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Dynamics within a Single Molecular Layer. Aggregation, Relaxation, and the Absence of Motion

J. C. Horne and G. J. Blanchard*

Contribution from the Department of Chemistry, Michigan State University,
East Lansing, Michigan 48824

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Abstract: We report on the transient and steady-state optical responses of the chromophore 2,2′-bithiophene-5,5′-diylbis(phosphonic acid) (BDP) incorporated within a single zirconium-phosphonate layer as a function of chromophore density. While the dilute solution optical response of BDP reveals no anomalous behavior, its characteristics are substantially different when confined within a monolayer. We vary the concentrations of layer constituents to determine the extent of interaction between BDP moieties within a single monolayer. We observe limited initial aggregation of BDP, the extent of which is determined largely by the conditions under which the monolayer is formed. Over time, the fractional contribution of BDP aggregates to the total optical response decreases to a limiting value, implicating surface adsorption site density as the dominant factor in determining the morphology of the organobis(phosphonate) layer. Motional relaxation measurements of BDP within the layer show that the chromophores are immobile on the hundreds-of-picoseconds time scale of our experiments.

Introduction

Organized molecular assemblies have found use in numerous chemical and physical applications, such as device patterning, nonlinear optics, and tribology.[1−7] This class of interfacial materials have characteristically well-defined structures of controlled composition and, with a small amount of material, they offer a widely tunable range of chemical, electrical, and optical properties. Metal-phosphonate (MP) organic multilayer structures have been investigated extensively[8−24] and, like other self-assembling monolayers, show potential for use in surface modification,[25−28] electronic device,[29−31] nonlinear optics,[7,19,20] and molecular recognition applications.[32−37] Phosphonic acids form strong, sparingly soluble complexes with metal ions, giving them significant advantages over many self-assembled monolayer (SAM) systems, such as the thiol/gold SAMs, which have been shown to be labile.[38−40] MP structures are comparable to SAMs in ease of synthesis, which generally involves immersion of the functionalized substrate into a solution of the appropriate (α,ω)-organobis(phosphonate). MP multilayers are versatile in a chemical sense because the identity of individual layers can be controlled selectively as the structure is assembled and, in this way, chemical or electrical potential, as well as optical properties, can be built into the system in three dimensions rather than two. Langmuir−Blodgett films can also be assembled as

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* Author to whom correspondence should be addressed.

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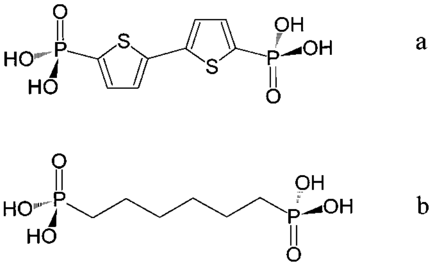
Scheme 1. Structures of Bis(phosphonates): (a) 2,2′-Bithiophene-5,5′-diylbis(phosphonic acid) (BDP) and (b) 1,6-Hexanediylbis(phosphonic acid) (HBPA)



ordered multilayer structures, but it is a relatively delicate process and, once formed, the films are not robust due to the weak nature of the associations between layers. For these reasons, MP multilayers are robust, nearly ideal model systems for the examination of energy relaxation both within and between individual molecular layers. This same structural motif holds significant technological promise for optical signal processing and information storage applications.

The connection between these apparently disparate uses for MP systems can be reconciled as follows. The density of optical information that can be stored within a single molecular layer is limited, and the spatial resolution or "bit size" available with optical approaches is determined by the diffraction limit for the optics used and the wavelengths of reading and writing light. One way to enhance the information density attainable within a specific volume is through the addition of a third dimension, but such an approach can also cause complications in control over material properties and basic physical processes. The ability to store information in a material optically depends on making a specific, stable modification to the optical response of a given layer of the material. The presence of other optically active constituents within the same layer or in neighboring layers creates the possibility of intra- or interlayer energy exchange processes, which serve to place limits on the utility of these materials for information storage applications.

We consider the interlayer and intralayer relaxation processes of MP assemblies separately because of the synthetic control we can achieve over these structures. In this initial work, we consider intralayer effects from a fundamental perspective using 2,2′-bithiophene-5,5′-diylbis(phosphonic acid) (BDP, Scheme 1) as the chromophore. Thiophenes are well understood[41] and, when phosphonated, form stable, relatively ordered layers because of their comparatively rigid structure, which prevents them from attaching to the surface at two points. To gain the information of interest here, we vary the concentration of the chromophore within a zirconium-phosphonate (ZP) monolayer. An optically inactive component can be used either for spacing between chromophore layers or for dilution of the chromophore within layers. In these experiments, we dilute the chromophore within a single layer using 1,6-hexanediylbis(phosphonic acid). This spacer molecule, in its all-*trans* form, is approximately the same length as the chromophore, so that the thickness of the monolayer is uniform (Scheme 1). We discuss below the extent of synthetic control we have over the composition of an individual layer, the steady-state optical response of BDP, and how it is related to the measured dynamical relaxation processes operating within the layer. Our data indicate that both aggregated and nonaggregated forms of the chromophore exist within a monolayer and that the relative amount of each is determined primarily by the silanized site density of the surface and not simply by the chromophore density.

Experimental Section

Synthesis of 2,2′-Bithiophene-5,5′-diylbis(phosphonic acid) (BDP). BDP was synthesized by modification of a published procedure on a longer (α,ω)-bisphosphonated thiophene oligomer.[18] All reagents were purchased from Aldrich Chemical Co. and used as received. Tetrahydrofuran (THF) was distilled over CaH_2 and then sodium, under N_2 atmosphere. 2,2′-Bithiophene (6.01 mmol) was dissolved in 200 mL of THF (under Ar) and cooled to −40 °C. An excess of *n*-butyllithium (25 mmol, 2.5 M in hexanes) was added to this solution, and the mixture was stirred for 90 min. A second solution of *n*-butyllithium (0.5 mmol) and bis(dimethylamino)phosphochloridate (25 mmol) in 20 mL of THF was added to the first via canula. The reaction solution was allowed to warm slowly to room temperature and was stirred for 3 days. The organics were extracted from water with ether, and the remaining aqueous layer was extracted twice with CH_2Cl_2. The combined organics were reduced in volume by rotary evaporation to about 1.5 g of a dark red oil. The tetraamide, a pale yellow solid which exhibited blue fluorescence on UV excitation, was collected chromatographically on silica plates (Fisher Scientific) using a mobile phase of 5EtOH:3MeOH: 2THF. The purified product was added to 100 mL of dioxane and dissolved at 80 °C. After the resulting mixture was cooled to room temperature, 50 mL each of water and concentrated HCl was added, and the solution was refluxed overnight. The solvent was partially removed, and a dark green-yellow solid was recovered in *ca.* 10% yield. Product identity was verified by ^{1}H NMR (DMSO-d_6): δ 7.3−7.5 (m).

Synthesis of 1,6-Hexanediylbis(phosphonic acid) (HBPA). All chemicals were purchased from Aldrich Chemical Co. Triethyl phosphite was dried over sodium and vacuum distilled. HBPA was prepared by the Michaelis−Arbuzov reaction of 1,6-dibromohexane (32 mmol) with excess triethyl phosphite (117 mmol).[22] The mixture was refluxed under Ar for 5 h to allow evolution of ethyl bromide. Excess triethyl phosphite was removed by vacuum distillation. Concentrated HCl (50 mL) was added to the colorless solution, which was then refluxed overnight. The resulting clear brown solution was cooled to room temperature. Upon cooling, a white precipitate (57% yield) formed which was collected by vacuum filtration and washed with acetonitrile. ^{1}H NMR (DMSO-d_6): δ 1.2−1.6 (m).

Metal-Phosphonate Multilayer Synthesis. Silica substrates, cut from quartz slides, were cleaned by immersion in piranha solution ($1H_2O_2$:$3H_2SO_4$) for 15 min,[42] rinsed with distilled water, hydrolyzed in 2 M HCl for 5 min, rinsed with distilled water, and dried under a N_2 stream. The substrate surface was silanized by refluxing in 1% v/v (3-aminopropyl)trimethoxysilane (Petrarch) in anhydrous octane under an Ar atmosphere for 10 min,[18] followed by thorough rinsing with reagent grade *n*-hexane. This amine primer layer was derivatized to the phosphonate by reaction with 100 mM $POCl_3$ (Aldrich) and 100 mM 2,4,6-collidine (Aldrich) in anhydrous acetonitrile under Ar for 1 h and rinsed with solvent grade acetonitrile. The phosphonic acid surface was zirconated overnight with a 5 mM solution of $ZrOCl_2$ in 60% EtOH/H_2O. Subsequent layers were added by sequential reaction with bis(phosphonate) (1.25 mM in 95% EtOH, 3 h at 55 °C) and zirconium (5 mM in 60% EtOH, 30 min) solutions, with extensive rinsing (H_2O) between each step. The pH of the solutions was maintained between 2 and 4.

Steady-State Optical Spectroscopy. The absorption spectra of BDP monolayers were measured using a Hitachi U-4001 UV−visible spectrophotometer. The samples were held vertically in place at 45° with respect to the incident beam and were collected with 5 nm spectral resolution. The emission spectra of the monolayers and solutions were collected using a Hitachi F-4500 fluorescence spectrophotometer. Monolayer samples were excited at 320 nm through a 10 nm slit. The emission bandpass was adjusted according to spectral intensity. The samples were held vertically, at 45° with respect to the excitation beam propagation in such a way as to minimize reflection of excitation radiation into the emission collection optics.

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(42) *Caution! Piranha solution is extremely corrosive and is a potent oxidizer.*

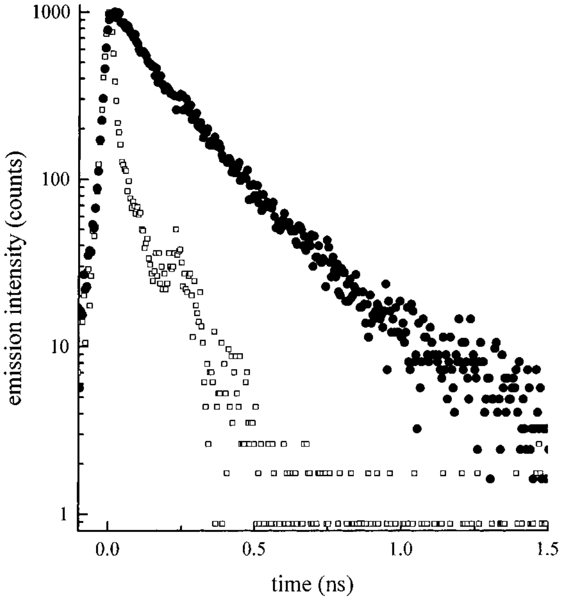

Figure 1. Example of excited state population decay (●) and instrument response function (□) for BDP in ethanol.

Time-Correlated Single Photon Counting Spectroscopy. The spectrometer we used for the fluorescence dynamics measurements of BDP solutions and monolayers has been described in detail before,[43] and we present here a brief overview of the system. The light pulses used to excite the sample are generated with a cavity-dumped, synchronously pumped dye laser (Coherent 702-2) excited by the second harmonic of the output of a mode-locked CW Nd:YAG laser (Quantronix 416). All samples were excited at 320 nm (Kiton Red, Exciton; $LiIO_3$ Type I SHG). Monolayer samples were held approximately horizontally, with 5° tilts away from horizontal in two directions: toward the excitation beam and toward the detector. Fluorescence from the sample was imaged through a reflecting microscope objective. Lifetimes were collected across the emission bands at 54.7° with respect to the excitation polarization for solutions and without polarization bias for monolayers. Fluorescence was collected at 390 nm (5 nm FWHM bandwidth for solution, 20 nm for monolayers) with polarizations of 0° and 90° for rotational diffusion dynamics measurements on all samples. A representative lifetime decay and instrument response function (~35 ps FWHM) are shown in Figure 1.

Data Analysis. The lifetimes we report here were fit to sums of exponentials using Microcal Origin software and are reported as the values and uncertainties of the fit to individual decays. Rotational diffusion information for solution measurements is reported as the average of six data sets with their associated 95% confidence limit uncertainty. For monolayers, eight pairs of alternating parallel and perpendicular scans were used to produce an average anisotropy function. $R(0)$ was determined to ±0.01 by regression of data at times after the instrument response, and several data sets were averaged for each sample.

Calculations. Semiempirical calculations[44−48] were performed using Hyperchem Release 4.0 (Hypercube, Inc.) on an IBM compatible PC (Gateway 2000 P5-120). The PM3 parametrization, used for these calculations, is a modification of the AM1 parametrization that treats molecules containing heteroatoms, such as sulfur, more accurately than previous parametrizations. An initial optimization of the structure was performed using a molecular mechanics routine (MM+)[49] followed by geometry optimization at the semiempirical level using an SCF algorithm. The torsion of the 2,5′ BDP σ bond was set at 10° increments, and semiempirical optimization was performed until the lowest energy conformation for the fixed interring bond torsion was attained. The heat of formation and $S_0 \leftrightarrow S_1$ transition energy were calculated for each geometrically optimized conformation.

Results and Discussion

We are concerned with understanding the optical response of (α,ω)-bisphosphonated chromophores, specifically oligomeric thiophene derivatives, as constituents of metal-phosphonate multilayer structures. As discussed above, the structural regularity attainable in these systems allows for the selective examination of intermolecular interactions between layers and within layers. Our initial work in this area focuses on the simplest case, that of a single layer containing a variable chromophore density. We want to discern, ultimately, how intermolecular interactions and photophysical processes within one layer will affect the optical response of, and relaxation dynamics within, more complex layered structures.

There are several factors that can, in principle, contribute to the optical response of this system. One factor is the stoichiometry of the monolayer deposition, which we can determine using UV−visible absorption spectrometry. The spontaneous emission response of the monolayer is also a rich source of information on how the components of the monolayer are assembled and how they interact. Fluorescence lifetime and reorientation dynamics data obtained using transient emission spectroscopy provide insight into the local environment(s) of the chromophores within a monolayer. Semiempirical calculations performed on the chromophore aid in our interpretation of the experimental data and thus our understanding of monolayer properties. We consider in the following sections each of these aspects in the characterization of mixed ZP monolayers.

Stoichiometry of Monolayer Formation. Little is known about the competition between different bis(phosphonate)s for active metal ion sites. There is some evidence that the formation of different mixed monolayers does not follow the stoichiometry of the solution from which they are formed precisely,[50] and thus we need to determine whether or not such is the case for the BDP/HBPA system. In addition to complications arising from competition for binding sites, the stoichiometry of a multicomponent deposition solution may not be reflective of the resulting monolayer concentration if solution phase aggregation of one or more of the constituents is occurring. For these reasons, it is important to establish a direct means of calibration for this particular system. To study the deposition stoichiometry of mixed monolayers relative to the solution from which they are formed, we varied the proportions of the chromophore (BDP) and the optically inactive component (HBPA) in ethanol solution and compared these data to absorbance measurements of the resulting monolayers. The total concentration of bisphosphonates (BDP + HBPA) in the deposition solutions was 1.25 mM, with the concentration of BDP fixed in increments from 1.25 mM (100%) to 0.0125 mM (1%). The absorption spectra of the resulting monolayers are shown in Figure 2. These data are background subtracted using a separate primed and zirconated substrate as the background (Figure 2 inset). This background spectrum is identical to that of a pure HPBA monolayer. The raw spectra exhibit a slight sample-to-sample variation in absorbance baseline, which can be attributed to slight absorptive differences between individual quartz substrates and positioning of the sample in the instrument. To correct for this baseline variation, the absorbances reported in Figure 3 are the differences between the absorbance at λ_{max} and the interpolated baseline. A linear regression fits the data well, indicating that

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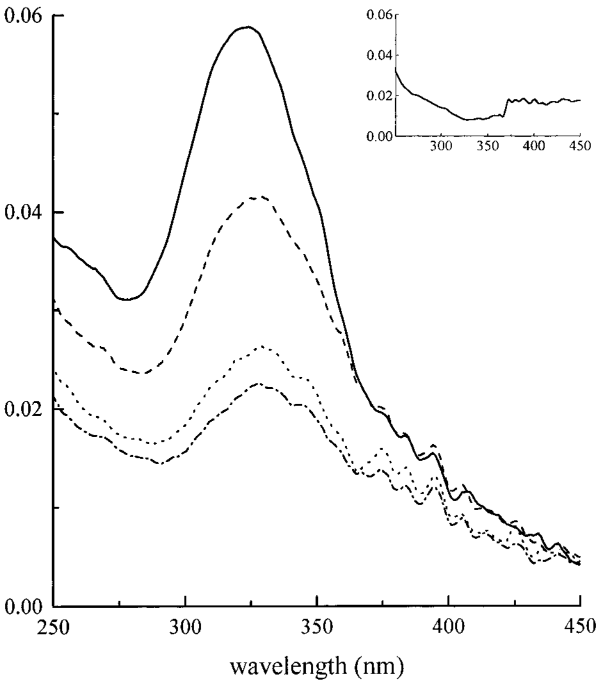

Figure 2. Background corrected absorbance spectra of BDP monolayers: (—) 100%, (- - -) 58%, (• • •) 34%, (- • -) 26%. Inset: Background spectrum.

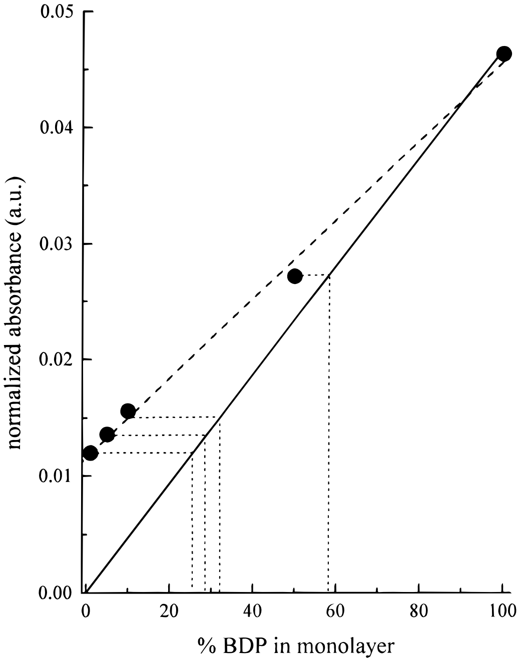

Figure 3. Dependence of monolayer absorbance on concentration of BDP in deposition solution. Solid line: Beer's Law predicted dependence, Dashed line: regression of experimental data.

Table 1. Comparison of Fractional BDP Concentrations in Deposition Solution and in the Resulting Monolayer, Determined According to Absorbance (see text for a discussion)

%BDP in deposition solution	%BDP in monolayer
100	100
50	58
10	34
5	29
1	26

there is a direct relationship between the deposition stoichiometry and the fractional concentrations of the components present in the deposition solution. These data reveal that the correspondence between solution composition and monolayer composition is not one-to-one. Beer's law requires there to be no residual sample absorption at [BDP] = 0, and the experimental background corrected data produce a linear regression to a measurable absorbance. Clearly for [BDP] = 0, $A_{BDP} = 0$, and the regression to a non-zero intercept implies that monolayer composition is offset from solution composition. In other words, for low fractional BDP concentrations (<1%), the relationship between solution and monolayer composition is curvilinear. From these data we can establish a working relationship between solution and layer composition that is straightforward. For monolayer formation where BDP is the only phosphonate-containing constituent in the deposition solution, we assert that a limiting layer of the chromophore is present, and we know experimentally that a pure HBPA monolayer represents a zero-absorbance condition. We further assert that Beer's Law holds for this system so that the absorbance of monolayers formed from mixed solutions is indicative of the chromophore concentration. For high fractional chromophore coverage, a direct correspondence between solution and monolayer composition is recovered, but for lower fractional coverage, we find significant preference for adsorption of BDP compared to HBPA (Table 1). This is not an unexpected result. For many ionic association processes, the formation constant of the complex depends sensitively on the identity of the species involved, and there is no reason to expect that not to be the case here. This result is observed, at least in part, because there is a ~25-fold stoichiometric excess of BDP relative to the number of substrate active sites (~1.5×10^{15}) for the 1% BDP deposition solution. This ratio correlates remarkably well with the observed monolayer concentration for this solvent system. We expect that it would be possible to achieve lower fractional coverages of the SiO_x surface by using smaller absolute amounts of BDP in the deposition solution, and we recognize that the relative efficiency of adsorption of both species will be determined by the solvent system.

The monolayer emission intensities varied with each sample but did not follow any trend, suggesting that the quantum efficiency of the monolayer samples is related to some factor(s) in addition to the amount of chromophore present. Part of the variation, again, may be due to inconsistency in the positioning of the sample. The relatively complicated behavior of the emission response for this system is also not a surprising result, and the details of this complexity contain useful chemical information as we will discuss below.

Monolayer Composition. The dilute solution behavior of BDP is typical of a simple chromophore. Its absorption and emission spectra have well-defined bands, and it exhibits a single-exponential fluorescence intensity decay in time. With monolayer samples, a double-exponential decay is observed, with a fast component that is the same as the solution lifetime, ~200 ps, and a slow component, ~1 ns, as shown in Figure 4. This decay functionality is observed for all monolayer samples, and the time constants recovered for each component are the same over the entire concentration range studied, as shown in Figure 5a,b. We observe that, as we collect lifetime data at several wavelengths within the BDP emission band, the form of the decay changes, as indicated Figure 6. Fitting these data recovers the same two time constants, but the fractional contribution of each decay component varies as a function of the wavelength at which the data are collected. Specifically, the relative contribution of the longer lifetime increases on the red side of the emission band for all samples (see Figure 7a,b).

Such behavior has been observed previously for different chromophores imbedded in ZP layers, although its origin was

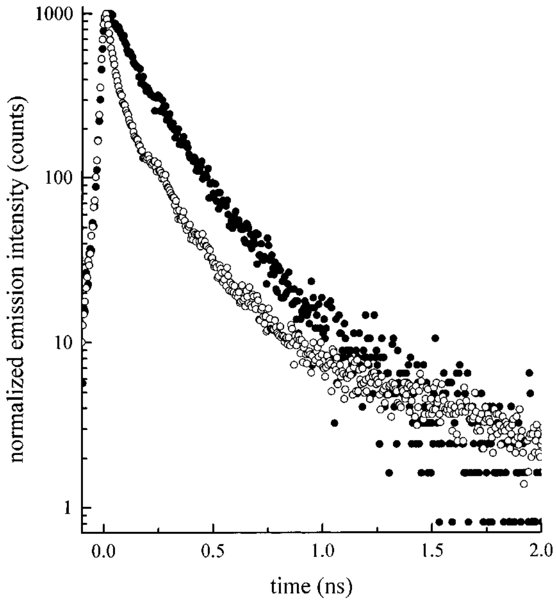

Figure 4. Representative fluorescence lifetimes of (●) solution and (○) monolayer.

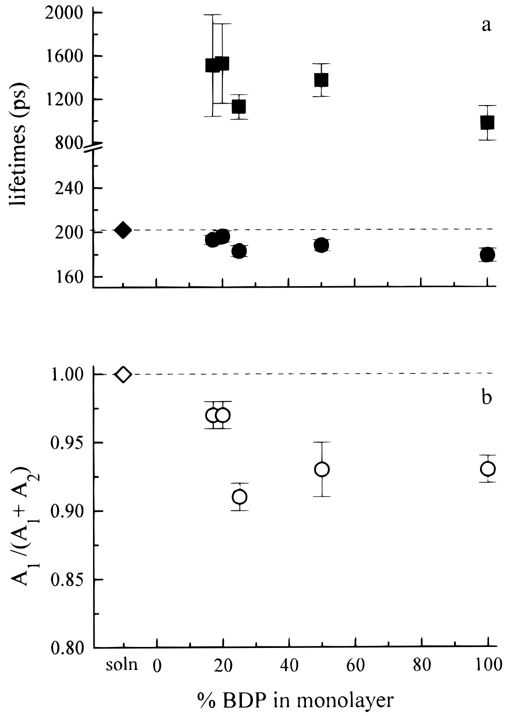

Figure 5. (a) Fluorescence lifetimes of BDP monolayers and solution at 400 nm. The data were fit to the function $f(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau 2)$. (b) Normalized prefactors of fast exponential decay component for data taken at 400 nm.

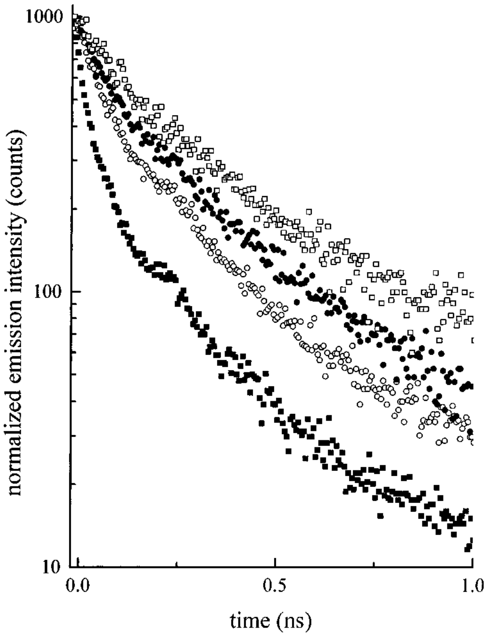

Figure 6. Fluorescence lifetime decays of BDP monolayers at (■) 390 nm, (○) 475 nm, (●) 525 nm, and (□) 575 nm.

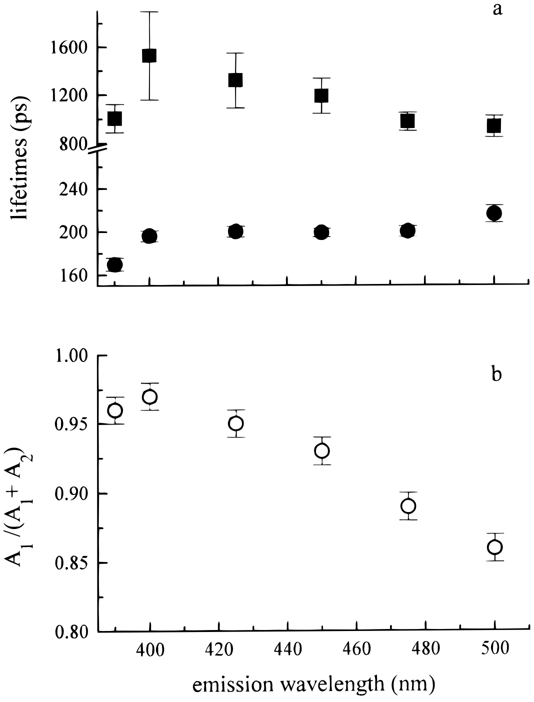

Figure 7. Emission wavelength dependence of (a) lifetimes and (b) normalized fast exponential prefactors for 29% BDP monolayer.

not determined.[12] One explanation for the existence of two lifetime components in these monolayers is the interaction of the chromophore with active hydroxyl sites on the silica surface. Wang and Harris found a similar lifetime behavior for pyrene on silica and determined that it was due to the existence of two distinguishable active silanol sites on the surface.[51] To explore the possible role of chromophore−substrate interactions, we synthesized a multilayer structure with a ∼26% BDP layer spaced away from the SiO_x surface by three HBPA layers. This structural motif prevents the chromophore from interacting with the surface. The same lifetime measurements were made, and the results were identical to those of the monolayers that were not isolated from the substrate, indicating that the presence of the second lifetime component is not the result of a single chromophore interacting with different silica sites on the same surface. Another possibility is that we are observing excitation transport, or "hopping", within the layer. If this were the case, the lifetimes would change as a function of chromophore concentration within the monolayer. More concentrated chromophore layers would exhibit longer lifetimes, or a wider distribution of lifetimes, because the exciton would "hop" from one chromophore to the next until it found a trap site. It is likely that such a process would not lead to a double-exponential decay functionality. Thus these complex monolayer decay properties cannot be accounted for by either chromophore-substrate interactions or simple excitation transport.

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(51) Wang, H.; Harris, J. M. *J. Phys. Chem.* **1995**, *99*, 16999.

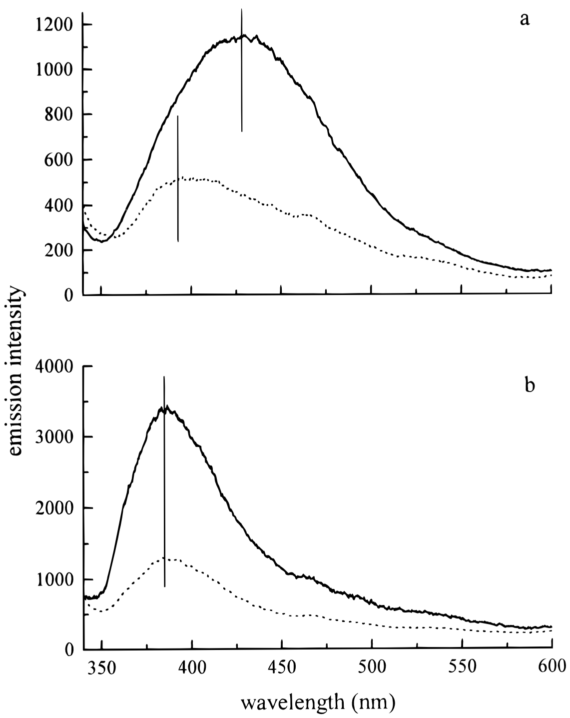

Figure 8. Emission spectra of fresh samples (solid lines) and aged (2 months) samples (dashed lines) for (a) aggregate-like and (b) monomer-like samples. The vertical lines are guides for the eye to the band maxima.

We consider next the possibility that we are observing emission from an aggregate or excimer moiety that forms at short intermolecular spacings, such as are found in a monolayer. Aggregation has been observed for several molecules, such as pyrene, which is known to form excimers in concentrated solutions and at solid interfaces.[52] The steady-state emission spectra of the monolayer samples are consonant with this explanation, as we find two distinct classes of spectra, one which has been observed at all chromophore concentrations and is similar to the dilute solution spectrum and one seen for chromophore monolayer concentrations above 34% (see Figure 8a,b). This latter feature, which we designate as the aggregate spectrum, is broader and red shifted by about 50 nm from the dilute solution, or monomer, spectrum. The intensity of the monomer emission spectrum is several times that of the aggregate spectrum, although quantitative intensity comparisons are difficult. We observe both monomer and aggregate peaks in the 100% BDP (1.25 mM) deposition solution, implying that the resulting monolayer will be comprised of both monomer and aggregate, with the ratio of the two forms being determined, at least initially, by their deposition kinetics. We note that, occasionally, a monolayer synthesized from concentrated BDP solution yields a monomer-like spectrum, which we believe is due to incomplete monolayer formation.

The monolayer aggregate spectra anneal over time to more monomer-like spectra, but samples that were characterized initially by a monomer-like emission response stayed the same except for diminution of intensity, as seen in Figure 8. There is evidence in the literature that the packing density of the organic portions of the ZP structures is mediated by the lateral spacing of the inorganic interlayer linking functionalities.[13,53,54] The ZP lattice has been shown to cause disorder in layers because the spacing it enforces is larger than the molecular area of most organic moieties.[9,55] This means that the spacing between individual chromophores may be larger than the intermolecular distance that is optimum for aggregate formation, so that, even if the chromophores are deposited onto the surface as pairs, they are likely to separate over time, giving rise to the spectral “annealing” we observe. This finding is fully consistent with our FTIR data on HBPA monolayers on SiO_x (not shown), indicating some structural heterogeneity within the layer. Also, we detect an apparent photodegradation of the chromophores within the layer (Figure 8a) which may indicate that the aggregates, as well as the monomer, are being destroyed, resulting in a sample with a higher proportion of monomer and a spectrum reflecting that change.

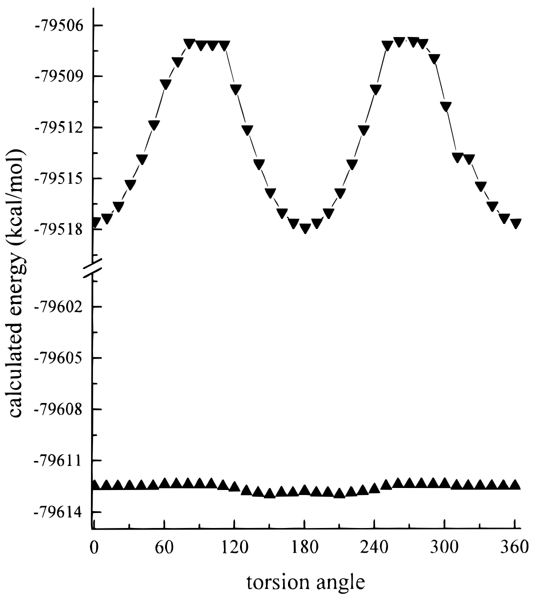

Figure 9. Calculated rotational energy barriers for BDP: (▲) S_0 and (▼) S_1.

We expect that, on the basis of the ionic nature of the metal-phosphonate bond(s), surface dissociation and diffusion will play a role in achieving the annealed condition for these layers. Our linear response data, however, do not provide significant insight into the role of diffusion for this system. If bound BDP aggregation was mediated by surface diffusion, we would observe aggregate-like absorption spectra in proportion to the surface concentration of the BDP for the annealed layers. Instead, we observe that the stable long-term condition for these films is in the form of monomeric chromophores, regardless of the initial BDP concentration. While the implications of these data remain to be explored more completely, it is clear that, for this system, surface diffusion is not the only process at work in determining the absorption properties of these films.

The existence of two measurably different spectra based on two chromophore species can be understood from a structural perspective with the aid of semiempirical calculations. We calculated the interring rotational energy barriers for both the ground state and the first singlet excited state of BDP, as shown in Figure 9. The S_0 potential energy surface is essentially independent of thiophene interring torsion angle, with rotational barriers of less than 1 kcal/mol. However, the S_1 surface has 12 kcal/mol barriers at 90° and 270° (rings perpendicular). The

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energetic minima occur at 0°, the *anti* conformer, and 180°, the *syn* conformer, where the molecule can adopt a quinoid-like S_1 resonance structure. In a system where there is freedom of motion, such as in solution, the conformational distribution of the chromophore is unbiased with respect to interring rotation prior to excitation. Upon excitation, the conformational distribution of BDP is biased toward the S_1 minima, where the molecules take on the planar, quinoidal structure. Planar BDP chromophore pairs are more likely to aggregate than nonplanar species if they are in close proximity, by a dipole coupling mechanism. In a monolayer, we expect different behavior because the chromophores are not able to rotate freely (*vide infra*). In the monomer limit within a monolayer, chromophores are spaced such that the probability of intermolecular interactions between chromophores is low, so the chromophores are excited from an average of all conformations, resulting in an emission spectrum with a distribution of energies skewed to high energies by S_1 emission contributions from twisted conformers. In more concentrated monolayers, chromophores are likely to be close enough to allow interaction which would serve to fix the molecules in more planar conformations and result in the lower energy spectrum. In addition, aggregation is expected to yield a spectral red shift, as is seen for the pyrene excimer.[52]

Rotational Dynamics. The rotational dynamics of the chromophores within a monolayer are an information-rich component of the optical response. Molecular reorientation measurements are well established as sensitive indicators of intermolecular interactions.[56−61] Most rotational diffusion measurements are performed on probe molecules in solution, where the orientational distribution of the chromophore can be completely random, while for a (partial or complete) monolayer of the same molecule, we expect its motional freedom to be constrained both by surface attachment and by interactions with neighboring molecules. For such a system, the hindered rotor model is appropriate for interpreting anisotropy data.[62,63] In this model, the surface-bound probe molecule is confined to a cone of rotation, where the base of the cone is defined by the attachment point of the probe to the surface and the cone semiangle is designated as θ_0. The optical and geometric properties of the tethered probe molecule also affect the form of the experimental signal. We select a nonrandom orientational distribution of chromophores within the monolayer with a laser pulse and monitor the change in emission intensity as a function of time following excitation. This measurement is made for emission signals polarized parallel and perpendicular to the excitation polarization, and these data are combined to produce the induced orientational anisotropy function, *R*(*t*), (Figure 10):

$$R(t) = \frac{I_{||}(t)\ \text{-}\ \mathrm{I}_{\perp}(t)}{I_{||}(t) + 2I_{\perp}(t)} \qquad (1)$$

The function *R*(*t*) is related to the properties of the probe molecule through[63]

$$R(t) = 2/5P_2(\cos\delta)\langle P_2[\mu(0)\cdot\mu^*(t)]\rangle \qquad (2)$$

where δ is the angle between μ and μ^*, the excited and emitting transition moments and P_2 is the second-order Legendre polynomial. For the hindered rotor model, it is important to consider two limiting cases, $t = 0$ and $t = \infty$. At $t = 0$, where the second term in eq 2 is unity, the information available from the measurement is determined by the optical properties of the probe molecule and thus we can determine δ directly. For BDP in solution we measure $R(0) = 0.24$, yielding $\delta = 31° \pm 2°$. At $t = \infty$, any rerandomization of the chromophores will be complete and the information available from the measurement is related only to the average tilt angle of the chromophore ensemble within the layer according to the hindered rotor model.[63]

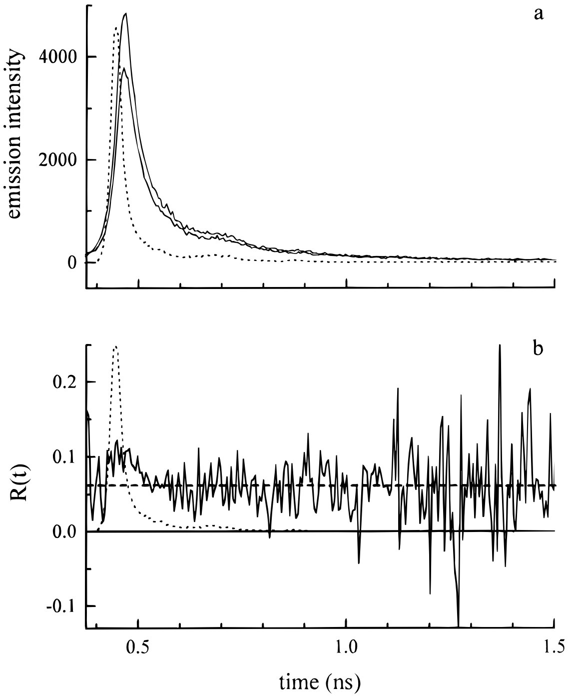

Figure 10. Reorientation data for a 26% BDP monolayer. (a) Raw transient signal intensities for emission polarized parallel (upper) and perpendicular (lower) to excitation pulse polarization. Included is the instrumental response function. (b) Induced orientational anisotropy function derived from the data presented in panel a and regressed fit.

$$R(\infty) = 2/5P_2(\cos\theta_{\mathrm{ex}})\, P_2(\cos\theta_{\mathrm{em}})\langle P_2(\cos\theta)\rangle^2 \qquad (3)$$

In eq 3, θ_{ex} is the angle of the excited transition moment with respect to the cone center axis, θ_{em} is the emitting transition moment angle with respect to this same axis, and θ is the average tilt angle of the chromophore within the cone. The terms for θ_{ex} and θ_{em} are, together, representative of the angle δ, and for simplicity, we take $\theta_{\mathrm{ex}} = 0$ and $\theta_{\mathrm{em}} = \delta$. From these quantities we can extract the average tilt angle, θ, from the experimental data.

In the hindered rotor model, there can also be a measurable relaxation associated with the randomization of chromophore orientations within the confining cone, with the time constant of this relaxation being related to the motion of the chromophore about its tether and the semiangle of the cone. It is evident from the experimental data presented in Figure 10 that we do not detect a transient relaxation of the chromophore within the monolayer, once contributions from the instrumental response function are accounted for. This finding is important in and of itself because it implies the rigidity of these systems on a nanosecond time scale, and from the infinite time response, we can derive useful information on the average tilt of the chromophore in the cone.

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Table 2. Dependence of Infinite Time Anisotropy on Fractional Composition of Monolayer

%BDP	$R(\infty)$
100	0.06 ± 0.01
58	0.05 ± 0.01
34	0.07 ± 0.01
26	0.05 ± 0.01

It is fair to question whether the absence of a decay in $R(t)$ is reflective of the absence of dynamics or the presence of unresolved, fast motion. We expect that the motion of BDP in a low-viscosity solvent will place a qualitative lower bound on the time constant for any such motion in the monolayer. For BDP in 95% ethanol, the reorientation time we measure, $\tau_{OR} = 299 \pm 41$ ps, is on the same order of magnitude as the monomer lifetime. This reorientation time is significantly slower than would be predicted by the Debye−Stokes−Einstein model[64] in the stick limit[65] (60 ps), and we attribute this difference to partial deprotonation of the terminal phosphonate moieties. Ionic charge will give rise to strong association with the solvent, slowing rotation of the chromophore. In a monolayer, the dynamics are expected to be mediated by attachment of the chromophore to the substrate as well as by dipole−dipole interactions between molecules and by the proximity of its neighbors. We expect that, if the chromophore were to exhibit a dynamical response within the monolayer, it would occur on a time scale at least similar to that seen for BDP in ethanol, if not longer. We believe that the absence of a measurable decay in $R(t)$ is indicative of a highly rigid environment. We recover the same value for the steady-state anisotropy for all monolayer concentrations studied, as shown in Table 2, another indication that the chromophores are unable to randomize on the time scale of the BDP excited-state lifetime. From the monolayer data, $R(\infty) = 0.06 \pm 0.01$, yielding $\theta = 35° \pm 2°$. This value for the tilt angle is similar to that recovered for alkanediylbis(phosphonate)s[14] but, for the BDP chromophores, indicates that organization within the layer is not determined fully by the structure of the (presumably all-*anti*) chromophore, which would suggest a tilt angle of ∼17°. It appears that there is either a contribution to the measured tilt angle of BDP from the metal-phosphonate coordination or from intermolecular interactions between the organic functionalities of the bis(phosphonate) species. Unfortunately, we do not have sufficient knowledge of the surface roughness or active site spacing to resolve this question, especially in light of the several possible coordination numbers of Zr^{4+}.[66]

We can use the rotational dynamics results to clarify some ambiguity about the origin of the aggregates. One explanation for the presence of aggregate is that all of the chromophore within the layer is initially monomer. Upon excitation, BDP relaxes to its S_1 conformational minima, where it is planar, and if other planar chromophores are in close proximity, they will aggregate. The second possibility is that the chromophore is prealigned as aggregates in solution and is deposited onto the surface as such. We found no evidence of motion in the dynamical data, likely ruling out the possibility that aggregate formation in BDP monolayers is driven by optical excitation. We note also that, if aggregation were mediated by excitation of BDP, then the measured population relaxation dynamics would be more complex than the double-exponential decay functionality we recover, and we would expect a chromophore concentration dependence, which we fail to observe. We believe that the deposition of preformed aggregates is more likely, based on both the dynamics data and the observation of monomer and aggregate bands in concentrated BDP deposition solution spectra.

Conclusions

Our initial investigation of the optical response of a chromophore-containing ZP monolayer indicates that these assemblies are ideal for the selective examination of interlayer and intralayer energy relaxation phenomena. We have demonstrated control over the concentration of chromophore in the layer, which is limited by the higher affinity of BDP for the metal binding sites. Some degree of aggregation occurs in the BDP monolayers, as verified by the presence of the two species detected with both the steady-state and fluorescence lifetime spectroscopies. The presence of aggregated chromophore does affect the population relaxation dynamics within the monolayer, but in a way that can be monitored. The time constants for the fluorescence decays remain concentration independent, ∼200 ps for the monomer and ∼1 ns for the aggregate, although the contribution of each species' lifetime varies across the emission band. The rotational motion data are constant within the chromophore concentration range 26%−100% BDP. We find a steady-state anisotropy of ∼0.06, consistent with the restrictions of monolayer attachments and interactions, from which we determine an average tilt angle of 35°. The absence of rotational motion demonstrates that the chromophores are in a highly rigid environment on the hundreds-of-picoseconds timescale of our experiments. This finding will simplify the interpretation of results on interlayer transport within multilayer structures because the chromophores should be even more restricted in an environment with attachments at both phosphonate functionalities.

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