.0 at room temperature for the purposes of Table II and a value of 0.87 at room temperature for the purposes of Table III (see below). Values of these room-temperature relative fluorescence yields are estimated to be accurate to $\pm 15\%$.

Measurements of fluorescence vield as a function of temperature employed a Janis liquid nitrogen cryostat capable of temperatures between 90 and 300 K. Yields were measured relative to roomtemperature yields by one of two methods. For the low-concentration PIC samples (0.125 mole fraction and below), a single sample was cooled to 90 K, warmed to 150, 210, and 270 K, and then cooled again to 90 K, with emission spectra recorded at each temperature. Reproducibility of the two 90 K runs was used as a measure of a successful determination. The excitation wavelength for these samples was 500 nm. For PIC samples of 0.25 mole fraction and above, problems with exposure-dependent decreases in intensity led to poor reproducibility of the integrated intensities for the two 90 K runs. As a result, fresh samples were used for each temperature and only the 90 and 270 K temperatures were studied quantitatively. For these samples, the excitation wavelength was 530 nm. Integrated intensity values were corrected for changes in intensity with exposure by multiplying by the ratio of the fluorescence peak intensity as the spectrum was initially scanned to the intensity of this peak at the end of the scan. At each temperature, the yield of a coating of $3.4 \times 10^{-10} \text{ mol/m}^2$ Rhodamine B in 10.8 g of gelatin/m² was used as an internal reference. In both single- and multiple-sample methods, relative yields were determined by integrating the emission, subtracting the integrated background emission from an undyed sample, and dividing by the absorptance at the excitation wavelength. The absorptance at 90 K was estimated from the room-temperature values by assuming that the integrated absorptance in the region of the PIC light absorption remained constant with temperature and that the excitation spectrum in this region mirrored the absorptance. The 90 K absorptance at the excitation wavelength was then calculated by comparing 90 K and room-temperature determinations of the ratio between the intensity value for this wavelength in the excitation spectrum and the integrated intensity of the excitation spectrum in the PIC region. With this method, changes in absorptance with temperature were judged to be small, in a range between 0 and 20%. In these temperature-dependence studies, the fluorescence yield of the 0.005 mole fraction PIC sample was found to decrease by 0.87 as temperature was increased from 90 to 270 K. Consequently, for the comparisons in Table III, the low-temperature fluorescence yield of this sample was assumed to be 1.0, giving a room-temperature yield of 0.87. For the data in Table III, values of the low-temperature fluorescence yields are estimated to be accurate to $\pm 25\%$ relative to each other and relative to their corresponding room-temperature vields

mode-locked argon ion laser coupled to a synchronously-pumped cavity-dumped rhodamine dye laser capable of producing 10-ps pulses at 3.8 MHz from 530 to 640 nm. The excitation intensity at the sample was below 10⁸ photons cm⁻² pulse⁻¹. Fluorescence was detected through a 10-nm bandpass interference filter by a Hamamatsu Model R2809U-01 microchannel plate photomultiplier tube operated at 3200 V. The signal was amplified with two ENI 600 P amplifiers and sent to a Tennelec Model 455 constant-fraction discriminator. A photodiode (Optoelectronics Model PD30) laser reference, time delay, time-to-amplitude converter, biased amplifier, multichannel analyzer, and laboratory computer completed the apparatus. The observed decays were analyzed in terms of sums of exponential decays by an iterative convolution and nonlinear least-squares fitting program employing Marquardt's algorithm.²⁵ The full width at half-maximum of the instrumental response was 80 ps, allowing deconvolution of decays as short as 40 ps with confidence. Temperature-dependence studies of the fluorescence decay also used the Janis liquid nitrogen cryostat.

Photographic sensitivity as a function of wavelength was measured by exposing samples for 10 s in a calibrated spectrograph with tungsten illumination. The film plane was fitted with a neutral filter providing a stepped series of optical density perpendicular to the direction of spectral dispersion. The samples were developed for 20 min at 20 °C in EAA-1 (Elon/ascorbic acid) developer,²⁶ fixed, and washed. The photographic sensitivity was obtained at 10-nm intervals from 400 to 700 nm from the reciprocal of the exposure (in $ergs/cm^2$) necessary to produce 0.15 optical density above minimum density at each wavelength.

In order to calculate the photoinduced electron-transfer rate from the adsorbed dye aggregate to AgBr, a direct proportion is assumed between the photographic sensitivity and the yield of electron injection from the dye. Further, it is assumed that photographic detection efficiency will be the same for an electron injected by the dye as for a conduction band electron resulting from AgBr band gap excitation. The relative quantum efficiency for spectral sensitization ϕ_s is then the ratio of photographic efficiency for exposure at the dye wavelength to the photographic efficiency for direct exposure of the AgBr at 400 nm:²⁷

$$\phi_{\rm s}(\lambda) = 400 S_{\lambda} A_{400} / \lambda S_{400} A_{\lambda} \tag{1}$$

where S is the photographic sensitivity defined above and A is the fraction of light absorbed. A correction of 0.05 was made to the A_{400} value to correct for the absorption by gelatin and film base at 400 nm. Values for ϕ_s presented in Table II are the average of multiple measurements made from 500 nm to the short-wavelength edge of the J-aggregate peak. The ϕ_s values from the J-aggregate peak or its long-wavelength edge were judged unreliable due to the relatively wide bandpass of the exposing spectrograph and the spectrophotometer compared with the sharp J-aggregate absorption edge. Values of ϕ_s are estimated to be accurate to $\pm 15\%$.

Results and Discussion

Figure 2 shows the absorptance spectra of a representative series of coatings of octahedral silver bromide microcrystals dyed with PIC diluted with varying amounts of its azacyanine analogue. Table I contains the values for the wavelength maxima corresponding to the two dyes in a similar series of coatings. At high levels of azacyanine, a monomer-like 537-nm PIC absorption, corresponding to isolated guest molecules of PIC within the azacyanine J-aggregate host, is observed. As the concentration of the diluent dye is decreased, the PIC spectrum red-shifts and narrows, indicating a larger average size for the J-aggregate. At 1.00 mole fraction PIC, the familiar 576-nm J-aggregate is seen. The red shift in the PIC J-aggregate spectrum with decreasing azacyanine concentration is paralleled by a blue shift in the

Fluorescence decays were measured by the time-correlated single-photon-counting method. The excitation source was a

⁽²⁵⁾ Bevington, P. R. Data Reduction and Error Analysis for the Physical

Sciences; McGraw-Hill: New York, 1969.
 (26) James, T. H.; Vanselow, W.; Quirk, R. F. PSA J. 1953, 19B, 170.
 (27) Spence, J.; Carroll, B. H. J. Phys. Colloid Chem. 1948, 52, 1090.



Figure 2. Absorptance spectra of coatings of 0.38-µm AgBr octahedral microcrystals dyed with PIC diluted with varying amounts of its azacyanine analogue. The total surface coverage of both dyes was held constant at 60% monolayer. Silver coverage in these coatings was 1.08 g/m².

TABLE I: Spectral Shifts with Aggregate Dilution

PIC mole fraction	λ_{max} , nn	n	PIC	PIC	
	azacyanine	e PIC E_{max} , cm		"average" N	
0.06	447	537	18 620		
0.125	446	541	18 480	1.1	
0.25	445	547	18 280	1.4	
0.375	444	552	18110	1.7	
0.50	441	559	17890	2.4	
0.625	439	565	17700	3.7	
0.75	436	570	17 540	7.0	
0.875		572	17 480	10.5	
1.00		576	17 360	8	

azacyanine peak, corresponding to a decrease in the average size of the azacyanine J-aggregate. Note that the absorption maximum for the azacyanine, with a J-aggregate peak at 447 nm, lies at significantly higher energy than the PIC maximum, giving good separation between the electronic transition energies in the two dyes.

To obtain a very approximate estimate of the size variation for the PIC aggregate in this series of coatings, we use the formula for the energy of the electronic transition as a function of aggregate physical size, developed for the simple case of a one-dimensional aggregate with circular boundary conditions:²⁸

$$E_{\rm N} = E_1 - ((N-1)/N)(E_1 - E_{\infty})$$
(2)

where E_N is the transition energy of an aggregate of size N, E_1 is the transition energy of an isolated molecule, and E_{∞} is the transition energy of an infinite chain. These size values are included in Table I. While this formula is clearly an oversimplification for the two-dimensional aggregates on the AgBr surface, it provides a qualitative picture of how the average PIC aggregate size is changing for the dilution series.

The effect of changing aggregate size on the room-temperature fluorescence lifetime of the PIC dye can be seen in Table II. At very high dilution, 0.005 mole fraction PIC, the emission lifetime is relatively long, 1.53 ns, and the decays are fit well by a single exponential. As the PIC concentration is increased and small PIC aggregates begin to form, the decays become more complex and the average lifetime, obtained by forcing the decay to fit a single exponential, shortens. At high mole fractions of PIC, where the PIC J-aggregate size is large, the decay is again approximated by a single exponential and is very short. If the relative quantum yield of fluorescence for the PIC dye were constant through this concentration series, this lifetime shortening would represent a significant enhancement in the radiative rate constant, $k_{\rm f}^{\rm J}$, of the J-aggregate. In selecting this mixed-aggregate system to study the size dependence of the J-aggregate dynamics, we had initially considered that the nonradiative processes in PIC would not be perturbed as the concentration of azacyanine diluent was changed, since the structures of the two dyes are very close.

TABLE II: Room-Temperature Fluorescence Lifetimes and Relative Quantum Yields of PIC

PIC mole fraction	av $ au_{f}$, ns	rel ϕ_{f}	$k_{\rm f}^{\rm J}/k_{\rm f}^{\rm M}$	photographic ϕ_{s}	k _s , s ⁻¹		
0.005	1.53	1.00		0.23	1.5×10^{8}		
0.03	1.48	0.89	0.92	0.25	1.6×10^{8}		
0.125	1.05	0.56	0.82	0.26	2.5×10^{8}		
0.25	0.762	0.40	0.80	0.23	3.0×10^{8}		
0.50	0.185	0.16	1.3	0.15	8.0×10^{8}		
0.75	0.073	0.099	2.1	0.091	1.3×10^{9}		
1.00	0.047	0.057	1.9	0.076	1.6×10^{9}		

Table II also contains results for the relative fluorescence quantum yield, ϕ_f , as a function of PIC mole fraction. Yields are given relative to the lowest concentration sample, 0.005 mole fraction PIC, and can be seen to decrease strongly as PIC concentration is increased. Evidently, the excited state of PIC has a nonradiative relaxation process with a rate which increases significantly with PIC concentration. Consequently, the major portion of the lifetime decrease observed with increasing PIC concentration is a result of the increase in this nonradiative process. However, since the radiative rate constant is proportional to the fluorescence quantum yield ϕ_f divided by the fluorescence lifetime τ_f , the radiative rate constant k_f^J for any given PIC concentration can be calculated relative to the radiative rate constant k_f^M for the PIC monomer from

$$k_{\rm f}^{\rm J}/k_{\rm f}^{\rm M} = \phi_{\rm f}^{\rm J} \tau_{\rm f}^{\rm M}/\phi_{\rm f}^{\rm M} \tau_{\rm f}^{\rm J}$$
(3)

where the values for τ_f and ϕ_f for the 0.005 mole fraction sample are used as the monomer reference. This ratio is equivalent to $N_{\rm eff}$, the effective number of molecules involved in the coherent decay of the J-aggregate. Values of k_f^J/k_f^M are included in Table II and are approximately 1 for PIC concentrations up to 0.5 mole fraction.²⁹ The ratio increases to 2 for the 0.75 and 1.0 mole fraction samples, indicating a small enhancement of the radiative rate constant for these larger J-aggregates.

These results for the PIC J-aggregate size series indicate that the dominant feature controlling the excitation dynamics at room temperature is the size-dependent nonradiative relaxation process rather than the J-aggregate superradiance. If, as predicted by our earlier theoretical studies, the superradiance at room temperature is significantly disrupted by interaction with phonons, study of the excitation dynamics at lower temperatures might reveal a larger value for the superradiance. In addition, examination of the temperature dependence of the nonradiative relaxation process would be expected to yield information about the nature of this process. Consequently, fluorescence decay and relative quantum yield measurements were made for the concentration series in Table II over the temperature range from room temperature to 90 K.

Figure 3 illustrates the fluorescence spectra obtained at 270 K and approxinately 90 K for 0.005, 0.125, 0.50, and 1.00 mole fraction PIC samples, while Table III contains the corresponding fluorescence lifetime and relative quantum yield data for these four samples. The other concentrations and temperatures examined show intermediate behavior relative to the specific data given in the figure and table. As described in the Experimental Section, the relative quantum yields are referenced to the low-temperature value for the 0.005 mole fraction sample, assumed to be equal to 1.00. As can be seen from the figure and the table, the behavior of this lowest concentration sample is relatively simple-the shape of the fluorescence spectrum is not changing significantly with temperature, the decays can be fit to a single exponential, and the small decrease in fluorescence yield as temperature is increased is accompanied by an proportional decrease in fluorescence lifetime. The lifetimes monitored at an emission wavelength of 620

⁽²⁹⁾ Since lifetimes for the middle concentrations (0.125–0.50 mole fraction PIC) are better fit with a two-component lifetime, a more exact procedure for calculating k_f^{J}/k_f^{M} would be to use only the short-component lifetime (assumed to be that of the aggregate) and to correct the relative ϕ_f to reflect only the yield of this short component. Following this procedure gives values for k_f^{J}/k_f^{M} which are essentially identical to those given in Table II.

⁽²⁸⁾ McRae, E. G.; Kasha, M. J. Chem. Phys. 1958, 28, 721.

TABLE III: Fluorescence Lifetimes^a and Yield^b as a Function of Temperature

PIC mole fraction	<i>T</i> , K	rel $\phi_{\rm f}$	emission λ , nm	τ_1 , ns	X_1^c	τ_2 , ns	X_2^c	τ_3 , ns	X3 ^c
0.005	95	≡1.00	570	1.78	1.00				
			620	1.92	1.00				
	300	0.87	570	1.53	1.00				
			620	1.63	1.00				
0.125 110 270	110	0.60	570	0.55	0.31	1.77	0.69		
			620	0.79	0.25	2.03	0.75		
	270	0.49	570	0.45	0.24	1.25	0.76		
			620	0.71	0.43	1.39	0.57		
0.50	95	0.38	570	0.13	0.37	0.49	0.41	1.33	0.22
			620	0.35	0.26	1.36	0.74		
	270	0.14	570	0.14	0.76	0.43	0.24		
			620	0.13	0.68	0.44	0.32		
1.00	90	0.11	570	0.050	1.00				
			620	0.097	0.34	0.92	0.66		
	270	0.050	570	0.047	1.00				
			620	0.039	1.00				

^a Fluorescence lifetimes measured with 540-nm excitation. ^b Fluorescence yields measured with 500 nm excitation (0.005 and 0.125 mole fraction) or 530 nm excitation (0.50 and 1.00 mole fraction). ^cX represents the fraction of photons having a given lifetime.

nm are slightly longer than the lifetimes monitored at 570 nm. Even at 90 K, the bandwidth of the emission is quite broad, 1010 cm^{-1} full width at $^{2}/_{3}$ maximum (FW2/3M).³⁰ The value of 1.78 ns for the 90 K lifetime monitored at 570 nm is very close to the 1.73-ns value obtained by Dorn and Müller³¹ for PIC monomers in glycerol at 84 K. This agreement suggests that, at these temperatures, there is little electron transfer from the excited monomer-like PIC molecules to the AgBr conduction band.

As the PIC concentration is increased to 0.125 mole fraction, the room-temperature fluorescence spectrum shifts to slightly longer wavelength and narrows somewhat, indicating emission from small PIC aggregates. As the temperature is decreased, a dramatic change is seen in the fluorescence spectrum: a broad structureless band grows in at long wavelength, obscuring the peak of the aggregate emission. The decays are complex, but can be approximately fit with the sum of two exponentials. The value for the longer lifetime component increases significantly as the temperature is lowered, and the overall relative quantum yield also increases. In addition, somewhat longer lifetimes are observed when the emission is monitored at 620 nm than at 570 nm.

At a PIC concentration of 0.50 mole fraction, the room-temperature emission is further shifted to long wavelength and its shape is close to that for the undiluted J-aggregate. At low temperature, a broad band at long wavelength is again evident, but the J-aggregate emission remains clearly visible and is relatively narrow, 260 cm⁻¹ FW2/3M. The fluorescence lifetimes at this temperature indicate that the lifetime of the J-aggregate is quite short and dominates the emission at 570 nm, while the broad-band emission, which dominates at 620 nm, has a much longer lifetime. At room temperature, both emission wavelengths show mainly the decay of the J-aggregate, with a lifetime which is not significantly different from that found at the lower temperature. The total fluorescence yield at low temperature is a factor of 2.7 higher than at room temperature.

The undiluted J-aggregate at 1.0 mole fraction has a behavior fairly similar to the 0.50 mole fraction sample. The room-temperature emission spectrum shows only the fluorescence of the aggregate, but at 90 K, evidence of the broad long-wavelength band can be seen, now significantly less intense than the aggregate emission. The width of the J-aggregate emission has narrowed to 130 cm⁻¹ (FW2/3M) at 90 K. Fluorescence decays monitored at 570 nm give the lifetime of the J-aggregate emission, which is essentially the same at both temperatures and shorter than the lifetime for the 0.50 mole fraction sample. The low-temperature lifetime measured at 620 nm has a much longer component



Figure 3. Fluorescence spectra for varying mole fractions of PIC as a function of temperature. Dotted lines are spectra at 270 K and solid lines are spectra at approximately 90 K: (a) 0.005 mole fraction PIC, $\lambda_{ex} = 500$ nm. (b) 0.125 mole fraction PIC, $\lambda_{ex} = 500$ nm. (c) 0.50 mole fraction PIC, $\lambda_{ex} = 530$ nm (d) 1.00 mole fraction PIC, $\lambda_{ex} = 530$ nm. Silver coverages were 1.08 g/m² for (a) and (b) and 0.54 g/m² for (c) and (d).

⁽³⁰⁾ The full width at $^{2}/_{3}$ of the maximum intensity is chosen to characterize the bandwidths through the concentration series in order to give a width which does not include either the vibronic shoulder or the long-wavelength structureless emission.

⁽³¹⁾ Dorn, H.-P.; Müller, A. Chem. Phys. Lett. 1986, 130, 426.

corresponding to the broad-band emission but this component is not observed at room temperature, where the lifetime seen is that of the J-aggregate. The total fluorescence yield at low temperature is approximately 2.3 times higher than at room temperature.

These fluorescence data as a function of temperature and PIC concentration suggest strongly that energy transfer to a trap state is the nonradiative process that is causing the strong decrease in room-temperature fluorescence yield with increasing PIC concentration. Emission from this trap is assumed to be the source of the broad, featureless band seen to long wavelength of the aggregate emission at low temperature. This trapping species is apparently present at quite low concentrations since it cannot be observed in either the absorptance spectra or the fluorescence excitation spectra. However, as the PIC concentration increases, giving larger average J-aggregate size, energy migration among the PIC molecules increases, making encounters with the trap and subsequent fluorescence quenching more probable. Since this energy migration is expected to have little temperature dependence over the temperature range studied, the quenching of the J-aggregate fluorescence as measured by the aggregate's fluorescence lifetime also does not change significantly with temperature.

The characteristics of the trap state which can be inferred from the kinetic and spectral data are as follows. For any given PIC concentration, the peak of the emission from the trap occurs at longer wavelengths than the PIC J-aggregate emission. As PIC concentration is increased, giving larger J-aggregate size and a longer wavelength J-aggregate peak, the emission of the trap also shifts to longer wavelengths. At room temperature, radiationless deactivation of the excited state of the trapping species occurs very rapidly and little or no emission from the trap is seen. At 90 K, the extent of radiationless deactivation of the trapping species appears to depend on aggregate size, with faster deactivation and lower emission yields for larger aggregate sizes. This change in characteristics of the trap emission with PIC concentration indicates that the trap is not a simple adventitious impurity or a state associated with the silver bromide microcrystals. Further confirmation of this conclusion comes from the recent observation by Terpstra and Wiersma³² of a similar broad long-wavelength emission in the low-temperature spectra of PIC aggregates formed on glass by Langmuir-Blodgett monolayer techniques. As a result, identification of the trapping species as a defect state associated with the J-aggregate seems a reasonable assumption.

The possibility that this defect state might be an arrangement of PIC molecules in a "sandwich dimer" configuration is an interesting hypothesis. Such arrangements, where the transition dipoles in the molecules are perpendicular to the line connecting their centers, are commonly observed for dye molecules in solution and might occur at the domain boundaries of the surface-adsorbed J-aggregates. These dimers have a strongly allowed transition shifted to the blue and a formally forbidden transition shifted to the red of the monomer absorption peak.²⁸ The analogue of this red-shifted transition in the proposed defect state might be a possible excitation trap. The experimental basis for this speculation about the nature of the defect state can be found in the spectroscopy of dimers of PIC in solution. Formation of PIC dimers in water has been studied by Kopainsky et al.³³ using absorption spectroscopy. Under the conditions required to obtain maximum dimerization with no apparent J-aggregation, the absorption spectrum consists of a blue-shifted dimer band at 480 nm, together with the monomer band at 522 nm.³⁴ Using these conditions, we have examined the room-temperature emission spectrum for excitation at 480 nm, as shown in Figure 4. The emission is a broad, featureless band with a quantum yield of approximately



Figure 4. Room-temperature fluorescence spectrum of 1×10^{-3} M PIC in ultrapure (Millipore) water, $\lambda_{ex} = 480$ nm. The spectrum was obtained in an 0.5-mm cell using front surface excitation.

10⁻⁴ and a peak at wavelengths longer than the emission from the very small amount of J-aggregate also present in the solution. (The J-aggregate can be seen in emission even when not visible in absorption because its fluorescence yield is much higher than that of the dimer.) Measurement of the fluorescence decay for emission in the dimer band at 610 nm gives a fluorescence lifetime of 10 ps or less. These results show that the emission characteristics of this solution sandwich dimer have many of the features observed for the emission from the trap found in the surface-adsorbed J-aggregates. Consequently, the hypothesis that this trap has structural features in common with the sandwich dimer seems a reasonable one.

The data in Figure 3 and Table III also provide information about the temperature dependence of the enhancement in radiative rate observed for the undiluted J-aggregate at room temperature. At 90 K, the total fluorescence yield of the 1.0 mole fraction PIC sample increases by a factor of 2.3 over the room-temperature value. However, part of the yield increase is emission from the trap, which is nonradiative at room temperature. When the PIC emission is examined at intermediate temperatures, a rough estimate of the band shape of the J-aggregate emission at 90 K can be made and the yield separated into the J-aggregate component and the trap component. Depending on the band shape chosen, the J-aggregate fluorescence yield at 90 K ranges between 0.057 and 0.074. Use of eq 3 then gives an enhancement of the J-aggregate rate between 2.0 and 2.6, at most a small increase over the value observed at room temperature.

This rather weak superradiance is in contrast to the results of DeBoer and Wiersma¹⁸ for PIC J-aggregates in ethylene glycol/water glass, where an enhancement in radiative rate of ~ 120 was measured at temperatures below 50 K. Above this temperature, the radiative rate was observed to decrease with increasing temperature, with an enhancement between 4 and 6 seen at 200 K (the temperature above which the glass begins to melt). However, our data have many features in common with the observation of Kemnitz et al.²¹ of weak temperature dependence and short lifetimes in the fluorescence decay of a thiacarbocyanine J-aggregate on AgBr. There are, of course, significant differences between J-aggregates formed in solution and those formed by adsorption to the surface of a silver bromide microcrystal. The solution J-aggregates have frequently been modeled as one-dimensional structures, 35,36 but on the basis of the results of Marchetti et al.³⁷ and the threadlike structures observed by optical microscopy,³⁸ an elongated three-dimensional microcrystal seems more likely. The J-aggregates on surfaces have been assumed to have a two-dimensional structure,³⁹ and the recent experiments

⁽³²⁾ Terpstra, J.; Wiersma, D. A. Presented at Charge Transfer in Restricted Geometries, 2nd Symposium on Photoinduced Charge Transfer, University of Rochester, Rochester, NY, July 1991; poster paper 38.

⁽³³⁾ Kopainsky, B.; Hallermeier, J. K.; Kaiser, W. Chem. Phys. Lett. 1981, 83, 498

⁽³⁴⁾ While Kopainsky et al. argued that the 522-nm band is also associated with the dimer, its coincidence with the monomer band and its relative weakness in the excitation spectrum of the dimer emission make an assignment of residual monomer more plausible.

⁽³⁵⁾ Norland, K.; Ames, A.; Taylor, T. Photogr. Sci. Eng. 1970, 14, 295.
(36) Scherer, P. O. J.; Fischer, S. F. Chem. Phys. 1984, 86, 269.
(37) Marchetti, A. P.; Salzberg, C. D.; Walker, E. I. P. J. Chem. Phys.

^{1976, 64, 4693.}

⁽³⁸⁾ Scheibe, G. In Optische Anregung Organisher Systeme; Foerst, W., Ed.; Verlag-Chemie: Weinheim, 1966; p 109

Excited-State Dynamics for J-Aggregates on AgBr

of Maskasky^{40,41} on large AgBr microcrystals have confirmed this assumption for silver halide surfaces. While both types of PIC J-aggregate have absorption maxima near 575 nm, the bandwidth of the surface-adsorbed aggregates is larger, suggesting the presence of more disorder. The observation of broad bandwidths and short fluorescence decays for J-aggregates in Langmuir-Blodgett monolayers^{10,20} suggests that these aggregates have more in common with the AgBr-adsorbed aggregates than with the solution aggregates.

As discussed in the Introduction, the J-aggregate superradiance can be limited by exciton-phonon coupling. For the data of DeBoer and Wiersma,¹⁸ the temperature dependence of $N_{\rm eff}$ and its low-temperature limit could be modeled using the theory of Spano et al.¹⁹ for the effect of exciton-phonon coupling on the J-aggregate radiative dynamics. Coupling to a 240-cm⁻¹ optical phonon gave a reasonable fit to the experimental data. If we assume that the same phonon is responsible for reducing $N_{\rm eff}$ for the surface-adsorbed J-aggregates to a value of 2.0 at room temperature, unrealistically high values of the exciton-phonon coupling are required and a large increase in $N_{\rm eff}$ at 90 K is predicted. Instead, the very weak temperature dependence of the superradiance over the range we have studied suggests that strong coupling to a low-frequency acoustic or optical phonon may be controlling the limiting value of $N_{\rm eff}$, N^* . In this case, N^* is given by the approximation⁷

$$N^* = 2.16\rho^{-1/3}$$
 for $kT/\Omega \gg 1$ (4)

where $\rho = F^2 k T / (V^2 \Omega)$, F is the exciton-phonon coupling strength, $\hbar V$ is the dipole-dipole interaction energy, and Ω is $\Omega_{\rm ac}$ or $\Omega_{\rm op}$, the frequency of the acoustic or optical phonon. For V = 600 cm^{-1} and $N^* = 2$ at 300 K, this relation gives $N^* = 3$ at 90 K and a value for F^2/Ω of 2.2×10^{-3} . This value for N* is consistent with the experimental determination, given the $\pm 25\%$ error in the low-temperature relative quantum yields. Exact calculation using the procedures described in ref 7 confirms that acoustic phonons up to 30 cm⁻¹ in frequency obey this scaling relationship and give $N^* = 2$ at room temperature and $N^* = 3$ at 90 K for appropriate values of F. Consequently, a significant difference in excitonphonon coupling can explain the large variation in the extent of superradiance observed between PIC J-aggregates in solution and on AgBr surfaces. The physical reason for this difference is not clear but may well be related to differences in dimensionality and microscopic structure of the two types of aggregates.

The inhomogeneous broadening observed for the surface-adsorbed PIC J-aggregates represents another factor with the potential to limit the aggregate superradiance. At room temperature, the fluorescence emission for the 1.0 mole fraction PIC sample has a bandwidth of 360 cm⁻¹ (FWHM), significantly broader than the fluorescence from solution J-aggregates, which typically have a bandwidth of 210 cm⁻¹ at this temperature. At 90 K, the fluorescence of the undiluted PIC aggregate on AgBr narrows to 170 cm⁻¹, but the excitation spectrum of this emission has a significantly larger width, 470 cm⁻¹. Spano and Mukamel⁹ have shown that the lifetime of an aggregate of physical size N having an inhomogeneous broadening σ is a function of the scaled variable $N^{3/2}\sigma/V$. Figure 4 of ref 9 provides a numerically calculated plot of $N_{\rm eff}$ vs this scaled variable, which can be used to estimate the lifetime of aggregates with size N and inhomogeneous broadening σ/V . Assuming the width of the 90 K excitation spectrum represents an upper bound on the inhomogeneous broadening of the undiluted PIC aggregate, minimum values of Neff for various sizes N can be estimated from this plot. The limiting value of $N_{\rm eff}$ is found to be about 8 for large N. A similar limiting value for $N_{\rm eff}$ is obtained using an expression given by Fidder et al. based on a fit to results of numerical simulations of the effects of inhomogeneous broadening on aggregates with $N = 250.^{11}$ Consequently, disorder alone is not sufficient to explain the small value of $N_{\rm eff}$ observed at 90 K.

An important motivation in studying the size dependence of the J-aggregate excited-state dynamics is to understand how aggregate size influences the efficiency of electron transfer from the aggregate to the AgBr conduction band. This efficiency can be measured photographically by determining the relative quantum yield of spectral sensitization ϕ_s , defined as the ratio of the ability of photons absorbed by a dye to produce a photographic image to the ability of photons absorbed by the silver halide to produce this image. The effect of changing PIC aggregate size on ϕ_s at room temperature is included in Table II. The value for ϕ_{e} is relatively constant for dilute aggregate samples up to 0.25 mole fraction PIC. As the number of larger aggregates increases with increasing mole fraction PIC, the spectral sensitizing efficiency of PIC decreases smoothly, reaching 0.08 at the limit of pure PIC. Overall, a factor of \sim 3 decrease in spectral sensitizing efficiency is observed for the pure PIC J-aggregate compared with the diluted aggregate samples. The values of the rate constant for spectral sensitization k_s in Table II are calculated from the relative sensitization efficiency ϕ_s and the average fluorescence lifetime (best single-exponential fit). The value of the sensitization rate constant is 1.5×10^8 s⁻¹ for very dilute PIC on AgBr and increases 10-fold to $1.6 \times 10^9 \,\text{s}^{-1}$ as the PIC mole fraction is increased to 1. Thus, the moderate decrease in ϕ_s with increasing aggregate size is the result of a strong increase in the sensitization rate constant offset by an even larger increase in competing radiative and nonradiative processes, as reflected in the overall excited-state decay rate.

Bird⁴² had previously suggested that partitioning of the J-aggregate by spacer molecules would increase spectral sensitizing efficiency by restricting the mobility of excitons to smaller domains, each of which would be less likely to contain within its boundaries an energy-quenching site such as an impurity molecule. Our results demonstrate this type of "supersensitization" in the increase seen in ϕ_s as aggregate size is decreased. However, our data further indicate that a significant reduction in sensitization rate constant can be an additional consequence of reducing the aggregate size. The explanation for the decrease in k_s with decreasing aggregate size may also be related to the confinement of the exciton to smaller domains. We speculate that increased exciton mobility in larger aggregates enhances the rate of electron transfer by increasing the probability of the exciton reaching a site favorable for electron-hole separation and subsequent electron injection into the conduction band. The importance of electron-hole separation as the critical process competing with radiative and nonradiative decay is supported by the existence of the well-known supersensitizing ability of low-oxidation-potential "hole-trapping" dyes when added in very low concentrations to PIC J-aggregates.43

In their work with 5,5'-dichloro-9-ethyl-thiacarbocyanine Jaggregates, Kemnitz et al.²¹ observed an electron-transfer rate which depended weakly on aggregate size. In contrast to our results with PIC, the spectral sensitization rate decreased with increasing aggregate size of the thiacarbocyanine J-aggregate. At the same time, the sum of the radiative and nonradiative rates increased 1 order of magnitude as estimated aggregate size increased from $N \sim 5$ to $N \sim 20$. Thus, most of the observed decrease in the spectral sensitization efficiency with increased aggregate size is attributable to the increase in the rate of competing processes and not to a change in electron-transfer rate.

Summary and Conclusions

From these studies of PIC fluorescence as a function of temperature and aggregate dilution, the following qualitative picture of the excitation dynamics emerges: At 0.005 mole fraction, the PIC molecules are isolated, monomer-like species within the azacyanine J-aggregate structure. As judged from the spectral width of the emission, their environment is somewhat heterogeneous, presumably because of variations in the silver halide surface. At 0.125 mole fraction, a majority of the PIC molecules are still

⁽³⁹⁾ Bücher, H.; Kuhn, H. Chem. Phys. Lett. 1970, 6, 183.
(40) Maskasky, J. E. Langmuir 1991, 7, 407.
(41) Maskasky, J. E. J. Imaging Sci. 1991, 35, 29.

⁽⁴²⁾ Rosenoff, A. E.; Norland, K. S.; Ames, A. E.; Walworth, V. K.; Bird, G. R. Photogr. Sci. Eng. 1968, 12, 185.
(43) Gilman, P. B., Jr. Photogr. Sci. Eng. 1974, 18, 418.

monomer-like, but a moderate number of dimers and trimers with the J-aggregate configuration have formed from statistical associations. In addition, a few defect states, possibly having a sandwich dimer configuration, have formed. Energy transfer from the monomer-like species to the dimers, trimers, and defect states causes the bulk of the fluorescence to come from these states. The defect-state emission dominates at 90 K, where it has a reasonably high quantum yield, while the room-temperature emission comes mainly from the small aggregates, since the defect state relaxes nonradiatively at this temperature. At 0.50 mole fraction, most the PIC molecules have formed small J-aggregates and extensive energy migration among these aggregates causes significant energy transfer to the defect states, resulting in a low yield of J-aggregate emission at room temperature. At 90 K, emission occurs from both the J-aggregates and the defect states, but an increased rate of nonradiative relaxation for the defect states formed at this concentration causes the overall yield of fluorescence to be lower than for the 0.125 mole fraction sample. For the undiluted PIC J-aggregates, the increased range of energy migration results in further quenching of the room-temperature J-aggregate fluorescence by the nonradiative defect states. At 90 K, the quenching persists and some emission from the defect states can be seen. The overall yield of fluorescence at this temperature remains quite low, presumably because the defect states associated with the undiluted J-aggregate have significant nonradiative relaxation at this temperature. One focus of our future work will be development of a better understanding of the nature of the defect states and a more quantitative model for their effect on the excitation dynamics of PIC J-aggregates.

While energy transfer from the J-aggregates to the defect state is the dominant factor controlling the size-dependent excitation dynamics, a weak superradiant enhancement of the J-aggregate radiative decay is also present for the samples containing the larger aggregates. The values obtained for this enhancement are much smaller than those observed for PIC J-aggregates in solution but can be rationalized by postulating strong coupling of the J-aggregate exciton to a low-frequency phonon. While the much larger disorder present in the surface-adsorbed J-aggregates may also be a factor in limiting the superradiance, disorder alone is not sufficient to explain the differences in enhancement observed between these aggregates and the solution aggregates.

Both the energy transfer to the defect states and the enhanced radiative rate of the large J-aggregates compete with the desired process of electron transfer from the aggregate excited state to the AgBr conduction band. Consequently, the relative quantum efficiency of spectral sensitization by the dye decreases as the aggregate size increases. However, this decrease is not as large as would be expected because the electron-transfer rate constant from the aggregate size. Better understanding of the reasons underlying this size dependence of the J-aggregate electron-transfer rate constant is another area for future work.

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Medium Effects on Photoinduced Electron Transfer in Langmuir–Blodgett Films

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The Langmuir-Blodgett technique has been used to prepare films in which electron donor and acceptor layers are separated by a spacer layer one molecule thick in which both the length and the electronic nature of the molecules were changed without altering donor or acceptor layers. A thiacyanine dye located at the hydrophilic interface acted as an excited-state electron acceptor. The donor layer incorporated a long-chain carboxylic acid derivatized with a ferrocene chromophore at the hydrophobic interface as a ground-state electron donor. By monitoring the quenching of the thiacyanine fluorescence by the ferrocene as a function of the composition of the spacer layer, the influence of the medium on the electron-transfer process was determined. For both series of saturated fatty acids and *trans*-stilbene-derivatized fatty acids the rate of electron transfer decreased with increasing separation distance of donor and acceptor, but the rate of attenuation was greater for the saturated fatty acids. Although the data do not conform to a simple exponential attenuation of electron transfer with separation distance, it is possible to fit it to this form by assuming that about half the excited thiacyanine dye is inactive in the electron-transfer process, or by assuming two populations which quench differently due to their different lifetimes. Both treatments lead to very low attenuation coefficients (β) for the fatty acid and *trans*-stilbene spacers; within the context of this analysis the attenuation coefficient is about 50% greater for the saturated fatty acids than the *trans*-stilbene spacers.

Introduction

Langmuir-Blodgett (LB) assemblies, prepared by sequential transfer of spread, compressed monolayer films formed at the air-water interface, have proven to be useful media for examining a variety of intermolecular interactions.¹ The ability to construct a variety of functionalized amphiphiles and to incorporate them at fixed distances from other reagents has led to a number of studies of both long- and short-range phenomena. Particularly interesting have been studies carried out in LB assemblies in which the distance dependence of excited-state quenching via energy and electron transfer has been investigated. On the one hand, studies of singlet-singlet energy transfer via long-range resonance interactions in LB assemblies have shown generally good agreement between theory and experiment; indeed LB assemblies have proven to be an almost ideal medium for investigating this phenomenon which proves elusive for investigation in many other situations due to the presence or predominance of other competing deac-

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⁽¹⁾ Recent monographs reviewing the field are: Langmuir-Blodgett Films; Roberts, G. G., Ed.; Plenum: New York, 1990. Ulman, A. An Introduction to Ultrathin Organic Films; Academic: New York, 1991.