Orientational and Vibrational Relaxation Dynamics of Perylene and 1-Methylperylene in *n*-Alcohols: Probing the Balance between van der Waals and Hydrogen-Bonding Interactions

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We report on the rotational diffusion and vibrational population relaxation dynamics of perylene and 1-methylperylene in the primary normal alcohols methanol through *n*-decanol. The rotational diffusion dynamics of the two chromophores are the same to within the experimental uncertainty for *n*-propanol through *n*-decanol. We observe a double exponential decay of the induced orientational anisotropy for 1-methylperylene in all of the alcohols and for perylene in *n*-propanol through *n*-decanol. These data are consistent with previous literature reports on perylene in high-viscosity solvents and on 1-methylperylene in *n*-alkanes longer than *n*-octane. These data also reveal a substantial difference in the behavior of perylene in *n*-alkanes and *n*-alkanols. Both chromophores reorient as oblate rotors in the *n*-alkanols, with the aspect ratio of the oblate ellipsoid describing their motion depending on the solvent aliphatic chain length. The vibrational population relaxation dynamics of the two probe molecules differ significantly, not only because of the difference in the nature of the solvent−solute coupling but also because of subtle differences in the organization of the solvent around the two chromophores. These data reflect the importance of solvent self-association in determining the local environments of these two chromophores.

Introduction

Understanding the details of solvent−solute interactions has received a great deal of attention by the chemistry community because of the importance of these interactions in determining properties such as chemical reaction yield and kinetics or the ability to isolate one compound from another. Interactions between solutes and their surrounding solvent molecules are difficult to resolve because, unlike in solids, the spatial relationships between the molecules are not fixed on time scales that can be accessed using structural measurements such as X-ray diffraction or multidimensional NMR spectrometry. Intermolecular interactions in the liquid phase are more complex than those in the gas phase because of their characteristic strength, the property that gives rise to the liquid phase and at the same time prevents a simple statistical description of collisional interactions from providing adequate insight. For these reasons, time domain spectroscopies have found particular favor in the investigation of solvation processes.

There are essentially three time-resolved spectroscopic approaches to the measurement of solvent−solute interactions. These are measurement of the time-delayed fluorescence Stokes shift (TDFSS) of selected solutes,[1−10] rotational diffusion[11−31] and vibrational population relaxation.[32−44] Of these, TDFSS measurements have provided the most insight into the early-time separation of inertial and diffusive contributions to solvent reorganization about excited solute molecules, and at the same time these reports have proven to be the most controversial in terms of their interpretation.[45−49] Perhaps the most significant issue that needs to be addressed regarding TDFSS measurements is the lack of generality of the effect. Despite the broad conclusions drawn from these experimental results, only a handful of chromophores with complicated spectroscopic responses are known to exhibit resolvable transient Stokes shifts.[2,50] The two other approaches to the measurement of

solvent−solute interactions do not offer the same time-resolution as the TDFSS measurements, but the phenomena of rotational diffusion and vibrational relaxation are not limited to a few chromophores; these are general effects, and the characteristic time scales over which they proceed are consonant with chemical reaction processes. We concentrate here on the rotational diffusion and vibrational population relaxation dynamics of perylene and 1-methylperylene in the *n*-alkanols methanol through *n*-decanol. We have chosen these probe molecules because they are relatively well characterized[29−31,39−41,43,44] and because literature reports on their solution-phase dynamical behavior leave open some significant questions.

Perylene has been studied more extensively than 1-methylperylene. Several reports on the reorientation dynamics of perylene point to solvents in which a two-component anisotropy decay is seen[30,31] and others where there is only a single decay.[29] It is important to understand the fundamental basis for these results and the data we present here provide some insight into this matter. Comparing the reorientation behavior of perylene with that of 1-methylperylene allows us to evaluate whether there is a measurable contribution from (weak) dipolar solvation effects in addition to the dominant van der Waals interactions. We reported previously that the reorientation of perylene in *n*-alkanes pentane through hexadecane yielded single-exponential anisotropy decays[29] and the nature of the solvent−solute frictional interactions changed as the length of the solvent molecule became similar to that of the solute. For 1-methylperylene in these same solvents, we found that there was a clear break in the anisotropy behavior at the same point, but the measured change was not simply a change in the frictional boundary condition; it was a shift in the functionality of the anisotropy decay from single to double exponential.[42] Such a change is consistent with a substantial alteration of the way in which the 1-methylperylene chromophore reorients in the longer alkane solvents. These data point to a qualitative change in the nature of solvent−solute interactions that depends on the relative

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lengths of the molecules, but a broader picture of the solvation of these two molecules has yet to emerge.

We have measured vibrational population relaxation from the $\sim$1375 cm^{-1} ring breathing modes of perylene and 1-methylperylene to understand the role of "structural" factors in mediating solution-phase vibrational excitation transport. We have found that both the spatial separation between vibrational donor and acceptor moieties and their relative orientation are important in mediating vibrational excitation transport.[44] Interestingly, it is not the acceptor density that determines the efficiency of transport. The ability of the donor and acceptor vibrational coordinates to align with one another mediates vibrational excitation transport for 1-methylperylene in the alkanes. In contrast to the reorientation measurements, the vibrational population relaxation dynamics of these two chromophores cannot be compared directly because the efficiency of donor−acceptor coupling is determined by the symmetry of the chromophores.[42] Using our two-pulse measurement scheme, systems that possess a center of inversion, such as perylene, will necessarily couple to the solvent bath modes according to the modulation of the solute's quadrupole moment. For donors without a center of inversion, such as 1-methylperylene, the modulation of the solute dipole moment by vibrational motion mediates excitation transport. These two coupling processes operate over different length scales (r^{-8} vs r^{-6}), and thus it is not possible to compare results directly. Despite the differences of scale, the solvent-dependent trends observed in the T_1 data for the two molecules provide insight into the average spatial relationship between donor and acceptor functionalities in solution.

Comparison of the reorientation and vibrational population relaxation dynamics we report here for perylene and 1-methylperylene in the *n*-alkanols yields significant information on the nature of the solvent−solute interactions that the chromophores experience. A key difference between the *n*-alkanes and *n*-alkanols is the extent to which solvent self-association determines their properties.[21,51] We find from the reorientation measurements that self-association of the alcohols determines the immediate environment of the chromophores to a significant extent, especially for the longer *n*-alkanes. The vibrational population relaxation data suggest that, for the longer *n*-alkanols, perylene appears to associate with the nonpolar aliphatic chains while the more polar 1-methylperylene interacts with the solvent alcohol functionality. These results are not surprising but do reveal the point at which solvent size, relative to the chromophore, becomes important for amphiphilic systems.

Experimental Section

Laser System. The picosecond pump−probe laser spectrometer used for both the reorientation and vibrational population relaxation measurements has been described in detail previously,[52] and we present only a brief outline of its performance characteristics here. A mode-locked CW Nd:YAG laser (Coherent Antares 76-S) produces 30 W of average power (1064 nm, 100 ps pulses, 76 MHz repetition rate). The output of this laser is frequency-tripled to produce $\sim$1.3 W of average power at 354.7 nm. The third harmonic light is used to excite two cavity-dumped dye lasers (Coherent 702) synchronously. Both lasers operate with Stilbene 420 laser dye (Exciton). The output of each laser is $\sim$100 mW average power at 8 MHz repetition rate with a pulse that produces a 7 ps fwhm autocorrelation trace using a three plate birefringent filter. The pump laser wavelength was set between 429.7 and 438.9 nm, depending on the chromophore and solvent, while the probe laser was set

in the range 456.7−463.1 nm. The pump wavelength was chosen to access the 0−0 transition of the chromophore and the probe wavelength to stimulate emission from the $S_1^{v=0}$ state to the $S_0^{v=1}$ state, where the vibrational resonance of interest is the 1375 cm^{-1} $v = 1$ ring breathing mode. These wavelengths were used for the vibrational relaxation and the reorientation measurements. Our previous work has demonstrated that the ground-state and excited-state reorientation behavior of perylene are identical,[29] and we assume that this is also the case for 1-methylperylene. The probe laser polarization was set alternately to 0° and 90° relative to the pump laser polarization for the reorientation measurements and to 54.7° for the vibrational relaxation measurements. The time resolution of this system, $\sim$10 ps, is determined by the cross-correlation between the pump and probe laser pulse trains. Detection of the transient signals was accomplished using a radio and audio frequency triple-modulation scheme, with synchronous demodulation detection.[53−55] Each reported time constant is the average of at least six individual determinations that are themselves the average of 7−10 time-scans.

Steady-State Spectroscopy. The steady-state absorption spectra of both chromophores in the *n*-alkanols were recorded with 1 nm resolution using a Hitachi U-4001 spectrometer. The spontaneous emission spectra for the same solutions was obtained with 1 nm resolution using a SPEX Fluorolog2 model F111AT spectrometer. These data were used to determine the appropriate laser wavelengths for each chromophore/solvent pair. The absorption and emission spectra for perylene and 1-methylperylene in *n*-pentanol are shown in Figure 1. We understand the details of these spectral profiles and describe them in the next section.

Chemicals and Sample Handling. Perylene (99.5%, sublimed) was obtained from Aldrich Chemical company and used as received. 1-Methylperyelene was synthesized by using the procedure of Peake et al.,[56] which is selective for methylation at the 1-position. Perylene is reacted with $CH_3Li/LiBr_{(eth)}$ in dry THF at −78 °C, followed by quenching with solid I_2 and reduction with $Na_2S_2O_3$. All chemicals used in the synthesis were purchased from Aldrich in the highest purity grade available. THF was dried over $Na_{(s)}$ and distilled prior to use. Initial purification of the product was accomplished with column chromatography (SiO_x column, 95:5 hexane/ethyl acetate). The product fraction was recrystallized according to the procedure specified by Zieger et al.[57] The recrystallized product was pure by ^1H NMR, UV−visible absorption spectroscopy, and mass spectrometry.

Results and Discussion

The focus of this work is on understanding the solvent−solute interactions of perylene and 1-methylperylene in the *n*-alkanols. Placing our results in the context of previous work on these same chromophores will allow us to gain insight into the dominant intermolecular interactions of these probe molecules. While the majority of the information on the solvation behavior of these probes is obtained from the time domain measurements, it is important to understand their steady-state optical responses because they are reflective of the average environment they experience.
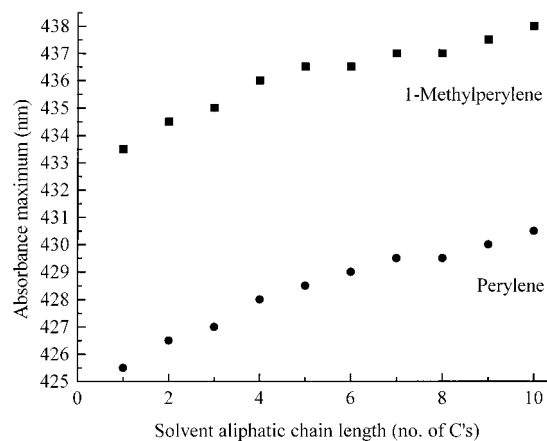
Steady-State Linear Spectroscopy. Among the reasons for using perylene and 1-methylperylene for these studies is the well-behaved optical response of each molecule. The quasimirror image absorption and emission spectra demonstrate the relatively small role that vibronic coupling plays in these data,[58] and the Stokes shift of 1-methylperylene compared to that of perylene

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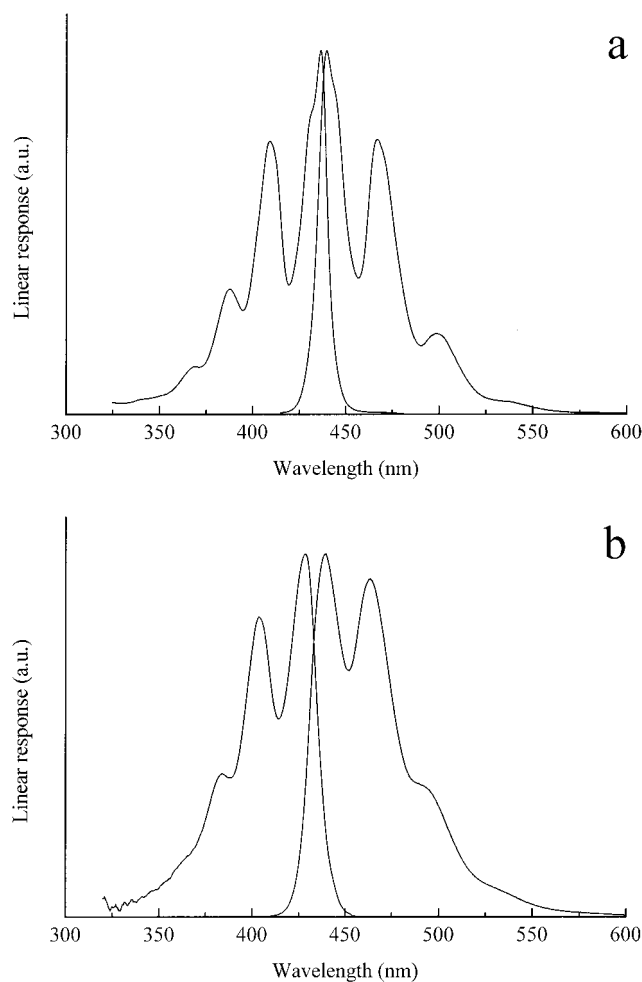
Figure 1. (a) Absorption and emission spectra of perylene in *n*-pentanol. (b) Absorption and emission spectra of 1-methylperylene in *n*-pentanol. Intensities have been normalized for presentation.

Figure 2. Dependence of perylene and 1-methylperylene absorption maxima on solvent alcohol aliphatic chain length. When normalized for wavelength shift relative to their absorption spectra in methanol, the solvent dependencies are identical for both chromophores.

points to the presence of a small but finite permanent dipole moment in 1-methylperylene. PM3 semiempirical calculations indicate $\mu \approx 0.24$ D in the S_0 and 0.53 D in the S_1 for 1-methylperylene.[59]

The linear responses of solutes can provide significant insight into the dielectric properties of the solvent. For example, the absorption maximum of the polar chromophore oxazine 725 exhibits a solvent polarity-dependent red shift in *n*-alkanol solvents up to *n*-heptanol.[24] Comparison of those data to the oxazine 725 absorption maximum in DMSO reveals that at least one contribution to the polarity-dependent spectral shift is solvent H-bonding. For the chromophores we use here, H-bonding almost certainly does not play the same role, but it is clear that there is a solvent dependence to their absorption maxima. Before considering this point, we need to account for the differences in the linear response of perylene and 1-methylperylene. The absorption maximum of perylene is red shifted from 1-methylperylene for a given solvent, and the individual features in the 1-methylperylene spectra are less well-defined. We understand these differences as arising from the fact that the methyl group on 1-methylperylene causes the two naphthalene moieties to be cocked at ~20° with respect to one another.[60,61] The resulting slight break in conjugation causes the blue shift and the reduction in symmetry causes additional vibrational resonances to become allowed, adding to the greater width of the absorption and emission spectral features. The solvent dependence of the absorption maxima of perylene and 1-methylperylene is shown in Figure 2. First, we note that the

solvent dependences for perylene and 1-methylperylene appear to be identical and, if plotted in terms of relative shift with respect to the band position in methanol (not shown), the results for the two chromophores are identical. We understand these shifts in the context of the chromophore ground and excited states being solvated more efficiently with increasing aliphatic chain length of the alkanol solvent. The excited states of the chromophores are solvated more efficiently than the ground states, presumably because van der Waals interactions between the solvent aliphatic chains and the chromophore π^* states are stronger than those for the ground state. These data are reminiscent of those for oxazine 725 in the same solvents, except that we do not see a saturation in the spectral red shift with increasing aliphatic chain length here. We interpret this difference in terms of the affinity for the ionic dye oxazine 725 for the alcohol functionality and the preference of perylene and 1-methylperylene for the aliphatic portion of the solvent. These data suggest that the balance of interactions between the different functionalities of these solvents will be important in understanding the transient data we consider next.

Molecular Reorientation. Of the time domain spectroscopies used in the study of solvent−solute interactions, molecular reorientation measurements are supported best by a theoretical framework for the interpretation of the experimental data.[62−67] The starting point for relating reorientation data to solvent and solute properties is the modified Debye−Stokes−Einstein (DSE) equation,[62,63,65−67]

$$\tau_{OR} = \frac{\eta V f}{k_B T S} \qquad (1)$$

In eq 1, η is the solvent viscosity, V is the solute hydrodynamic volume (225 Å^3 for perylene and 243 Å^3 for 1-methylperylene),[68] f is a frictional interaction term to account for frictional contributions to solvent−solute interactions, k_B is the Boltzmann constant, T is the temperature, and S is a shape factor to account for the nonspherical shape of the solute. The DSE equation is clearly not intended to account for specific molecular-level interactions between molecules, and it is clear that any description of solvation phenomena based on solvent bulk properties must be incomplete. These limitations notwithstanding, the modified DSE model provides remarkably close agreement with many experimental results and it thus serves as a useful starting point in any discussion of reorientation measurements.

Experimentally, the time-dependencies of the stimulated gain signal on the probe beam, polarized parallel ($I_\parallel(t)$) and perpendicular ($I_\perp(t)$) to the pump beam, are used to extract information on the rerandomization of the anisotropic distribution of chromophores selected by the pump pulse.

$$R(t) = \frac{I_\parallel(t) - I_\perp(t)}{I_\parallel(t) + 2I_\perp(t)} \qquad (2)$$

The most common result for reorientation measurements is to recover an experimental $R(t)$ function that decays as a single exponential, with the time constant of this decay being taken as τ_{OR}. Such data are often interpreted in the context of eq 1. There are a number of experiments, however, where $R(t)$ is found to decay with a multiple exponential functionality,[22,30,42,69] or depends on the manner in which the chromophore is excited.[11,31] In these cases, eq 1 is clearly not sufficient. Chuang and Eisenthal have formulated the relationship between $R(t)$ and solute properties such as the angle between the excited and probed one-photon transition moments and the actual anisotropy in the diffusion constant.[64] They found that $R(t)$ can decay with as many as five exponential components, although the most common case is that of a single exponential. In cases where more than one decay component is resolved, it is possible to interpret the details of the reorientation dynamics in substantial detail.

We consider that the chromophores have their π-system in the approximate xy plane, with x being the long, in-plane axis, and z is perpendicular to the π-system plane. For each chromophore, our intention is to assign the coordinate system such that the x-axis coincides with the absorption transition moment. For perylene, this assignment is coincident with specific bond axes because of its high symmetry, while for 1-methylperylene it is not, since the π-system for this chromophore is nonplanar. We can relate the experimental reorientation times to the shape of the volume swept out by the rotating molecule.[64] We describe this volume in terms of either a prolate ellipsoid, characterized by rotation primarily about its long in-plane axis, $D_x > D_y \approx D_z$, or an oblate ellipsoid, characterized by rotation about the axis perpendicular to the chromophore π-system, $D_z > D_x \approx D_y$.

oblate:
$$R(t) = 0.3 \exp(-(2D_x + 4D_z)t) + 0.1 \exp(-6D_x t) \quad (3)$$

$$\text{prolate: } R(t) = 0.4 \exp(-6D_z t) \qquad (4)$$

In eqs 3 and 4, we have used the quantity D_x. We have also assigned the molecular axis along which the transition moments lie to be the x axis, and for this assignment, the reorientation measurements will not contain any explicit information on D_x. In the limit of an oblate rotor, where $D_x = D_y$, we could equally well have made this substitution in eqs 3 and 4. To allow more obvious comparison with our previous reports, we continue to use the quantity D_x.

For both perylene and 1-methylperylene in the n-alkanols, we measure experimental $R(t)$ functions that are fit best by the sum of two exponential decays (Figure 3) (Table 1). The solvent dependence of the fitted times is presented in Figure 4. Our findings are in agreement with several other results reported for perylene in viscous solvents[30,31,69] and for 1-methylperylene in n-alkanes longer than n-octane.[42] Our previous work showed that perylene exhibits a single-exponential anisotropy decay in the alkanes n-pentane through n-hexadecane and 1-methylperylene exhibits a single-exponential decay in n-alkanes up to
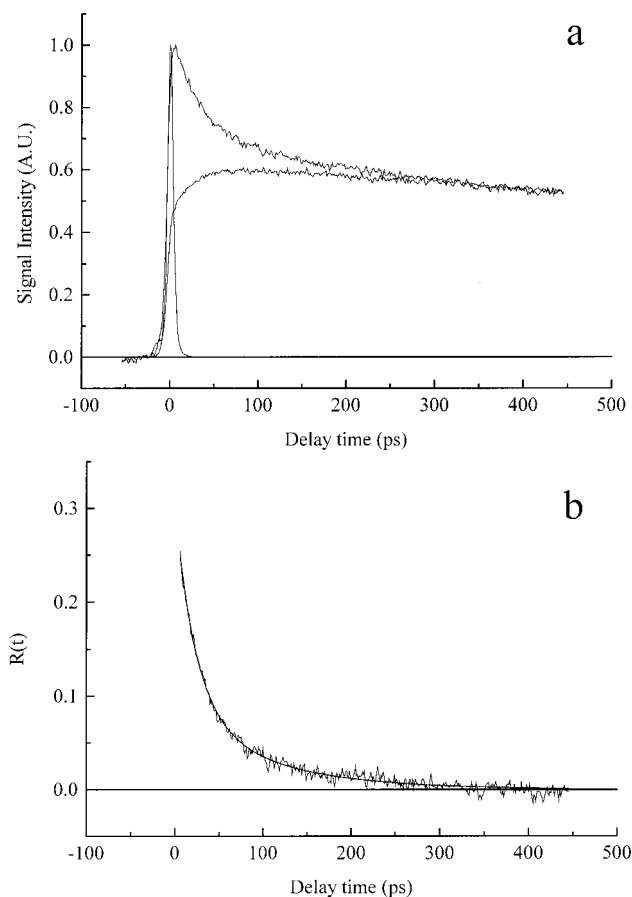
Figure 3. (a) Experimental $I_\parallel(t)$ and $I_\perp(t)$ scans for 1-methylperylene in n-pentanol, along with the instrumental response function. These data are typical of those recorded for reorientation measurements. (b) Anisotropy function, $R(t)$, for the data shown in (a). The decay is fit to the function $R(t) = R_1(0) \exp(-t/\tau_1) + R_2(0) \exp(-t/\tau_2)$.

and including n-octane.[29,42] As indicated by eqs 3 and 4, for our experimental conditions, a single-exponential decay of $R(t)$ indicates that the chromophore reorients as a prolate rotor and a double exponential decay indicates reorientation as an oblate rotor. It is important to consider both the information content of the data we report here and how these results augment our earlier reports on the reorientation of these chromophores in the n-alkanes.

Using eq 3 to interpret our data, we can obtain the quantities D_z and D_x. We show the diffusion constants as a function of solvent aliphatic chain length in Figure 5a and their ratio in Figure 5b. These data on 1-methylperylene are consistent with those reported in the n-alkanes because, in both cases, they trend toward an increasing ellipsoidal aspect ratio with increasing solvent aliphatic chain length. In our previous work,[42] for n-alkanes octane and shorter we recovered a ratio $D_z/D_x < 1$, and in this work, D_z/D_x ranges from $\sim$4 to $\sim$8.5. Also, in the n-alkanes, we see that the ellipsoid aspect ratio saturates at $\sim$8.5 for sufficiently long alkanes.[42] For 1-methylperylene in n-decanol, $D_z/D_x \approx 8.5$. It is not clear that this is a saturation value because we have not used longer n-alkanols because n-dodecanol has been shown to form a mesophase between 24 °C and 30 °C.[21] Clearly, the data on 1-methylperylene in the two families of solvents are not identical, but this is not surprising because of the important role that the alcohol functionality plays in mediating persistent organization.[51,70] The close correspondence between the two bodies of data, however,

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TABLE 1: Reorientation Times and Zero-Time Anisotropies for Perylene and 1-Methylperylene in the *n*-Alkanols[a]

	perylene				1-methylperylene			
solvent	$R_1(0)$	τ_1 (ps)	$R_2(0)$	τ_2 (ps)	$R_1(0)$	τ_1 (ps)	$R_2(0)$	τ_2 (ps)
CH_3OH	0.23 ± 0.06	17 ± 2			0.16 ± 0.04	11 ± 2	0.06 ± 0.01	34 ± 5
C_2H_5OH	0.11 ± 0.02	30 ± 6			0.25 ± 0.05	17 ± 2	0.07 ± 0.03	53 ± 13
C_3H_7OH	0.20 ± 0.05	16 ± 4	0.10 ± 0.03	59 ± 17	0.28 ± 0.03	18 ± 2	0.09 ± 0.03	62 ± 6
C_4H_9OH	0.17 ± 0.05	27 ± 8	0.06 ± 0.03	101 ± 39	0.19 ± 0.05	17 ± 3	0.12 ± 0.04	69 ± 14
$C_5H_{11}OH$	0.19 ± 0.09	21 ± 7	0.11 ± 0.03	82 ± 16	0.19 ± 0.06	21 ± 7	0.12 ± 0.05	81 ± 27
$C_6H_{13}OH$	0.19 ± 0.07	28 ± 6	0.11 ± 0.03	110 ± 22	0.21 ± 0.04	23 ± 7	0.13 ± 0.04	107 ± 26
$C_7H_{15}OH$	0.22 ± 0.05	35 ± 7	0.10 ± 0.03	168 ± 29	0.23 ± 0.03	29 ± 4	0.14 ± 0.02	139 ± 15
$C_8H_{17}OH$	0.21 ± 0.04	32 ± 5	0.11 ± 0.01	157 ± 15	0.18 ± 0.02	29 ± 5	0.14 ± 0.02	133 ± 15
$C_9H_{19}OH$	0.20 ± 0.05	33 ± 15	0.14 ± 0.04	146 ± 23	0.16 ± 0.04	28 ± 5	0.17 ± 0.03	132 ± 20
$C_{10}H_{21}OH$	0.20 ± 0.05	37 ± 7	0.15 ± 0.02	217 ± 45	0.21 ± 0.02	40 ± 6	0.11 ± 0.02	206 ± 21

[a] The data are the best-fit results of the data to the function $R(t) = R_1(0) \exp(-t/\tau_1) + R_2(0) \exp(-t/\tau_2)$. Times are given in picoseconds and the uncertainties listed are standard deviations ($\pm 1\sigma$) for at least six determinations of each quantity.
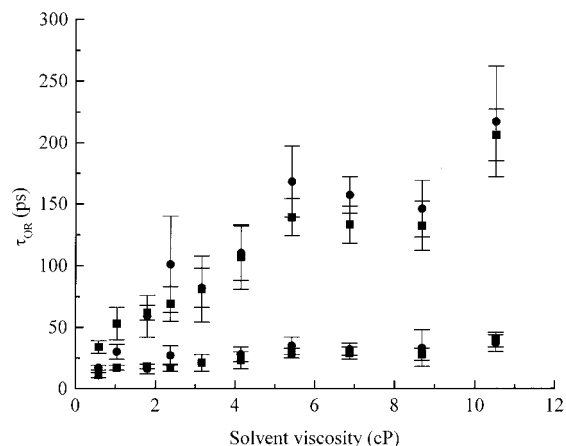

Figure 4. Reorientation time constants plotted as a function of solvent viscosity for perylene (●) and 1-methylperylene (■). The reorientation time constants are identical to within the experimental uncertainty for the two chromophores in the solvents used. The fast reorientation time is essentially solvent viscosity independent and the dependence of the slow reorientation time does not depend linearly on viscosity.

suggests that the same fundamental physical processes are operative in both systems.

The data on perylene in the alkanes and alkanols provide less in the way of direct correspondence. For *n*-alkanes up to *n*-hexadecane[29] and in methanol and ethanol, we recover a single-exponential decay, and for *n*-alkanols propanol through decanol, we find a two-component anisotropy decay. Perylene reorients as a prolate rotor in alkanes and as an oblate rotor in the alkanols *n*-propanol and longer. In methanol and ethanol, we recover what appears to be a single exponential decay, and note that our ability to distinguish between a fast second component and a single decay is limited by temporal resolution and signal-to-noise ratio. The apparently discontinuous change in D_z for perylene in ethanol and *n*-propanol (Table 2) suggests that we have not resolved the fast second component in $R(t)$ for the smaller solvents. We measure $D_z/D_x \approx 8.5$ for perylene in *n*-decanol and $D_z/D_x < 1$ for perylene in *n*-decane. This remarkable difference in aspect ratios for one chromophore in the different solvents underscores the important role that the presence of the alcohol group plays in the organization of the solvent.

It is interesting to note that, for both chromophores, the increasingly anisotropic environment formed with increasing solvent aliphatic chain length is characterized by a strong dependence of D_z on solvent identity and a much weaker solvent dependence of D_x (Figure 5a). The dominant constraint imposed on the chromophores is for reorientation out of plane, suggesting a layered or quasilamellar environment. This finding is consis-
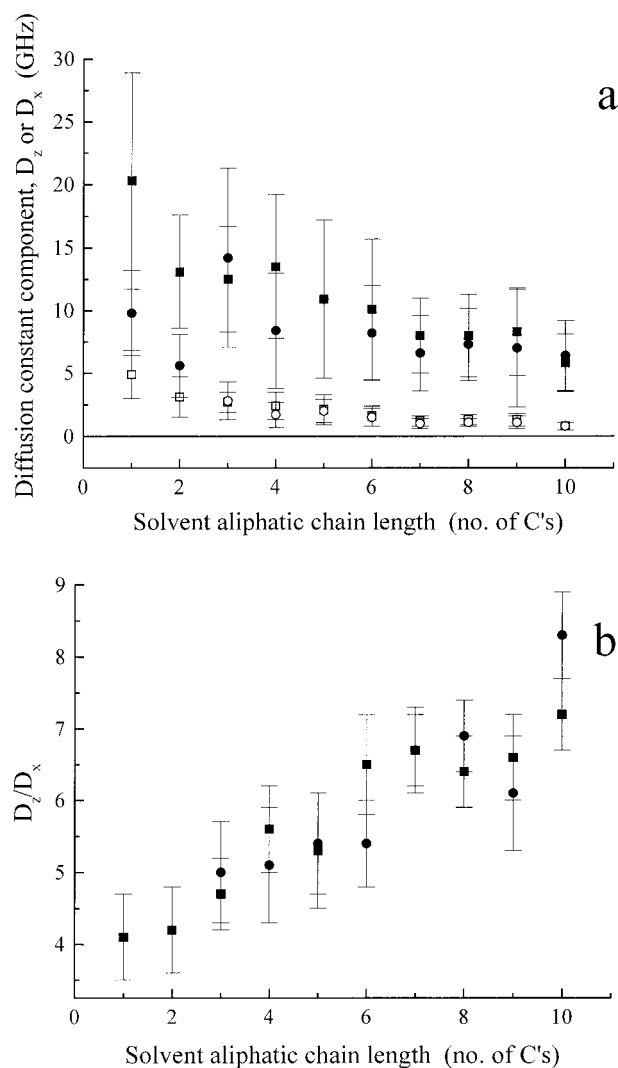
Figure 5. (a) Cartesian components of the rotational diffusion constant as a function of solvent aliphatic chain length for perylene ($D_z = ●$, $D_x = ○$) and 1-methylperylene ($D_z = ■$, $D_x = □$) in the *n*-alkanols. (b) The ratio D_z/D_x as a function of solvent chain length for perylene (●) and 1-methylperylene (■). These data indicate that the environment experienced by both chromophores is essentially identical and the structural anisotropy in the solvent cage increases with solvent aliphatic chain length.

tent with our results on 1-methylperylene in the *n*-alkanes, and the fact that we observe this phenomenon in all solvents argues for persistent local organization over a length-scale that is at least on the order of the chromophore (vide infra). We note also that this result is in excellent agreement with a recent report

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TABLE 2: Cartesian Components of the Rotational Diffusion Constant, *D*, for Perylene and 1-Methylperylene in the *n*-Alkanols[a]

	perylene			1-methylperylene		
solvent	D_x (GHz)	D_z (GHz)	$D_z/D_x{}^b$	D_x (GHz)	D_z (GHz)	$D_z/D_x{}^b$
CH_3OH		9.8 ± 1.2	<1	4.9 ± 0.7	20.3 ± 0.7	4.1 ± 0.2
C_2H_5OH		5.6 ± 1.1	<1	3.2 ± 0.8	13.1 ± 1.5	4.2 ± 0.3
C_3H_7OH	2.8 ± 0.8	14.2 ± 3.6	5.0 ± 0.4	2.7 ± 0.3	12.5 ± 1.4	4.7 ± 0.1
C_4H_9OH	1.7 ± 0.6	8.4 ± 2.5	5.1 ± 0.5	2.4 ± 0.5	13.5 ± 2.4	5.6 ± 0.3
$C_5H_{11}OH$	2.0 ± 0.4	10.9 ± 3.6	5.4 ± 0.4	2.1 ± 0.7	10.9 ± 3.6	5.3 ± 0.5
$C_6H_{13}OH$	1.5 ± 0.3	8.2 ± 1.8	5.4 ± 0.3	1.6 ± 0.4	10.1 ± 3.1	6.5 ± 0.4
$C_7H_{15}OH$	1.0 ± 0.2	6.7 ± 1.3	6.7 ± 0.3	1.2 ± 0.1	8.0 ± 1.1	6.7 ± 0.2
$C_8H_{17}OH$	1.1 ± 0.1	7.3 ± 1.1	6.9 ± 0.2	1.3 ± 0.1	8.0 ± 1.4	6.4 ± 0.2
$C_9H_{19}OH$	1.1 ± 0.2	7.0 ± 3.2	6.1 ± 0.5	1.3 ± 0.1	8.3 ± 1.5	6.6 ± 0.2
$C_{10}H_{21}OH$	0.8 ± 0.2	6.4 ± 1.2	8.3 ± 0.3	0.8 ± 0.1	5.8 ± 0.9	7.2 ± 0.2

[a] These quantities and their uncertainties are derived from the fitted time constants shown in Table 1. [b] The uncertainties in the quantities D_z/D_x were calculated from the standard deviations in the D_z and D_x data according to the formula $\sigma_{D_z/D_x} = (D_z/D_x)\sqrt{(\sigma_{D_x}/D_x)^2+(\sigma_{D_z}/D_z)^2}$.

by the Johnson group on two-photon excitation-induced anisotropy decays, where the form of the $R(t)$ function was found to depend measurably on the excitation polarization conditions.[31]

It is clear that the reorientation behavior of these two chromophores depends sensitively on the solvent in which they are dissolved. With only the reorientation data, it is possible to draw correlations between bulk solvent properties and microscopic reorientation behavior, but the extent to which these correlations can provide real insight into the relevant intermolecular interactions is limited. For this reason, we have also studied the vibrational population relaxation behavior of these chromophores in the same alkanol solvents. Those data, in conjunction with the reorientation measurements, provide additional insight into the average organization of solvents about the solutes.

Before we discuss our vibrational population relaxation data, we consider what is known about the solvent alcohols. NMR experiments have shown that, at room temperature, the dominant form of the *n*-alkanols is the trimer,[51] which is believed to exist in a ring-bound configuration.[21] This finding indicates that the solvent bath mode is heterogeneous on the length scale sensed by the solvent. Such local heterogeneity can, in principle, be sensed by vibrational population relaxation as we discuss below. Another significant implication of the presence of trimers in solution is that it makes the dominant form of the solvent have a hydrodynamic volume 3 times larger than that predicted from calculations of monomer solvent.[68] This is true in the limit of the characteristic lifetime of the solvent trimers being on the same order as the dynamics we measure. For the alkanols, the longitudinal relaxation time, τ_L, ranges from tens to hundreds of picoseconds as the aliphatic chain length increases.[70] With the larger effective solvent species, it is reasonable to expect more restriction of the chromophores, consistent with our findings of an effective oblate rotor shape in the *n*-alkanols and in the longer *n*-alkanes for 1-methylperylene.

Vibrational Population Relaxation Measurements. Vibrational population relaxation measurements provide information that is complementary to reorientation measurements. While these two measurements sense fundamentally different phenomena, both depend on the properties of the chromophore local environment. The reorientation data we present here indicate that, in the *n*-alkanols, both perylene and 1-methylperylene exist in environments that are restricted in such a way as to allow chromophore rotation primarily about an axis perpendicular to the π-system plane. The type of solvent local organization most consistent with these findings is that of a quasilamellar medium.

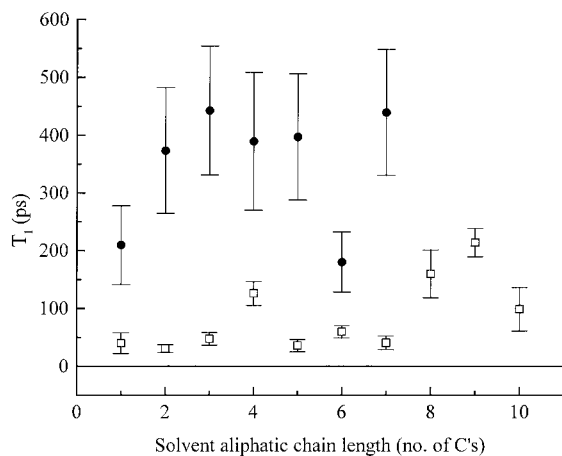**TABLE 3: Vibrational Population Relaxation Times, T_1, for Perylene and 1-Methylperylene in the *n*-Alkanols[a]**

	perylene	1-methylperylene
solvent	T_1 (ps)	T_1 (ps)
CH_3OH	209 ± 68	40 ± 18
C_2H_5OH	374 ± 109	31 ± 7
C_3H_7OH	443 ± 111	48 ± 11
C_4H_9OH	389 ± 119	126 ± 20
$C_5H_{11}OH$	397 ± 109	36 ± 11
$C_6H_{13}OH$	180 ± 52	60 ± 11
$C_7H_{15}OH$	439 ± 109	41 ± 12
$C_8H_{17}OH$	54 ± 24^b	160 ± 41
$C_9H_{19}OH$	72 ± 16^b	214 ± 25
$C_{10}H_{21}OH$	185 ± 74^b	99 ± 38

[a] Relaxation times are determined from at least six individual data sets, and the uncertainties are standard deviations. Times are values from fits of the experimental data to eq 5 and are given in ps. [b] Results of fits to eq 6.

As we had mentioned above, the alkanol solvents likely exist primarily as H-bonded trimers, and such a configuration will likely give rise to a microheterogeneous environment. With this picture in mind, we present our T_1 data (Table 3).

We have focused on the vibrational relaxation behavior of the perylene 1375 cm^{-1} and the 1-methylperylene 1370 cm^{-1} ring breathing modes.[39-44] We have chosen these modes because the terminal CH_3 group on the alkanol exhibits a rocking motion at ~1378 cm^{-1}, essentially degenerate with the solute donor mode. In this manner, measurement of T_1 as a function of alkanol identity can provide information on the spatial proximity and relative orientation of the donor and acceptor vibrational coordinates. The details of how the experimental technique operates have been presented elsewhere[39,71,72] and we forego a discussion of this matter here. The vibrational population relaxation time constants we report here are significantly longer for perylene than for 1-methylperylene in methanol through *n*-heptanol. We understand this effect in the context of the nature of the coupling between the donor and acceptor.[40,42] For molecules possessing a center of inversion, the lowest order multipole moment that can be modulated using our excitation scheme is the quadrupole moment. Assuming an IR-active acceptor mode, the intermolecular coupling will decay with donor−acceptor spacing as r^{-8}.[40] For a donor that does not possess a center of inversion, the excited vibrational resonance will modulate the dipole moment and the donor−acceptor coupling will depend on intermolecular distance as r^{-6}.[42] We have synthesized and use 1-methylperylene precisely because it is of lower symmetry than perylene, and we have shown that the coupling between the ring breathing mode and the solvent bath will be stronger than it is for perylene.

Because the theoretical framework for the interpretation of vibrational population relaxation in liquids is not well developed, we do not attempt to extract solvent−solute interaction information from single T_1 data points. Rather, we are interested in the solvent-dependent behavior of these time constants (Figure 6). We observe a break in the T_1 trend for both chromophores at *n*-octanol. For 1-methylperylene, we see an abrupt increase in T_1 with increasing alkanol chain length. We interpret this effect as a change in the proximity of the solvent acceptor mode relative to the solute donor mode. This finding suggests the association of the 1-methylperylene chromophore with the solvent alcohol functionalities. We can rationalize this assertion based on the fact that 1-methylperylene has a nonzero dipole moment and dipolar interactions must therefore contribute to the solvent−solute interactions at some level. When the alkanol chain becomes long enough that the terminal CH_3 group can,

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Figure 6. Vibrational population relaxation times for perylene (●) and 1-methylperylene (□) as a function of solvent aliphatic chain length.
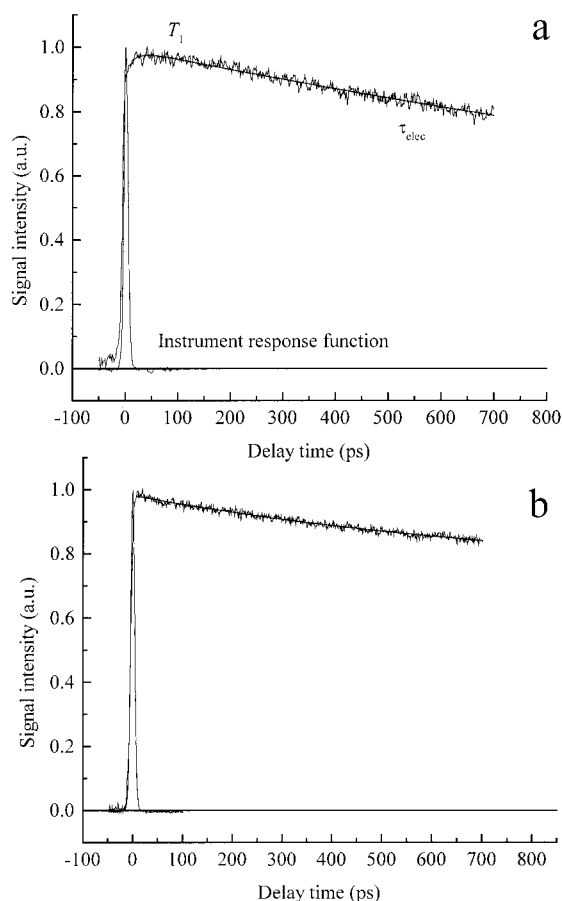
Figure 7. Magic-angle data for perylene in (a) *n*-pentanol and (b) *n*-decanol. Note the difference in the functionality of the population decay. See text for a discussion.

on average, be relatively isolated from the 1-methylperylene chromophore, the donor−acceptor coupling weakens, accounting for our experimental findings.

For perylene, the situation is not directly comparable. This is because the functionality of the population relaxation dynamics data changes for *n*-octanol through *n*-decanol. For solvents methanol through *n*-heptanol, we recover the expected form of the signal for a coupled three-level system (Figure 7a). We have reported on the details of this experiment previously[39,71,72] and forego a detailed discussion here.

$$S(t) = a \exp(-t/\tau_{ste}) - b \exp(-t/T_1) \qquad (5)$$

but for the longer alkanols the signal functionality changes to be a sum of exponentials (Figure 7b).

$$S(t) = a \exp(-t/\tau_{ste}) + b \exp(-t/\tau_2) \qquad (6)$$

where τ_2 is the fast decay time constant and τ_{ste} is the stimulated emission decay time constant. We have encountered this solvent-dependent changeover previously for tetracene in *n*-hexadecane[43] and understand it in the context of the solvent−solute interactions either providing or mediating an additional nonradiative decay pathway. In the previous work, we conjectured that intersystem crossing was responsible for the observed solvent-dependent change in the functionality of $S(t)$ because tetracene has a relatively low fluorescence quantum yield, ϕ_{fl}, and a modest intersystem crossing quantum yield, ϕ_{ISC}.[43,73,74] For perylene, ϕ_{fl} is ∼0.94, and this quantity depends only weakly on the identity of the solvent.[75] Intersystem crossing is thus not a likely explanation for the results we present here. Because the origin of this new relaxation pathway is not known, there is necessarily ambiguity in assigning the physical significance of the recovered time constant. We therefore will not attempt to cloud the discussion presented here with speculative interpretations of these data. The fact that we see a change in the interactions between perylene and its immediate environment at the same point that we observe a change for 1-methylperylene indicates that perylene is sensing either the same local environment as 1-methylperylene or its complement. For 1-methylperylene, the T_1 data are consistent with a measurable contribution from dipole−dipole solvent−solute interactions, but for perylene, there is no permanent dipole moment, precluding the contribution of such interactions. The complement to the environment sensed by 1-methylperylene would be for perylene to interact most strongly with the aliphatic portion of the solvent, and this suggestion is in intuitive agreement with the dominance of van der Waals interactions between (symmetric) PAHs and aliphatic solvents. Indeed, we observe this same behavior for tetracene only in long-chain aliphatic solvents.

Taken as a whole, the reorientation and vibrational population relaxation data for perylene and 1-methylperylene in the alkanols point to the importance of solvent self-organization in determining solvent−solute interactions. Alcohols are known to form persistent H-bonded networks with the lifetime of the network being proportional to the aliphatic chain length.[51,70] NMR data point to the dominance of H-bonded trimers in solution,[51] and with the assumption that the characteristic time constant of the H-bonded network is the same as the average lifetime for the trimers, it is likely that these species dominate the solvent−solute interaction dynamics we sense. The reorientation data suggest that both chromophores are constrained to reorient in an environment that is best described as quasilamellar.[42] The presence of solvent trimers implies structural heterogeneity on the length scale of the solvent molecules, with relatively hydrophobic and hydrophilic microenvironments in close spatial proximity. The vibrational population relaxation measurements suggest that 1-methylperylene associates with the more closely with polar portions of the solvent, and this segregation becomes pronounced for sufficiently large alkanol solvents. For perylene, it is likely that the chromophore associates with the less polar environment, although it would be necessary to assign some specific physical meaning to the second exponential decay seen for *n*-octanol through *n*-decanol to augment this assertion.

Conclusions

We have studied the rotational diffusion and vibrational population relaxation dynamics for perylene and 1-methyl-

perylene in a series of *n*-alcohols from methanol through *n*-decanol. We find evidence for solvent local organization, consistent with the relatively long-lived hydrogen-bonded complexes that characterize the alkanol solvents. This local organization constrains the chromophores to reorient as oblate ellipsoids. The reorientation times measured in each *n*-alkanol are the same for both chromophores. We conclude that, in these systems, the specific characteristics of the chromophore have less of an effect on the rotor shape than the hydrogen bond-mediated solvent transient structure.

The vibrational population relaxation times for perylene indicate that vibrational energy transfer is less efficient than it is for 1-methylperylene in *n*-alkanols. This is an expected result, and we understand it on the basis of the differences in the nature of donor−acceptor coupling for the two chromophores. For the alkanols, it is the strong, persistent solute−solute interactions that mediate the solvent−solute interactions we measure. For alkanes, the interactions between solvent and solute are on the same order as solvent−solvent interactions, allowing the structure of the solute to play a more deterministic role in the form of the recovered transient optical responses. We expect that, in systems where dipole−dipole interactions are significant but H-bonding interactions are largely mitigated, the difference in the dynamics of these two chromophores will become more pronounced.

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