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ARTICLES

Layered Nanocomposites of Aggregated Dyes and Inorganic Scaffolding[†]

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Layer-by-layer thin films were prepared by the alternate deposition of clay particles and ionic organic compounds from solution onto a rigid support. The organic component comprised a monomeric cyanine dye or poly-l-lysine with the same cyanine chromophore appended to it, a dye polymer. Physical measurements indicated that layers of the organic and inorganic materials could be deposited alternately in a repeated fashion with each layer only one to two nanometers thick. Within the film structure the cyanine chromophore exhibits J-aggregate spectroscopic properties, either as the result of adsorption to the clay in the case of the monomeric dye or because it preexisted in this form in the case of the dye polymer. This composite assembly can potentially serve as a model for a light-harvesting photoantenna system. We attempted to demonstrate that by capping the multilayer film with another layer of a different cyanine dye, whose J aggregate absorption band overlapped the fluorescence wavelength of the dye incorporated into the film, acting as an excitation energy donor. Efficient energy transfer was demonstrated for films containing no more than four dye layers for the monomeric donor dye or six layers for the polymeric donor dye. However, close examination of the absorption spectra of the donor−acceptor systems reveals that an interaction appears to occur in the assembly that results in excess acceptor dye being incorporated into the film. This raises the possibility that the acceptor dye penetrates into the film and mixes into the donor dye layers, calling into question whether long-range energy transfer occurs due to an antenna effect.

1. Introduction

The intermolecular self-association of organic dyes under the influence of environmental factors has been recognized and studied for many years. Hence, the self-association of organic photographic sensitizing (cyanine) dyes has been obtained and studied in different matrixes such as liquids,[1] in Langmuir−Blodgett films,[2] in polymer films,[3] on silver halide crystal surfaces,[4] and more recently in polymeric layer-by-layer assemblies.[5] This study combines the concept of spontaneous, self-organization of organic dyes into aggregates with the deliberate fabrication of lamellar structures. Choosing the proper inorganic scaffolding material may allow the desired dye aggregate packing to be stabilized on its surface. Using the layer-by-layer buildup approach developed by Decher et al.,[6] we are able to create three-dimensional arrays resulting in a packaged assembly of multicomposite materials with designed functionality containing dye aggregates exhibiting novel optical behavior. These inorganic−organic multicomposites are formed by intercalation of the guest species (cyanine dyes) into layered inorganic solids (clays), forming a unique nanostructure controlled by host−guest interactions.[7] The smectite family of layered clay minerals provides the appropriate features for inducing organization in organic guest molecules.[8] Among smectites, synthetic Laponite provides an advantage due to the small size of the aqueous colloidal particles. Also, the particular Laponite used (RDS) was modified by the manufacturer by treatment with pyrophosphate to graft P_2O_5 groups to the edges of the clay particles. This allows the material to form very stable colloids. It is well-known that the spectral properties of cyanine dyes are fundamentally modified by aggregation.[1−9] The aggregates formed by cyanine dyes are of special interest in the spectral sensitization of photographic processes.[10] These aggregates are called H- or J-aggregates, depending on whether their transition dipole moments are oriented in a head-to-head or head-to-tail manner, respectively. J-aggregates are characterized by an absorption peak bathochromically shifted compared with the monomer absorption, while that of H-aggregates is hypsochromically shifted.

Due to the commercial importance of cyanine dyes in photography, the study of energy transfer between J-aggregated cyanine dyes is of special interest. Studies have been carried out of energy transfer between cyanine dyes in LB films,[11] and mixed J-aggregates of cyanine dyes in layer-by-layer alternate assemblies.[12] Inorganic spacer layers have been shown to provide a more complete separation of donor and acceptor dyes than layers composed entirely of organic materials.[13] The use of cyanine dyes that are ordered into J-aggregates in such a composite layered structure can potentially provide a more

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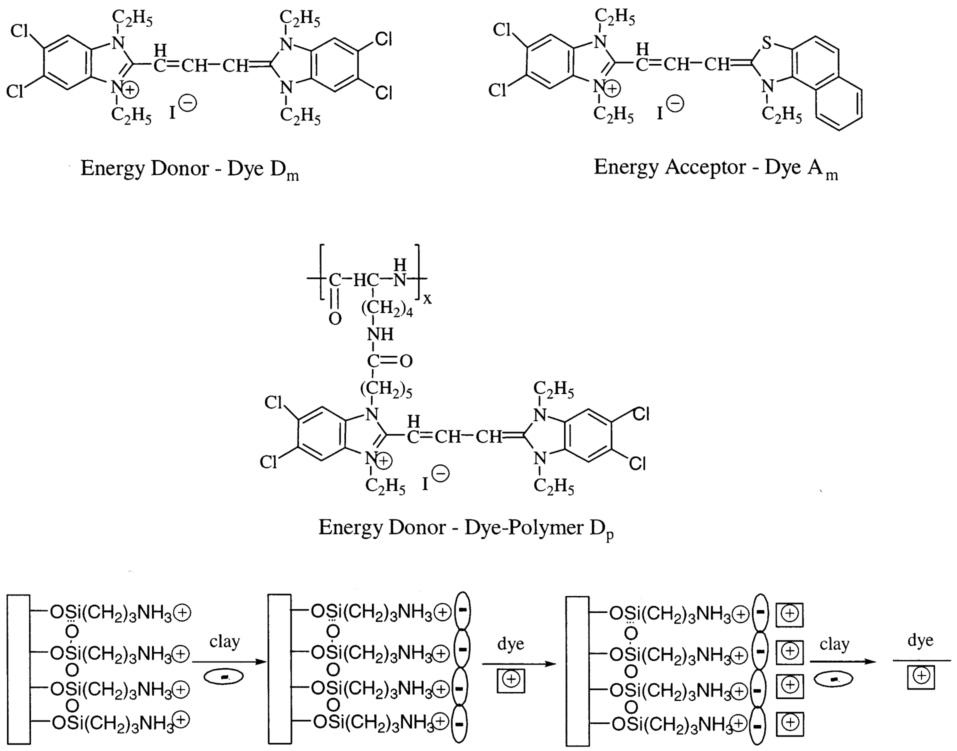

Figure 1. Structure of dyes used and multilayer deposition scheme.

effective antenna system than dilute chromophores in the organic matrix, because the absorption cross-section and the critical radius for energy transfer can be enhanced in the former. We have used in these experiments both monomeric cyanine dyes adsorbed onto clay supports as J-aggregates and also cyanine dyes appended to a polymer backbone, which induces their J-aggregation even in solution.[14 (b)] These polymeric materials with extensive, intrachain-chromophoric ordering have not been previously investigated in energy transfer experiments. In the present study, we find that assemblies containing only a donor cyanine monomer or a donor cyanine polymer exhibit a uniform buildup of the cyanine J-aggregate as measured by absorption, fluorescence, or ellipsometry. Addition of an outermost layer of acceptor results in efficient quenching of the donor fluorescence of up to several layers concomitant with sensitization of acceptor fluorescence. We show that this efficient sensitization most likely occurs through a process of interpenetration of the acceptor into the donor-dye clay such that regions of acceptor J-aggregate may occur close enough to the donor aggregates to allow efficient energy transfer to occur.

2. Experimental Section

The structure of dyes used is shown in Figure 1. The monomer dyes A_m and D_m were provided by Eastman Kodak Company Research Laboratories, whereas the dye polymers were synthesized by a procedure described elsewhere.[14] All solvents were 99% purity or higher and were purchased from Aldrich. All reactions were carried over in flame-dried glassware and under nitrogen atmosphere using chemical-grade anhydrous solvents. Liquid and thin film absorption spectra were measured using a Perkin-Elmer Lamba 19 UV/vis/NIR Spectrometer and emission spectra were measured using a SPEX Fluorolog 2 Spectrofluorimeter. The solutions were prepared using spectrophotometric grade solvents purchased from Aldrich and measured in high-quality quartz cuvettes. In the case of the thin film spectra, results were averaged for each measurement over five sets of data acquired in different regions of the film. The error in these measurements was calculated to be no more than 10−15%. The thin films were deposited on 1 cm × 3 cm glass plates. Silicon single-crystal wafer (100) substrates were also used for ellipsometric measurements. The substrates were modified using the following procedure: (1) The substrates were soaked in a 7:3 H_2SO_4:H_2O_2 solution at high temperature for 2 h, then in a 5:1:1 H_2O:H_2O_2:NH_4OH solution (at room temperature) for 1 h. (2) They were then rinsed with deionized water and dried under nitrogen and they were checked by contact angle measurements ($<1°$). (3) The substrates were silanized in a reaction kettle using a (0.5−1%) aminopropyl diethoxy methylsilane solution in anhydrous toluene (v/v) under a nitrogen atmosphere for 16 h. After silanization, the substrates were sonicated 30 min each successively in toluene, 1:1 toluene to methanol and methanol. The substrates were then dried in a stream of nitrogen and stored under vacuum for 16 h, after which they were ready to use. The modified substrates were tested again by ellipsometry in order to determine the thickness of the silane layer deposited. The ellipsometry measurements were performed using a GAERTNER Auto Gain Ellipsometer L116B. A silane layer thickness of no more than 7 Å ± 5% was measured, which corresponds to a monolayer. In preparation for the layer-by-layer depositions procedure, the substrates were protonated by immersion in a 0.03 M HCl solution (deionized water) for 10 min. For film fabrication, a silanized substrate was immersed in a Laponite clay solution (60 mg in 100 mL deionized water) for 10 min, then washed in deionized water, and dried using a nitrogen stream. The substrates were then dipped into the dye solution (5 mM in methanol) for 10 min, rinsed successively with deionized water in three separate beakers, and dried using a nitrogen stream. The succession of layer deposition is presented in the Scheme shown in Figure 1. The synthetic clay, Laponite RDS, was purchased from Southern Clays, Inc. The thickness of the deposited layers was measured by ellipsometry. The substrates bearing multilayers were freshly prepared and absorption and emission spectroscopy measurements were performed in each case, within five minutes of the layer deposition.

Picosecond fluorescence lifetime measurements were carried out on a time-correlated, single-photon counting laser system.[15] The 565 nm excitation source was a synchronously pumped Rhodamine 6G dye laser which is cavity dumped at a repetition rate of 1.9 MHz. A microchannel plate photomultiplier tube (Hamamatsu R1564U-07) was used to detect the fluorescence after its pass through a monochromator. Photon events were timed by an EGPE ORTEC TAC system and counts were accumulated in a PC equipped with a multichannel analyzer board interfaced with an Edinburgh Instruments Software package for fluorescence lifetime analysis. Data were taken with a resolution of 3.5 ps per channel and the instrument response was measured as no more than 80 ps at fwhm. The apparatus is described in more detail elsewhere.[15] Luminescence decays were analyzed in terms of the sum of exponentials using a nonlinear, least-squares iterative reconvolution procedure. When each one of the results was averaged from measurements coming from10 different samples, an error no larger than ±10% was obtained.

Fluorescence quantum yield measurements in the films were performed using as a standard the solution quantum yield of Rhodamine 6G (quantum yield in methanol is 0.9)[14] measured in a 0.2 mm path length cuvette, resembling the path length of the films deposited on the glass support. Its emission is in the same regime as that of the cyanine dyes being measured. The absorption of the standard was adjusted to the film absorption at the excitation wavelength and kept always below 0.1 in order to avoid reabsorption. The quantum yield analysis was done using a procedure described by Scaiano.[16]

3. Results and Discussion

3.1. Multilayer Buildup. Because the object of this work is to build cyanine dye-Laponite multilayers in order to use them in the study of energy transfer in antenna systems, the first issue was to demonstrate that we are able to build multilayers involving both monomer cyanine dyes and dye polymers. The layer thickness for the clay layers was measured by ellipsometry to be 12 Å ± 10%. The layer thickness for the monomer layers was measured by ellipsometry to be 13 Å ± 15%, and for the dye-polymer layers to be 16 Å ± 15%. These results indicate that somewhat more than a monolayer of dye is adsorbed for each clay layer. Precisely how much is difficult to say. The molecular dimensions from X-ray crystallography indicates that the monomer-dye layer would be about 10 Å thick for the molecule adsorbed with its long axis parallel to the substrate as is generally accepted for such surface packing.[17] Also, ellipsometry results showed that the increase in film thickness with the deposition of additional dye or clay layers is essentially linear for both monomer cyanine dye (D_m) and dye-polymer (D_p)(Figure 2). The linearity is better in the case of the dye-polymer multilayer buildup than in that of the monomercyanine dye. The better coating properties achieved by grafting the cyanine dyes onto the polymeric backbone and referred to previously,[14(b)] are evident here. The dye multilayer formation can also be followed by absorption and emission spectroscopy. It is expected that the absorption and emission intensity of the multilayer would increase linearly with each monomer dye or dye-polymer layer deposited as long as there is no interlayer interaction or, in the case of fluorescence, significant self-absorption. The behavior of the dye polymer and monomer dye confirms this expectation and is shown in Figures 3 and 4, respectively. The linear increase of the absorption signal with the number of layers shown in the insets in Figure 3a and 4a, does not pass through the origin, which may be attributed to reorganization of the dye-clay stacking following deposition of the initial layers. In the case of the dye-polymer layers, the absorption spectrum peaks at 561 nm for one layer and then shifts bathochromically with the addition of layers, reaching 565 nm after nine layers. This structure reordering of the aggregate packing results from a change in film thickness as has been reported for poly(phenylene vinylene) multilayers.[18] The same trend is observed in the case of the monomer-dye D_m, for which the absorption spectrum peaks at 568 nm for one layer and then shifts bathochromically with the addition of layers, reaching 572 nm after nine layers. The lower energy maximum for the latter suggests that there may be a higher J-packing order in the monomer dye-aggregate. The bandwidth of the absorption half-maximum in the case of the dye-polymer D_p decreases from 2315 ± 50 cm^{-1} after the deposition of one chromophore layer to 2085 ± 50 cm^{-1} following the deposition of nine chromophore layers. The bandwidth of the absorption half-maximum with additional dye-polymer D_p layers decreases monotonically (Figure 5). In the case of the monomer-dye D_m, the bandwidth of the absorption half-maximum decreases even more dramatically from 2777 ± 50 cm^{-1} after the deposition of one chromophore layer to 1454 ± 50 cm^{-1} after the deposition of nine chromophore layers indicating the greater lability of the monomer-dye aggregate ordering. These results are summarized in Table 1. This decrease in bandwidth of the absorption half-maximum with additional dye D layers is quite rapid for the first three layers then it reaches a plateau (Figure 5). The influence of substrate or adhesion layers on the ordering and packing of initial layers resulting in an anomalous thickness of the first layer has been encountered previously in layer-by-layer fabrication.[6c] In addition, further stabilization in the J-aggregation and the self-healing properties of the chromophore-clay multilayers due to the strong interlayer cohesion may play a role in the present system.

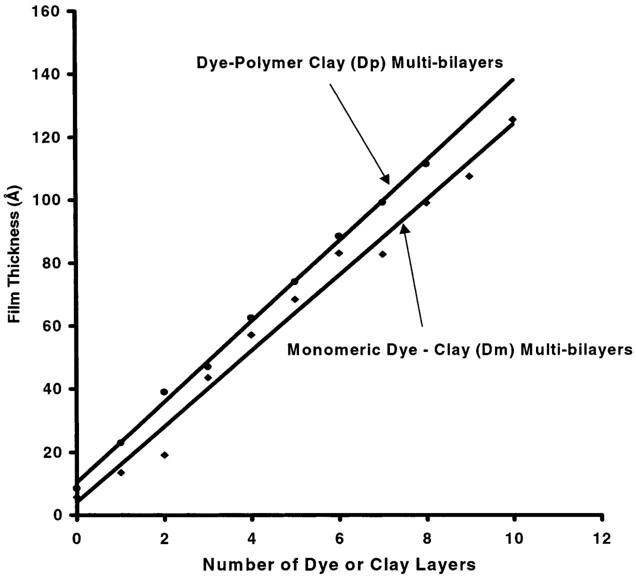

Figure 2. Ellipsometry results representing the film thickness of different number of dye or clay layers.

From Figure 3a, the increase in absorbance seen for the dye polymer with each successive dipping in the dye solution is 0.14. A closely packed monolayer of this same chromophore in a Langmuir−Blodgett film has been reported to have a maximum absorbance of 0.073.[19] Thus, a rough estimate is that the equivalent of about two monolayers of the chromophore are deposited for each clay layer in the present films incorporat-

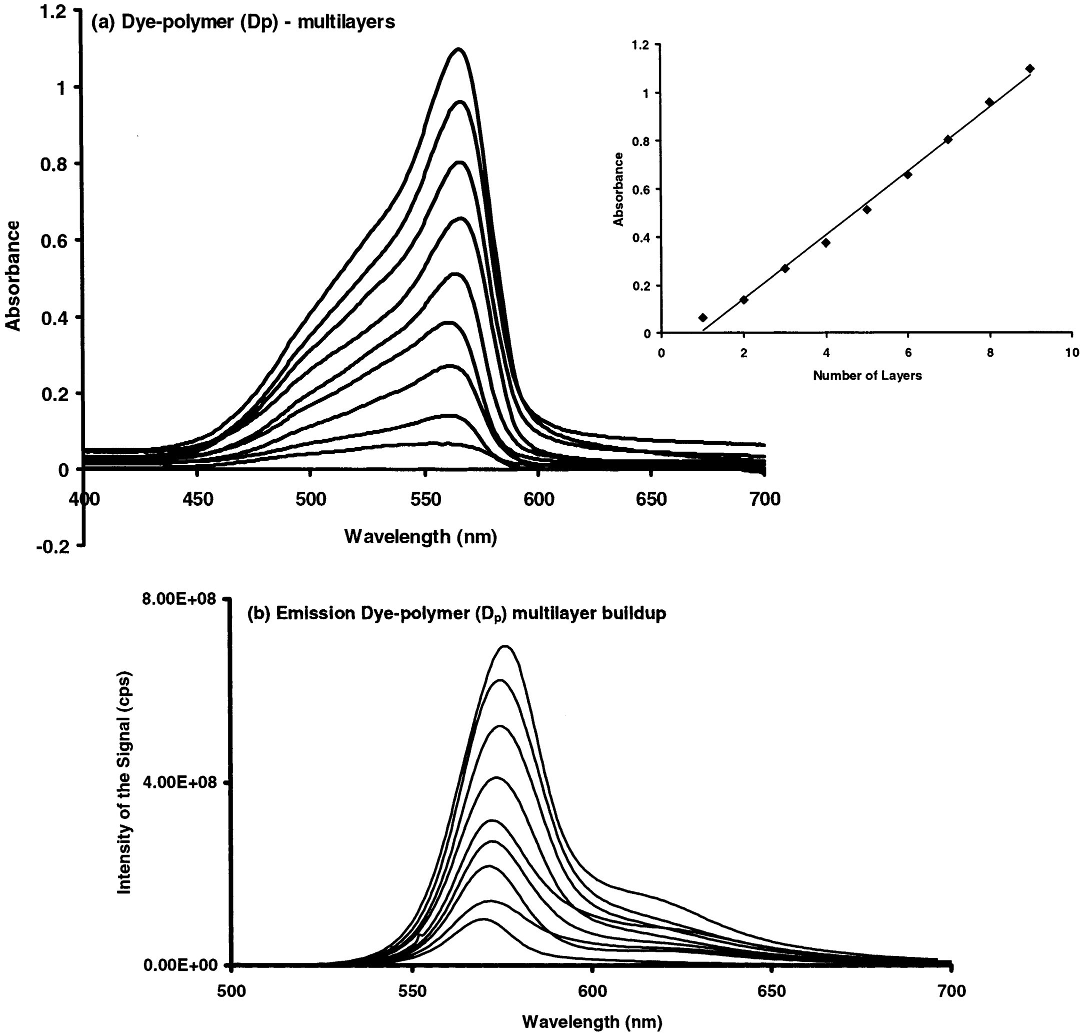

Figure 3. Absorption and emission spectra for the dye-polymer.

ing the dye polymer. For the monomeric dye this value corresponds to slightly more than three dye monolayers per clay layer. For the dye polymer, the result is consistent with the organic material coating both faces of each clay sheet. In the case of the monomeric dye, it appears that the chromophore stacks in more that a single layer on the surface of the clay. There is, in fact, evidence in the photographic literature that this dye has a propensity to form multilayer stacks in the J-aggregated state on the surface of silver halide.[20]

3.2. Photophysical Properties. *3.2.1. Single-Photon Counting Measurements.* Fluorescence decay lifetimes were recorded for single-layer monomer dye and dye-polymer films using single photon counting measurements. Analysis showed that the fluorescence decays for D_m and D_p were biexponential, with a short lifetime of 10 ± 20% ps attributed to the J-aggregate and a long-lived component of 60 ± 20% ps attributed to the residual nonaggregated chromophore. No significant difference between D_m and D_p was observed. The same trends were seen when fluorescence decays of the donor/acceptor systems described below were recorded. Because the fluorescence lifetimes of the donor and acceptor are quite close to each other, it was very difficult to resolve the spectra. Rather than observing a change in the donor lifetime upon addition of the acceptor, a decrease in the donor fluorescence signal intensity after the addition of the acceptor was observed. This result is consistent with the static type of quenching present in our system, but no further lifetime-analysis calculations were attempted using these data.

3.2.2. Quantum Yield Measurements. Fluorescence quantum yields of D_m and D_p were measured. The values given in Table 2 are very low, consistent with the short excited-state lifetime of these dyes in the J-aggregated state.

3.3. Energy Transfer. From the results presented above indicating the ability to successively deposit alternate layers of clay and dye monomer or dye polymer, it appeared attractive to construct assemblies incorporating an outermost layer of an energy accepting cyanine to investigate the possibility of energy transfer in these structures. It has been shown[12] that the singlet—singlet energy transfer process between the cyanine dyes coated in films occurs through a dipole—dipole or Förster mechanism which requires an overlap between donor emission spectrum and the acceptor absorption spectrum.[21] The cyanine dyes discussed above—monomer-dye D_m and dye-polymer D_p, which absorb in film at 568 and 561 nm and emit at 572 and 580 nm, respectively—were used as energy donors. As energy acceptor, we investigated the monomer-dye A_m whose J-aggregates on clay absorb in film at 605 nm. We were interested in the effectiveness of energy transfer between adjacent donor and acceptor chromophore layers, and also in studying the possibility of an antenna effect occurring whereby the excitation delivered to multiple donor layers can be harvested by energy transfer to a single acceptor layer. We anticipated the possibility that the dye-polymer Dp forms an extended J-aggregate and due to its polymeric character a more pronounced antenna effect might be observed compared to the monomer-dye D_m. However, as

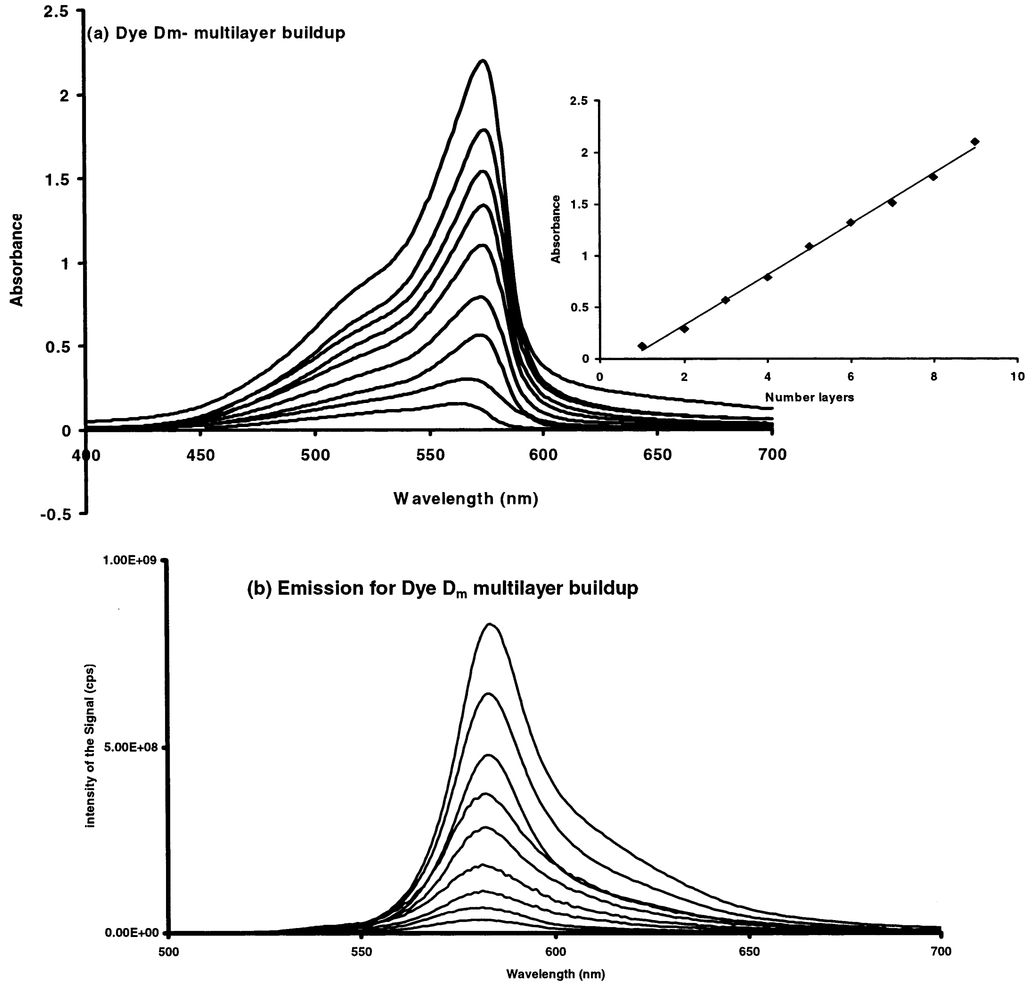

Figure 4. Absorption and emission spectra for the dye monomer.

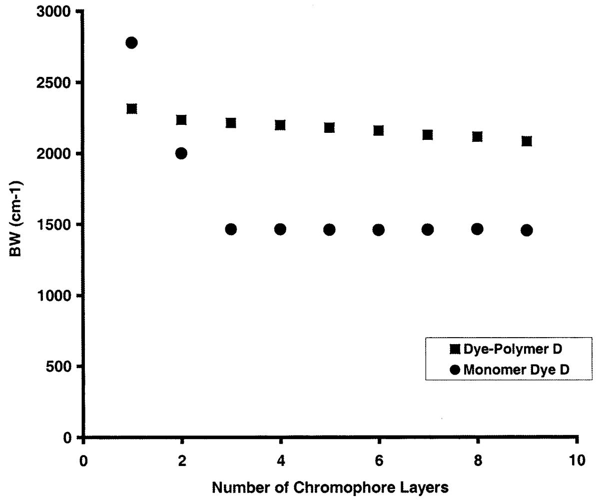

Figure 5. Total bandwidth variation with number of chromophore layers.

TABLE 1: Variations in the Absorption and Emission Wavelength Maxima, Plus Bandwidth Single Layer Compared with Multilayer Films

no. chromophore layers (film)	donor	λ_{max}(abs), nm	λ_{max}(em), nm	fwhm, cm^{-1}
1	dye-polymer	561	580	2315
1	monomer	568	572	2777
9	dye-polymer	565	583	2085
9	monomer	572	578	1454

TABLE 2: Directly Measured Fluorescence Quantum Yields (D_m = Monomer Dye Donor, D_p = Dye-Polymer Donor)

system	D_m	D_p
quantum yield	7×10^{-3}	4×10^{-3}

will be discussed below, the actual results make it doubtful that our system is sufficiently ordered to permit such analysis.

3.3.1. Spectroscopic Measurements. Measuring the steady-state fluorescence spectrum provides an indication of the singlet excited state population of cyanine dye ensembles. We compared the total fluorescence resulting from excitation of the energy-donor dye in the absence and presence of the acceptor. In each case incorporation of the acceptor was obtained by a usual dipping process with a terminal “coating” of the acceptor over the appropriate ensemble of donor dye monomer or dye polymer. Fluorescence spectra were recorded after the addition of each dye or clay layer. The excitation wavelength was in all cases 480 nm, where the acceptors absorbed only a small fraction of the light relative to the donor. In the case of assemblies incorporating the monomer cyanine-dye D_m and the monomer cyanine-dye A_m, almost all the donor fluorescence is quenched when the adjacent layer of the acceptor is present and the emission from the acceptor J-aggregate is observed (Figure 6b). The intensity of the emission increases with number of donor layers used (up to four layers); there is no further increase with increasing number of donor layers (more than four layers). For assemblies incorporating the dye-polymer D_p and the monomer cyanine-dye A_m, almost all the donor fluorescence is quenched when the acceptor is present, and emission from the acceptor

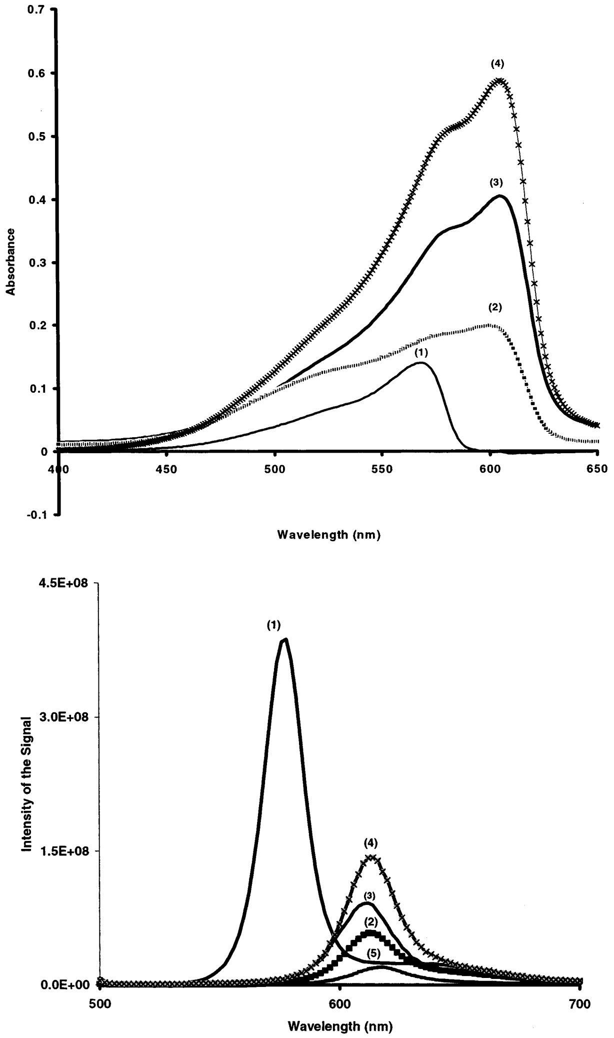

Figure 6. (a) Film absorption spectra of (1) D_m; (2) D_m/A; (3) $D_m/D_m/A$; (4) $D_m/D_m/D_m/A$; (b) Film emission spectra of (1) D_m; (2) D_m/A; (3) $D_m/D_m/A$; (4) $D_m/D_m/D_m/A$; (5) $A - \lambda_{exc} = 480$ nm.

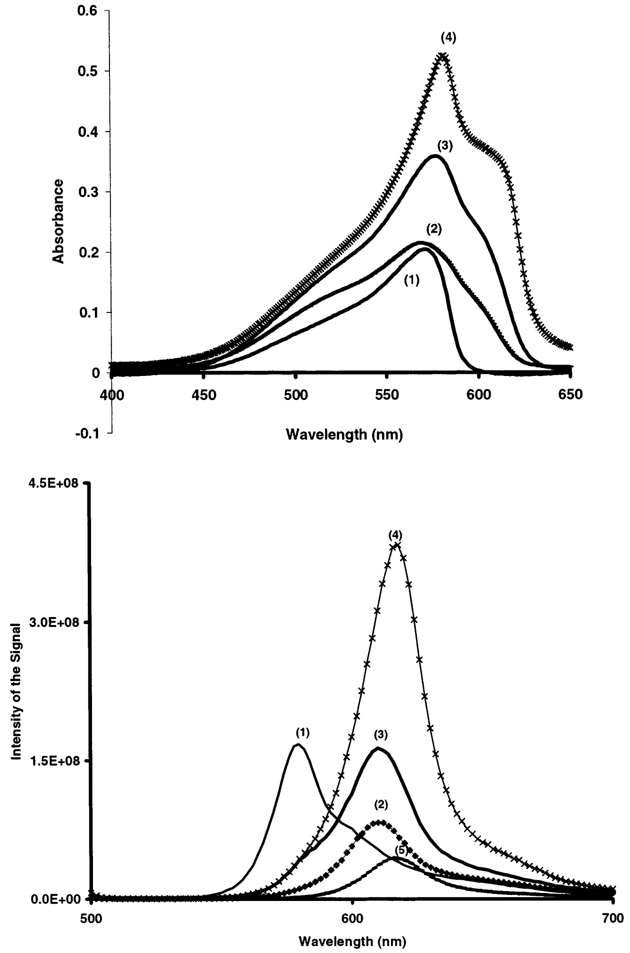

Figure 7. (a) Film absorption spectra of (1) D_p; (2) D_p/A; (3) $D_p/D_p/A$ (4) $D_p/D_p/D_p/A$; (b) Film emission spectra of (1) D_p; (2) D_p/A; (3) $D_p/ D_p/A$; (4) $D_p/D_p/D_p/A$; (5) A $-\lambda_{exc} = 480$ nm.

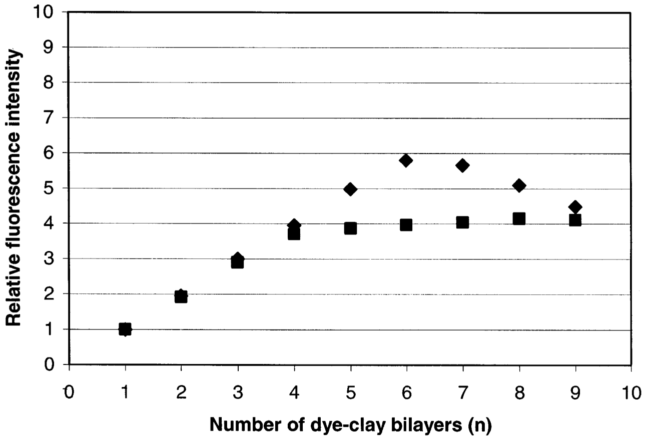

Figure 8. Acceptor emission at 610 nm as a function of number of donor dye-clay bilayer for a monomer dye (squares) and for a dye-polymer (diamonds).

is observed along with residual emission from the donor (Figure 7). The intensity of the acceptor J-aggregate emission increases with number of donor layers used (up to six layers) but does not increase further with additional dye-polymer energy donor layers. The dependence of acceptor emission as a function of the number of donor dye-clay bilayers is shown in Figure 8 for both monomer and polymer donor dyes.

An inspection of the absorption spectra in Figures 6a and Figure 7a indicates there is a lack of additivity of the donor and acceptor absorption spectra for both the acceptor plus donor (dye monomer) and the acceptor plus donor (dye polymer). The absorption spectra of the mixed ensembles were deconvoluted (Figure 9, parts a and b) in each case to three individual components: (component 1) a "Gaussian" corresponding to the J-aggregate absorption of acceptor occurring near 620 nm, (component 2) a "Gaussian" corresponding to the J-aggregate of the donor, and (component 3) a much broader "Gaussian" centered at shorter wavelengths (~540 nm). The actual and "fit" spectra are compared for the donor monomer/acceptor in Figure 9a and the corresponding deconvolution for the donor polymer/acceptor is shown in Figure 9b. The breadth of the latter peak (component 3) and its occurrence in a region where both monomers and other aggregates (for example "H" aggregates or dimers) absorb suggest that its composition may be difficult to determine. However, the first and second components from the deconvolution may be reasonably ascribed to "largely J-aggregate" of acceptor and donor, respectively. Figures 10 and 11 show how these components evolve as the composition of the ensemble is changed. In Figure 10 (donor monomer/acceptor) the absorption maxima of both of these peaks is shown to shift somewhat to the red as the number of layers of dye monomer (donor) increases. This suggests that the composition of the J-aggregates may be more complex than pure dye donor or pure dye acceptor; however, because the shift is rather small the absorptions may clearly be ascribed to species

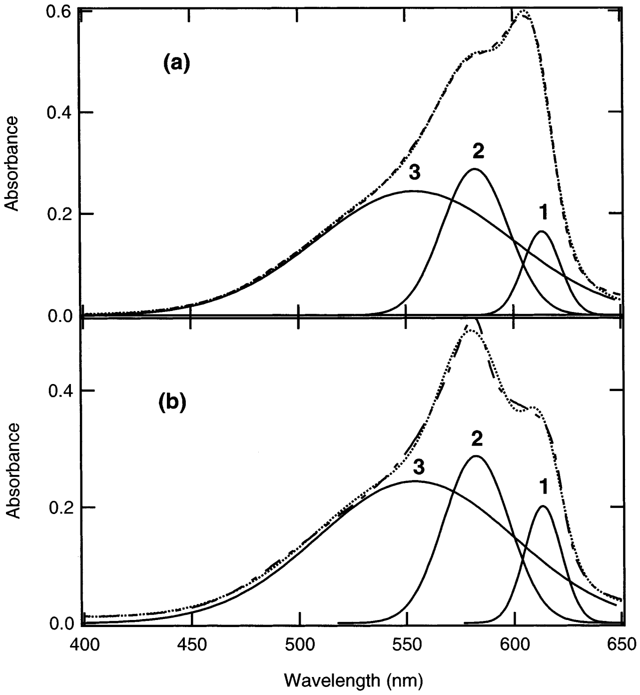

Figure 9. Deconvoluted absorption spectra for mixed assemblies composed of D/D/D/A: (a) donor monomer plus acceptor, (b) donor polymer plus acceptor.

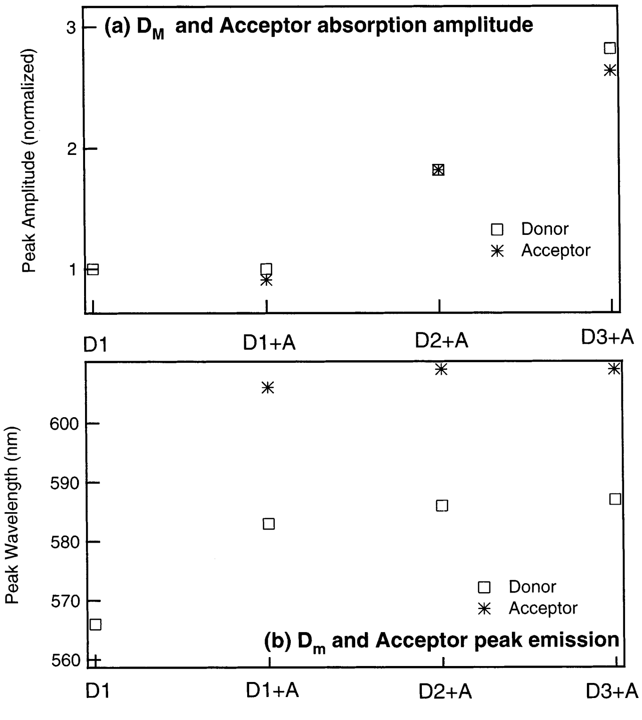

Figure 10. Peak amplitude (a) and peak maxima (b) for deconvoluted components of donor monomer plus acceptor assemblies.

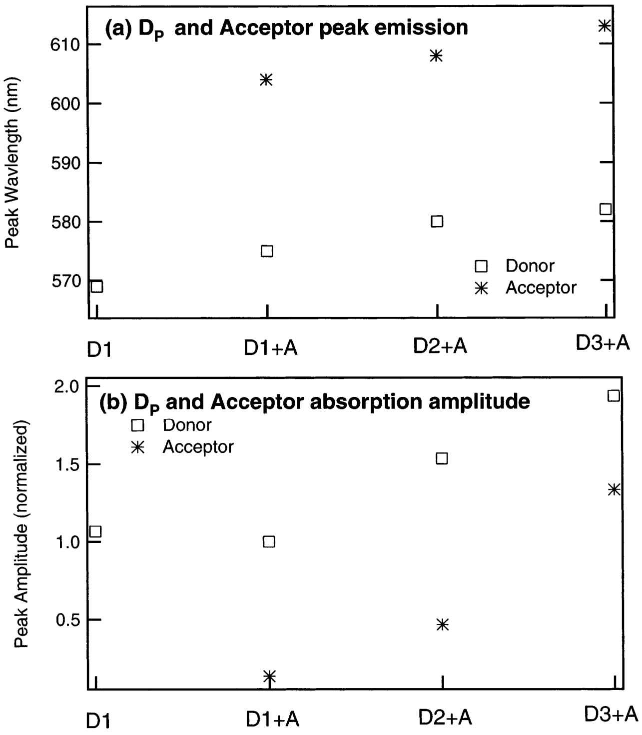

Figure 11. Peak amplitude (a) and peak maxima (b) for deconvoluted components of donor polymer plus acceptor assemblies.

where the “principal components” are mostly J-aggregate of one or the other cyanine. As shown in Figure 11, similar changes occur when the dye monomer is replaced by the polymer. Perhaps more instructive is the comparison of peak amplitudes as a function of number of layers of donor. For the dye monomer (Figure 10), the amplitude of the absorption peak ascribed to “mostly donor dye J-aggregate” is the same when a single layer of acceptor is added and shows, as anticipated, a linear relationship between the numbers of layers of dye donor in the total assembly. The slope of this plot is less than unity. More interesting, the amplitude of the “mostly acceptor dye J-aggregate” absorption shows a linear increase with number of donor layers in the ensemble. Qualitatively similar, but less pronounced behavior is observed for the ensembles containing dye polymer and the acceptor. The amplitude of the “mostly donor dye J-aggregate” absorption peak increases (as expected) with the number of layers of the donor; however, the slope of the plot is less than unity. Unexpectedly, the amplitude of the “mostly acceptor dye J-aggregate” absorption peak also increases with the number of layers of donor, even though in each case the acceptor was deposited in a single dipping process.

These observations indicate that the structures of the ensembles containing mixtures of both dye polymer and acceptor, and dye monomer and acceptor, may be much more complex than might be predicted on the basis of simple layer-by-layer assembly. The incorporation of increasing amounts of acceptor (in a single dipping step!) as the “dipped” assembly has increasing numbers of layers of donor (and clay) indicates that the acceptor may not be confined to the outer layer but is actually “invading” or interpenetrating the inner layers of the ensemble. Assembly invasion can also explain the very effective sensitization of acceptor J-aggregate fluorescence from several base layers of donor (for both the polymer and the monomer of the donor). However, this frustrates any quantitative analysis of donor J-aggregate − acceptor J-aggregate energy transfer in these assemblies and prevents a clear identification of any new long-range processes between the polymeric aggregates and the acceptor. Unfortunately, this situation has likely been exacerbated because we were forced to use a monomeric acceptor dye. The corresponding polylysine-based dye polymer did not form a robust J-aggregate when layered onto the donor-clay film and, as a result, was not spectroscopically able to act as an energy acceptor for the J-aggregated donor chromophore.

The invasion of the donor assemblies by the acceptor is an interesting process. At least three different mechanisms (and/or combinations thereof) might be proposed for the invasion.

A first mechanism could involve penetration of the acceptor into "inner layers" of the assembly during the dipping process followed by generation of "patches" of J-aggregate acceptor on vacant clay sites in the inner layers as well as on top of the outermost layer of clay. A second mechanism could involve a competitive desorption of donor and adsorption of acceptor, thus, leading to replacement of patches of donor with patches of acceptor. A third mechanism might involve growth of new aggregates of acceptor onto existing aggregates of donor without their displacement but with corresponding swelling or expansion of the existing (prior to exposure to the acceptor) assembly. These are complex interactions involving multiple component materials, and it is not possible from these initial experiments to determine the extent of these different processes in a quantitative way. It may be worthwhile to consider their likelihood from what we know of the properties of the dyes and the clay.

Although both donor and acceptor cyanines are expected to be relatively hydrophobic (large molecules, only a single, delocalized positive charge in each case), it might be expected that the acceptor is somewhat larger (additional phenyl ring) and consequently slightly more hydrophobic than the donor. This could result in it having a stronger tendency to adsorb to the clay than the donor. It is known that Laponite has a relatively low number of exchangeable cations,[14b] so that hydrophobic interactions play a larger role in adsorption than with other minerals having greater charge density. Thus, it is plausible that although the maximum amount of donor dye has been adsorbed to the clay, the acceptor could adsorb by displacement of donor dye. The estimates in section 3.1 that the extent of chromophore adsorption in the case of the dye polymer is essentially a complete monolayer coverage over the surface of the clay particles, and is even greater in the case of the monomeric dye, suggest that very little, if any, free clay surface is available upon which the acceptor dye could adsorb. The possibility that acceptor dye deposits onto the donor dye is also a plausible scenario. There is no independent information as to whether this happens for these particular donor and acceptor cyanine chromophores. But, as already stated, the monomeric donor dye has a tendency to form such multiple layers and appears to already do so in the present experiments. So, it is not unreasonable to suggest that the acceptor dye, which, if anything, has a greater tendency for hydrophobic adsorption than the donor dye, may also bind onto a preexisting layer of donor dye, either monomeric or the dye polymer. Thus, there is reason to believe that the acceptor dye may in fact penetrate into the multilayer film structure through one or more mechanisms and not remain isolated from the donor dye by an integral clay layer.

That layer-by-layer fabrication does not always lead to well isolated, sharply delineated periodic structures has been recognized for some time. More specifically, in the construction of donor–acceptor systems for energy transfer and light harvesting it has been determined, using the "spectroscopic ruler" of Förster theory, that for all-polymeric materials there is broadening or interpenetration of the chromophore distributions of several nanometers.[22] It has also been shown in films constructed from a polyelectrolyte and an oppositely charged small organic molecule that the latter penetrates to depths up to 20 nm into the film structure.[23] This is greater than the entire thickness of the present films. Because the adsorption of the small molecule was dependent on the fabrication conditions, the present system would not be expected to behave identically, but the results demonstrate that such molecules can easily penetrate a relatively thick film. On the other hand, Kaschak and Mallouk demonstrated that by using the inorganic spacer zirconium phosphate they were able to confine chromophores much more narrowly within a layer, to 6 Å or less.[13] It was that distinction between organic and inorganic interlayers that motivated us to attempt our experiment to build multiple donor, dye-clay bilayers. However, apparently because of the specific properties of the materials used, whether the clay, the polyelectrolyte, or the chromophore, it must be concluded that the present system is sufficiently disordered to short-circuit the long-range energy transfer process needed to concentrate the excitation energy in a single energy-acceptor layer that was the goal of the antenna system. The present architecture does not allow us to analyze the film structure by the spectroscopic ruler technique, since it does not include a systematic spacing of single donor and acceptor layers, but rather adds successively more donor layers to the structure, preventing a straightforward analysis via Förster theory. Standard macroscopic techniques of monitoring the film growth, through ellipsometry or absorption spectroscopy, failed to detect a problem or defects in the fabrication process. Only a close examination of the spectra of the complete system revealed that a nonadditive behavior was occurring with concomitant photophysical consequences.

Thus, the acceptor fluorescence intensities for monomeric and polymeric donors shown in Figure 8 as a function of the number of donor layers reflect a combination of interpenetration of acceptor dye resulting in efficient short-range energy transfer within mixed layers and long-range energy transfer from multiple donor layers to a partial layer of acceptor dye. Both processes cease to be effective beyond a certain number of donor layers, which is different for monomer and polymer donor dyes.

4. Conclusions

In this study, we demonstrated that we are able to build layer-by-layer systems using monomer cyanine dyes or dye-polymers and inorganic clay layers. The multilayers built using dye polymers showed better layer buildup than those built using monomer dye but, nonetheless, both types of chromophores used provided multilayers. Within the film structure, the cyanine chromophore exhibited J-aggregate spectroscopic properties, either as the result of adsorption to the clay in the case of the monomeric dye or because it preexisted in this form in the case of the dye polymer. Such composite assemblies were prepared in an attempt to demonstrate a light harvesting photoantenna system through long-range energy transfer by adding a layer of a different cyanine dye whose J-aggregate absorption band overlapped the fluorescence wavelength of the dye incorporated into the film acting as an excitation energy donor. Although efficient energy transfer was demonstrated for up to four donor dye-clay bilayers in the case of the monomeric dye and up to six donor dye-clay bilayers in the case of the dye polymer, it appears that this may not be due to long-range energy transfer. Analysis of the absorption spectra of the assemblies including the acceptor dye layer show evidence that more acceptor dye is adsorbed the greater the number of donor dye-clay bilayers. This indicates that some acceptor dye may penetrate into the assembly, increasing the likelihood that some acceptor dye may be in close proximity to the donor dye within the film structure rather than isolated in a spatially separate layer. This could cause efficient short-range energy transfer, leading to the observed sensitized fluorescence of the acceptor. These results provide a cautionary note in the fabrication of structured systems requiring the nanometer-level order of the molecular components needed to achieve cooperative performance.

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