Inter- and Intralayer Energy Transfer in Zirconium Phosphate−Poly(allylamine hydrochloride) Multilayers: An Efficient Photon Antenna and a Spectroscopic Ruler for Self-Assembled Thin Films

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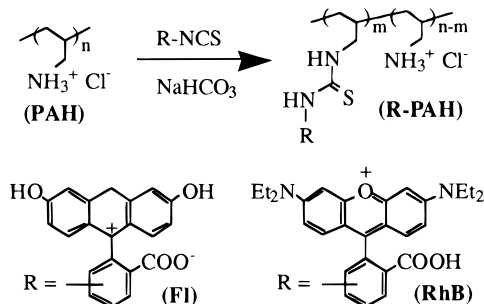*The Pennsylvania State University*
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Molecular self-assembly provides a useful synthetic route to many interesting supramolecular structures and devices.[1] Covalent[2] and ionic[3] self-assembly methods have been used to make multilayer thin films with cooperative electronic and optical properties, including electroluminescence,[4] second-harmonic generation,[5] and photoinduced electron transfer.[6] Because these effects depend critically on supramolecular structure, an important goal is to develop simpler and more reliable techniques for juxtaposing the active components—photoactive and electroactive molecules—in well-defined structural arrangements. Another ongoing challenge is the development of better tools for characterization of these assemblies on the nanometer length scale. Probes such as ellipsometry, X-ray diffraction, and UV−vis spectroscopy provide information that is averaged over macroscopic dimensions and are often unable to differentiate between possible structures.

Ionic multilayer films made from organic polyelectrolytes contain oppositely charged polymer strands that intertwine, and there are no sharp boundaries between sequentially grown layers.[7] Related thin films made from two-dimensional inorganic polyanions such as clays[8] and α-zirconium phosphate (α-ZrP)[9] are thought to be structurally analogous to ionic intercalation compounds, in which the stratification of inorganic and organic components is well defined. It is not known, however, whether the contents of these layers are mixed in the adsorption process. Each adsorption step appears to produce a single monolayer in some cases[9] and multiple layers in others.[8] In this paper, we report a study of α-ZrP/poly(allylamine hydrochloride) (PAH) thin films, in which energy transfer between fluorescent probes serves as a "spectroscopic ruler". A comparison of theoretical and experimental energy transfer efficiencies for many different layer sequences shows that there is little or no bilayer formation or interlayer mixing during the adsorption process. These results underscore the usefulness of this surface assembly technique for device applications. Specifically, this study shows that it is possible to construct solid state photon antenna composites with energy transfer efficiencies approaching unity.

The polycation PAH was tagged with fluorescein (Fl) and rhodamine B (RhB) using modified Schotten−Bauman conditions.[10] UV−vis absorption spectra gave chromophore loadings of ca. 1:20 and 1:50 for the Fl−PAH and RhB−PAH polymers, respectively. Sequential adsorption of these polymers and colloidal α-ZrP onto glass slides, using conditions similar to those described previously for α-ZrP/PAH films,[9,11] resulted in polymer coverages of $(3-4) \times 10^{-10}$ equiv/cm^2 on each side of the glass and ellipsometric film thicknesses (measured on silicon substrates) of 22 Å per anion−cation layer pair. The increase in thickness of these bilayers relative to α-ZrP/PAH (14−16 Å per layer pair) reflects the size of the probe molecules and possibly their effect on the coiling of the polymers at low ionic strength. There was no observable birefringence in the absorption spectra of these films, suggesting random chromophore orientation within the layers.

Energy transfer between Fl and RhB proceeds by a Förster mechanism, which provides a quantitative probe of intermolecular distances within supramolecular assemblies.[12] The rate of energy transfer can also reflect the sensitivity of probe

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(10) (a) Haugland, R. P. In *Molecular Probes Handbook of Fluorescent Probes and Research Chemicals*; Molecular Probes, Inc.: Eugene, OR, 1992−1994; p 20. (b) Half the stoichiometric amount of NaHCO$_3$ was added to an aqueous solution of 0.2 equiv/L PAH. To this solution was added a 10 mM solution of the isothiocyanate-functionalized chromophore in DMF, and the solution was incubated at room temperature in the dark for 2 h. The chromophore-derivatized PAH was then purified by adding acetone to precipitate the polymer from water (for RhB−PAH) or ethylene glycol (for Fl−PAH).

(11) A 7 mequiv/L solution of Fl−PAH in ethylene glycol was acidified with aqueous HCl to give the yellow color of the acidic form of Fl. This procedure redissolves any suspended polymer. Then, solid NaOH was added until the orange color of the basic form of Fl (p$K_a = 6.4$) began to appear. Substrates were incubated in this solution for 10 min and then rinsed sequentially with ethanol, water, and ethanol and dried in a stream of Ar. α-ZrP was adsorbed from 0.7 mequiv/L suspensions at pH 10, as described in ref 9. A similar procedure was followed for RhB−PAH, except that 4 mequiv/L aqueous solutions, pH 6.8−7.2, were used.

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Table 1. Comparison of Measured and Calculated Energy Transfer Efficiencies for Different Donor−Acceptor Gometries

system	χ measured (calcd[a])
RhB + Fl	0.89 (0.90)
RhB/Fl/RhB	0.82 (0.81)
RhB/RhB/Fl	0.72 (0.73)
RhB/PAH/Fl/PAH/RhB	0.39 (0.41)
RhB/PAH/PAH/Fl/PAH/PAH/ RhB	0.13 (0.11)
RhB/Fl	0.62 (0.70)
RhB/PAH/Fl	0.19 (0.27)
RhB/PAH/PAH/Fl	0.05 (0.06)
RhB/RhB/Fl/Fl	0.35 (0.36)[b]

[a] Simulation parameters: $R_o = 40$ Å, zero-layer interpenetration. / denotes an α-ZrP layer. [b] Calculated using $R_o = 40$ Å for both the Fl−Fl and Fl−RhB energy transfer reactions.

molecules to changes in polarity or local pH;[13] in the present case, however, the chemical environment was kept constant. By varying the number of α-ZrP/PAH "spacer" bilayers between layers containing Fl−PAH and RhB−PAH, it was possible to create assemblies in which the Fl to RhB distance was either smaller or greater than the Förster radius, which is ca. 40 Å.[14] Energy transfer efficiencies (χ) were calculated from steady-state emission spectra of the thin films. Values of χ obtained from the enhanced emission of the acceptor (RhB) and quenching of the donor (Fl) emission typically agreed within 2−5%.

Table 1 shows a comparison of χ values obtained experimentally and by Monte Carlo simulation of the energy transfer reaction for different layer sequences.[15] The agreement between experimental and calculated values is striking. This comparison provides an important check of the structural model of these films suggested by ellipsometry. Consider, for example, the sequence of three adsorption steps RhB−PAH, α-ZrP, Fl−PAH. If single smooth monolayers are deposited in each step, the structure is RhB/Fl, where / signifies an α-ZrP layer. On the other hand, if bilayers grow in each step but cover only 50% of the surface, the local geometry is RhB−RhB//Fl−Fl or RhB/ RhB/Fl/Fl (sequences like the latter have been suggested for silicate multilayers[8]). The observed values of χ rule out all but the first structure, for which good agreement ($\chi = 0.62, 0.70$) is found with theory. The last structure can be made deliberately in seven adsorption steps, and again the agreement between experiment and theory ($\chi = 0.35, 0.36$) strongly supports a model in which each adsorption step produces either a smooth polycation layer or a single layer of α-ZrP sheets.

When the donor−acceptor distance is comparable to or greater than the Förster radius, χ is also a sensitive function of the mixing of polycations or interpenetration of layers. Figure 1 illustrates this point for arrangements in which a single Fl−PAH layer is flanked by RhB−PAH layers with variable numbers of α-ZrP/PAH spacers between. Efficiencies were calculated for acceptor layer "widths" of 0, 6, 18, and 36 Å. At
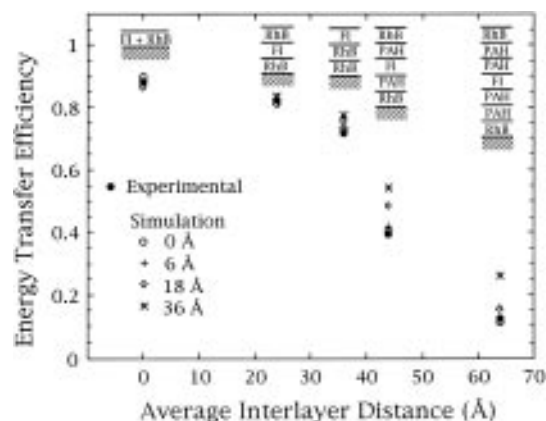
Figure 1. Energy transfer efficiency (χ) versus average donor−acceptor interlayer distance for Fl−PAH/α-ZrP systems containing two RhB−PAH layers and theoretical efficiencies obtained from Monte Carlo simulations. Calculated values are shown for several RhB−PAH layer widths.

short donor−acceptor distances, the mixing of layers has little effect on the calculated efficiencies. However, at larger distances there are significant differences, with only the zero-mixing cases (0 and 6 Å layer widths) providing good fits to the data. This calculation provides good evidence that a polycation layer, once adsorbed, does not desorb or mix with other polymer layers in the subsequent layer growth/washing steps.

To demonstrate the potential for making very efficient energy transfer assemblies by this technique, a system containing both donors and acceptors in the same layer was prepared by adsorption of a mixture of Fl−PAH and RhB−PAH solutions. In this case, both the simulated and experimental efficiencies were 0.89 (Figure 1). This is the theoretical limit for a single-layer system at this low (1:50) loading of RhB on PAH. Higher efficiencies should be attainable with higher acceptor loadings. Other systems with efficiencies as high as 0.95 were prepared by sandwiching one donor layer between three acceptor layers. We note that this assembly technique provides a structurally tunable and synthetically very simple alternative to other biomimetic light-harvesting systems, such as fluorescent donor−acceptor supermolecules,[16] polymers,[17] covalently bound mono-layers,[18] and Langmuir−Blodgett films.[19]

This comparison of experimental and theoretical energy transfer efficiencies has shown that it is possible to control the morphology of self-assembled ionic films deliberately and precisely on the angstrom length scale. Energy transfer efficiencies near unity are achieved with properly designed systems. The possibility of extending this work to the creation of more complex biomimetic systems, which combine both energy and electron transfer functions, is currently being explored.

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(15) Simulations were carried out using the Fortran program ETRANS on a Power Macintosh 8100/80. The algorithm involved generating an excluded-volume set of acceptor molecules with random x- and y-coordinates within a $2R_o \times 2R_o$ grid, and z-coordinates were fixed by the experimentally determined layer thicknesses. The density of acceptors was chosen to match the observed polymer coverage, and the Förster radius, R_o, was fixed at 40 Å. The energy transfer efficiency, χ, was calculated as $\sum(R_o/R)^6/(1 + \sum(R_o/R)^6)$, where R is the donor-acceptor distance. Ensemble averages of 1,000−10,000 configurations are given in Table 1 and Figure 1. R_o values of 35 and 45 Å resulted in significantly poorer fits to the data. For simulations of layer interpenetration, the z-coordinates of the RhB acceptors were allowed to assume random values of equal probability within a specified distance of the midpoint of the acceptor layer.

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