Local Viscosity of Binary Water+Glycerol Mixtures at Liquid/Liquid Interfaces Probed by Time-Resolved Surface Second Harmonic Generation

Piotr Fita, Angela Punzi, and Eric Vauthey*

*Department of Physical Chemistry, University of Geneva, 30 quai Ernest-Ansermet, CH-1211 Geneva 4, Switzerland*

The excited-state relaxation of malachite green and brilliant green in solvents of various viscosity has been investigated at liquid/liquid interfaces and in bulk solutions by surface second harmonic generation and transient absorption spectroscopy. Mixtures of water and glycerol in various proportions have been used as solvents of variable viscosity. Transient absorption measurements in bulk revealed that both dyes are suitable as a probe of local viscosity for water+glycerol mixtures and that two of three processes following the optical excitation exhibit the same power dependence on solvent viscosity. This observation leads to assignment of the processes to a twist and twist-back of the aromatic rings attached to the central carbon atom of the dye. Therefore, identification of the intermediate state observed in the radiationless deactivation pathway with the twisted form of the dye has been supported. The time profiles of the second harmonic signal recorded at water+glycerol/ dodecane interfaces have been found to be monoexponential at low dye concentrations (below 10^{-5} M) and biexponential at higher concentrations, and therefore the origin of the slower component has been attributed to the relaxation of dye aggregates adsorbed at the interface. The decay times measured at interfaces increased with increasing amount of glycerol in the mixture, but the rise was slower than in bulk solution. Therefore, the viscosity at the interfacial region, higher than that of the bulk solution, is mainly determined by structural modification of the solvent resulting from interactions between the two liquids that constitute the interface and addition of glycerol affects viscosity, only to a lesser extent. We have also shown that if the viscosity of the upper layer is much higher (at least 1 order of magnitude) than that of water or short alkanes, a slow-down of the relaxation is observed. This contradicts earlier findings and means that large amplitude motion of all three rings is involved in the deactivation of the excited molecule, but the rotation of the phenyl ring, which is smaller than the alkyl-substituted aniline groups, becomes a bottleneck for the relaxation in very viscous environments.

Introduction

A deep understanding of the physical and chemical properties of interfaces between different phases has great significance to various fields of chemistry and biochemistry.[1] Interfaces constitute the local environment for numerous chemical reactions and physical phenomena including such common and for everyday life important processes as corrosion of metal surfaces, acting of cleaning agents, or creation of foams and emulsions. Thus an in-depth knowledge of the interface may help to control the process according to the needs. Various water interfaces also play a key role in biological processes taking place at cell membranes, including the transport of medicines and the infection of cells by viruses. In this case, the knowledge of physical and chemical properties of the interface may help to design more effective drugs.

Unfortunately, the spectroscopic studies of interfaces are hampered by the fact that the number of molecules in the interfacial region is usually orders of magnitude smaller than the number of molecules in the continuous media surrounding the interface. Therefore, the linear response of the surface molecules is entirely buried under the response of the bulk molecules. In order to overcome this obstacle, special experimental techniques have been developed. These can be divided
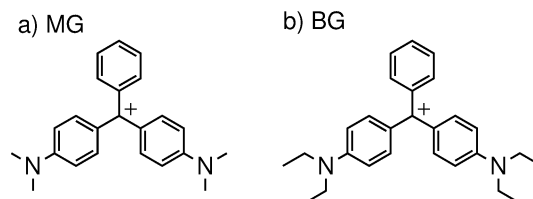
Figure 1. Chemical structures of MG (a) and BG (b).

into two groups: methods relying on the confinement of the probing light to the interfacial region utilizing evanescent waves[2–6] or near-field microscopy[7,8] and methods based on even-order nonlinear light-matter interactions, which are intrinsically insensitive to isotropic media. The latter category includes second-order techniques known as surface second harmonic generation (SSHG[9,10]) and sum-frequency generation (SSFG[11]), which have been widely used to probe stationary properties of interfaces.[11–18] Still, applications of time-resolved versions of SSHG and SSFG for studies of the dynamics of various photoinduced processes, especially at liquid interfaces, remain rather scarce.[19–24]

In many of the reported time-resolved experiments, physical properties of the interfacial region were investigated by analyzing electronic relaxation of malachite green (MG, Figure 1a), a dye which belongs to the family of the triphenylmethane (TPM) dyes,[25] adsorbed at the interface.[19–21,24,26,27] The first singlet

* To whom correspondence should be addressed. E-mail: Eric.Vauthey@ unige.ch.

excited state of MG undergoes ultrafast nonradiative relaxation, and its lifetime strongly depends on the solvent viscosity but is independent of the solvent polarity. For this reason MG has been the subject of numerous stationary and time-resolved spectroscopic experiments that aimed to describe its deactivation pathway.[28–35] It is generally agreed that the relaxation is intrinsically barrierless and involves rotation of the aniline or phenyl substituents. The friction exerted by the environment on the rotating rings accounts for the viscosity dependence of the excited state lifetime. Still, several questions regarding the relaxation mechanism remain unanswered. In particular, it is not clear whether the rotation of all three rings is required for the deactivation, and what is the exact nature of the intermediate state observed in the relaxation pathway. Despite these lacks in the knowledge on its photodynamics, MG makes a useful viscosity probe for liquids.

Time-resolved SSHG experiments by Eisenthal and co-workers revealed that excited state relaxation of MG adsorbed at a water/alkane or air/water interface is several times slower than that of MG dissolved in bulk water.[21] The decay times measured for both types of interfaces were comparable, and only a weak influence of the viscosity of the upper, nonpolar, phase has been observed for various water/alkane interfaces. Time-resolved measurements were supplemented by the analysis of the polarization of the second harmonic light radiated from the interface. It indicated that the phenyl group pointed toward the alkane phase, whereas the aniline substituents were submerged in water and the molecules were tilted by approximately 42° with respect to the interface normal. In light of this observation, the weak dependence of the excited state decay time on the viscosity of the upper (alkane) phase was interpreted by these authors as an evidence that only the aniline groups are involved in the excited state relaxation, and the phenyl ring does not play any significant role in the process. The slower decays measured with the molecules adsorbed at interfaces relative to those dissolved in bulk solutions were explained in terms of a higher viscosity of the interfacial region.

In the above-described experiments, the viscosity of the lower, aqueous phase has been kept constant, and the upper limit of the viscosity range of the alkanes was restricted to values approximately twice as high as the viscosity of water. Therefore, in our opinion, the experiments cannot be unambiguously interpreted as a proof that the rotation of the phenyl ring is not involved in the relaxation. Taking into account the smaller molecular volume of the phenyl ring compared to that of the aniline groups as well as a possible difference in the hydrodynamic boundary conditions, the rotation of the phenyl ring could be less affected by solvent friction. It is thus possible that, even in the most viscous alkane (pentadecane) used in the above-mentioned study, rotation of the phenyl ring is still faster than rotation of the aniline groups in water, and this accounts for the observed independence of the decay time from the alkane viscosity.

We decided to investigate this problem in more detail by extending the range of viscosities of the upper, nonpolar phase to check whether the lifetime of the excited state of the dye remains unchanged even for a very viscous upper phase. We also wanted to observe the influence of the viscosity of the lower, polar phase on the relaxation of the excited dye. In order to do this, we carried out a series of time-resolved SSHG measurements, where the nonpolar phase was, as in the experiments of Eisenthals' group, an alkane or a mixture of alkanes, and the polar phase was a mixture of water and glycerol. We selected the water+glycerol mixture as our adjustable-

viscosity solvent because it allows for the viscosity to be varied in a wide range by changing the proportions of the two liquids. At the same time, this mixture allows the more complicated case of multicomponent interface to be studied.

In addition to MG, the dye most commonly applied in time-resolved SSHG experiments, we also used another dye of this family, namely, brilliant green (BG, Figure 1b).[36] The only difference between MG and BG is the alkyl substituents on the aniline groups. The longer ethyl groups of BG should make it more sensitive than MG to the solvent friction, whereas both dyes show very similar spectral characteristics.

Prior to the SSHG experiments, we studied the excited-state dynamics of MG and BG in bulk water+glycerol solutions by transient absorption spectroscopy in order to verify their usefulness as viscosity probes for the water+glycerol/alkane interfaces. Our results throw a new light on the processes involved in the nonradiative deactivation as well as the nature of the intermediate state.

Experimental Section

Samples. MG oxalate was purchased from Fluka and BG was obtained from Waldeck, Division Chroma. For the preparation of the water+glycerol mixtures, deionized water, and an 86–88 wt % aqueous solution of glycerol (p.a.) from Acros Organics were used. The dynamic viscosity of the mixtures was calculated according to the empirical formula given by Shankar and Kumar.[37] The concentration of the dye in the water+glycerol solutions in both transient absorption and SSHG experiments was equal to 10^{-5} M and 2×10^{-5} M for MG and BG, respectively. At this concentrations no aggregates are expected to be formed in bulk solution, which has been confirmed by monitoring the stationary absorption spectra of the samples. The absorption spectra of the solutions corresponded to the spectra of the monocationic forms of the dyes, independently of the composition of the water+glycerol mixtures. No decomposition of the samples in time has been observed.

The following liquids were used as the upper layer for SSHG samples: *n*-hexane (Fluka, p. a.), *n*-heptane (Acros Organics, 99%+), octane (Aldrich, 98%), decane (Fluka, purum), dodecane (Acros Organics, 99%), tetradecane (Acros Organics, 99%), pentadecane (Aldrich, 98%), and paraffin oil (Fluka, for IR spectroscopy). All compounds were used as supplied.

Transient Absorption Spectroscopy. The experimental setup for transient absorption spectroscopy has already been described in detail elsewhere.[38] Briefly, the excitation pulses were generated by a home-built noncollinear optical parametric amplifier (NOPA) fed by a standard Ti:sapphire femtosecond amplified system (Spitfire from Spectra Physics) working at a 1 kHz repetition rate. The central wavelength of the pulses was equal to 615 nm, their duration was approximately 50 fs, and the energy at the sample position was in the range of 2–3 μJ. Transient absorption was probed with white-light supercontinuum pulses generated in a 3 mm-thick CaF$_2$ plate. The useful spectral range of the supercontinuum extended from 380 to 780 nm. The polarization of the probe pulses was at a magic angle relative to that of the pump pulses. After acquisition, all spectra were corrected for the chirp of the probe pulses. The samples were contained in 1 mm-thick fused silica cells and kept at room temperature. They were stirred by bubbling with nitrogen. The temporal resolution of the setup was better than 200 fs.

Surface Second Harmonic Generation. Time resolved SSHG measurements were carried out in the geometry shown in Figure 2. The sample was contained in a square glass cell with 40 mm side. The size of the cell was big enough to reduce
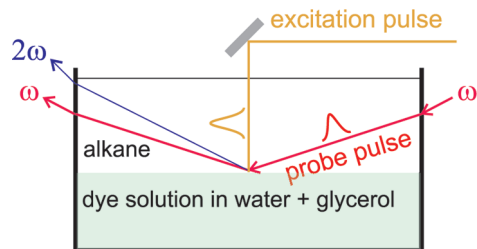
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Figure 2. Geometry of the time-resolved SSHG experiment.

the effect of the meniscus and ensure that the surface is sufficiently flat at the center. The probe pulses, delivered directly from the same Ti:sapphire amplifier used for transient absorption measurements, had an energy on the sample in the range of 10−100 nJ, a duration time of approximately 120 fs, and linear s-polarization. The angle of incidence of the probe pulses on the surface was close to 70° and, if possible, was set to be slightly greater than the critical angle for total internal reflection at the interface. The beam was focused with a 500 mm-focal length lens and just before the sample passed through an absorption filter to eliminate second harmonic light generated at the surface of metallic mirrors.

The second harmonic light generated at the interface was collected with a 100 mm-focal length lens, filtered from the accompanying scattered fundamental light with help of a BG23 filter and focused onto the entrance slit of a monochromator (0.25 m Cornerstone from Oriel) equipped with a photomultiplier tube (Hamamatsu, R446). The output signal was amplified and processed by a gated boxcar integrator and averager module (SR250 from Stanford Research Systems) and finally recorded by a computer.

The 615 nm-centered excitation pulses were generated by a commercial NOPA (Clark-MXR). The beam hitting the interface vertically from above was focused on the surface by two lenses, one spherical and one cylindrical, in order to match the shape of the elongated spot created on the surface by the probe beam. The energy of the excitation pulses on the sample was in the range of 1−2 μJ, and their polarization was circular. The excitation beam was reflected from a retroreflector placed on a motorized, computer-controlled translation stage, which allowed for control of the delay between probe and excitation pulses.

The sample was kept at room temperature (20 °C).

Results and Discussion

Transient Absorption Spectra. We carried out a series of transient absorption measurements with solutions of MG and BG in various water+glycerol mixtures: from pure water to a 40:60 vol mixture of water and stock solution of glycerol (86−88 wt % aqueous solution of glycerol). The latter corresponded to approximately 56% (wt %) of glycerol in water.

The general features of the transient spectra remained unchanged for the whole range of glycerol concentrations used and are well represented by the spectra measured in pure water (Figure 3a and Figure 4a for MG and BG, respectively).

The spectra of both dyes exhibit very similar shape and temporal evolution. Four spectral bands can be distinguished in the transient absorption data. Three of them (positive at 380−550 nm; negative at 550−630 nm and 700−760 nm) decay monotonically. In the 630−700 nm range, the negative signal decays, and a positive signal arises. For MG, these bands are typically ascribed to excited state absorption (380−550 nm), ground state bleaching (550−630 nm), intermediate state absorption (630−700 nm), and stimulated emission (700−760
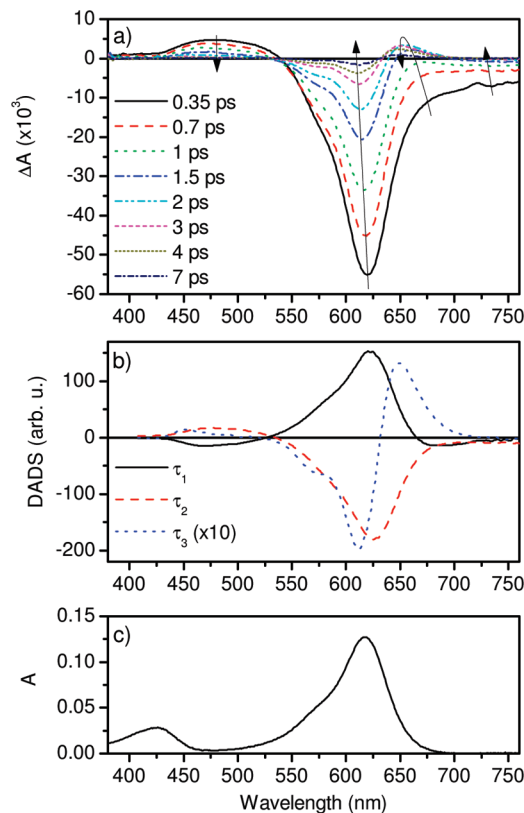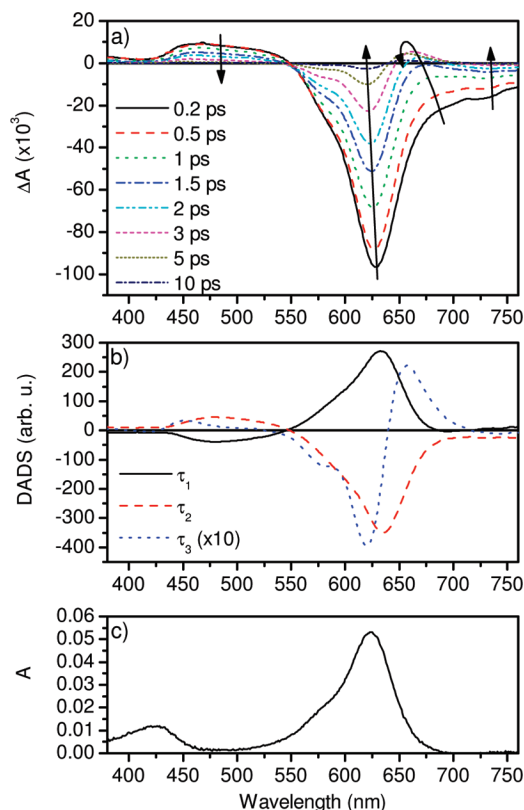

Figure 3. (a) Transient absorption spectra of MG in water at selected delays between excitation and probe pulses. (b) DADS obtained from global analysis of the transient absorption data. (c) Stationary absorption spectrum of MG.

nm).[24,35] Because of the very high similarity of the dyes, this assignement should be also correct for BG.

Time-resolved data in all water+glycerol mixtures were analyzed with help of the matrix-reconstruction global fitting algorithm.[39] For all samples, three distinct decay times were necessary to reproduce the data; the following values have been found for water solutions of the dyes: $\tau_1 = 0.33$ ps, $\tau_2 = 0.57$ ps, and $\tau_3 = 2.4$ ps for MG, and $\tau_1 = 0.63$ ps, $\tau_2 = 0.83$ ps, and $\tau_3 = 3.4$ ps for BG. The decay-associated difference spectra (DADS) in pure water are shown in Figure 3b and Figure 4b. As expected, the relaxation of BG is slower than that of MG as a result of the higher friction exerted by the solvent on the diethylaniline groups. The decay times obtained with MG agree very well with earlier findings.[24,31,33] The data reported for BG are scarce and refer only to single-color pump−probe experiments carried out at 635 nm[33] with a temporal resolution of approximately 30 fs. The authors have found two time constants shorter than 250 fs as well as three longer values: 0.55, 0.69, and 2.7 ps. In general, all three values are shorter than those measured in our experiment; the difference, however, is not very significant and may be attributed to the fact that they were measured in a single-color experiment, contrary to our broad-band measurement. The selected wavelength, 635 nm, made the single-color measurement particularly inaccurate, because in this spectral range the amplitude of the slowest decay component is close to 0 (compare the DADS corresponding to τ_3 in Figure 3b).

Similar measurements have been performed in various water+glycerol mixtures and the decay times extracted are shown in Figure 5 as a function of the viscosity. The shortest time constant (τ_1) is viscosity independent, while τ_2 and τ_3 exhibit a clear viscosity dependence.

Figure 4. (a) Transient absorption spectra of BG in water at selected delays between excitation and probe pulses. (b) DADS obtained from global analysis of transient absorption data. (c) Stationary absorption spectrum of BG.
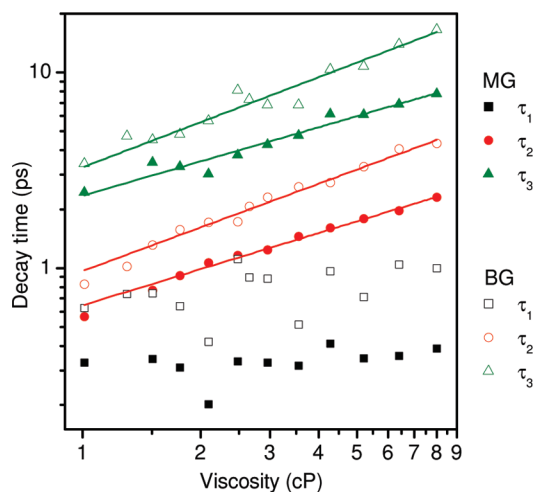
Figure 5. Decay times determined from transient absorption data with MG and BG (points) in water+glycerol mixtures of various viscosities, and best fits of eq 1 (solid lines).

The increase of τ_2 and τ_3 with increasing viscosity of the solvent has been also observed in the previous pump−probe studies of MG and BG[33] as well as of other triphenylmethane dyes (crystal violet and ethyl violet[34]) dissolved in various alcohols. However, the time constant of the fast rise of the signal, corresponding to τ_1, measured in those experiments was also solvent dependent, contrary to our observations. Our results, however, are not directly comparable to earlier measurements because of the difference in the nature of solvents: a mixture of two liquids in our case and pure alcohols in the previous studies.

TABLE 1: Best Fit Values of the Exponent α in Eq 1 Obtained from the Viscosity Dependence of the Decay Times τ_2 and τ_3

	MG	BG
τ_2	0.61 ± 0.02	0.74 ± 0.03
τ_3	0.58 ± 0.04	0.76 ± 0.05

The τ_1 time constant has been ascribed to structural relaxation of low-frequency vibrational modes of the molecule, which results from the fact that the equilibrium structure is different in the excited state and in the ground state. Thus some vibrational modes are out of equilibrium immediately after photoexcitation. Relaxation of these modes involves low-amplitude motions and might be influenced by the friction exerted on the dye molecule by the surrounding solvent molecules, which explains the observed solvent-dependence as well as different relaxation times for different dyes.[33,34] Slower relaxation observed for BG than for MG ($\tau_1 = 0.33$ ps and $\tau_1 = 0.63$ ps for MG and BG in water, respectively) might result from both a mass-effect (lower vibrational frequency) and a volume effect, because the solvent friction is higher for molecules with larger substituents on the aniline groups.
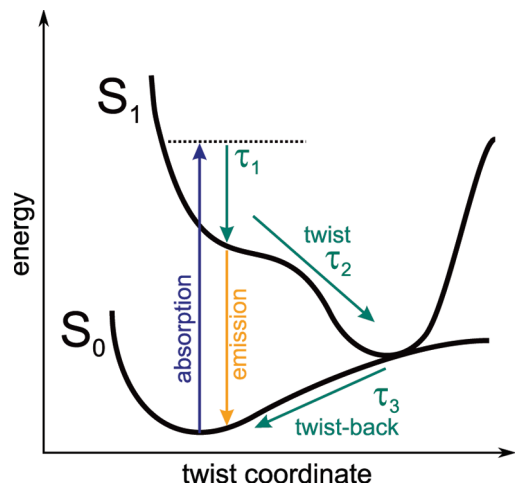
Low-amplitude vibrational and torsional motions involved in this relaxation are most likely affected by interactions with the nearest solvent molecules only. On this microscopic scale (the first solvation shell), the solvent friction may not be significantly modified by addition of the glycerol, even though it strongly increases the macroscopic viscosity, which explains the lack of the influence of glycerol on τ_1 in our studies. This comparison of the data obtained for pure solvents (alcohols) and for water+glycerol mixtures indicates the difference between the macroscopic viscosity and microscopic friction exerted on solute molecules.

The viscosity dependence of τ_2 and τ_3 can be described by the equation:[40]

$$\tau(\eta) \sim \eta^{\alpha} \qquad (1)$$

where η is the viscosity of the solvent. The values of the parameter α determined from fitting eq 1 to the data are presented in Table 1. It can be seen (Figure 5) that eq 1 fits very well to the data in the viscosity range studied here.

The values of α obtained here for MG are comparable to that determined by stationary polarization spectroscopy for MG dissolved in water+glycerol mixtures ($\alpha = 2/3$).[30] Strong dependence of τ_2 and τ_3 on the solvent viscosity (α close to 1) means that large amplitude structural motions (as opposite to low-amplitude motions related to τ_1) of the molecules are involved in the processes associated with these decay times, and the processes may be identified with the isomerization of the molecule in the high friction, low barrier regime.[41,42] Moreover, the α values associated with both time constants, τ_2 and τ_3, are equal within the limits of experimental error. If we assume the existence of a barrier for isomerization, this barrier, which determines α, would have to be similar in both electronic states where this process takes place. Because there is a large body of evidence indicating that the motion in the excited state is intrinsically barrierless,[43−45] it should rather be assumed that both processes are barrierless and controlled only by the friction exerted by the solvent. Therefore, the equality of α for both processes means also that the associated structural motion must be of the same nature. The lower value of τ_2 compared to that of τ_3 might be explained by a steeper potential in which the

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Figure 6. Ground- and excited-state potentials of MG and BG and the excited-state deactivation pathway explaining the same viscosity dependence of the formation and decay times (τ_2 and τ_3, respectively) of the intermediate state by its twisted character.
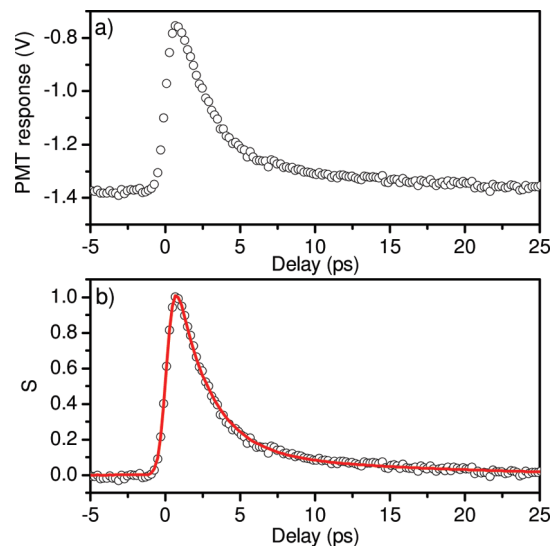

Figure 7. Measured (a) and normalized (b) intensities of the time-resolved SSHG signal for MG at a water/dodecane interface.

first twisting motion occurs. This is in good agreement with both quantum chemistry calculations[46] and experimental data[45] that point to a very shallow minimum of the ground-state potential as a function of the torsional angle. Still, the presence of a small barrier in the ground state as the origin of the observed slow-down of the back-twist cannot be completely excluded. The fact that α is higher for BG than for MG can be intuitively understood by the higher friction exerted by the solvent on the longer ethyl substituents of the former.

This observation throws a new light on the relaxation pathway of MG and BG, especially on the nature of the intermediate state. That state, often referred to as S_x, was ascribed by different research groups to either a twisted, propeller-like conformer of the ground state[29,33,34] or a vibrationally hot ground state.[47] Because τ_2 and τ_3 are the time constants of, respectively, population and decay of S_x, analogical structural motions must be involved in population and depopulation of this state. Namely, S_x is populated from the excited state by a twist of the phenyl and aniline rings and is depopulated to the ground state by a twist-back, flattening the structure of the molecule (Figure 6).

In our opinion, the equality of the exponents α obtained from eq 1 for the viscosity dependence of the buildup and decay times of the population of the intermediate state is a very strong argument supporting its twisted nature. Although in our previous work,[24] we suggested that some features of the DADS found in transient absorption spectra of MG are consistent with S_x being a vibrationally hot ground state, we believe that the arguments based on the current results prevail.

Apart from the above findings, the transient absorption experiments indicate that both dyes can be used as a reliable viscosity probe for the water+glycerol system under study. Both the longer time constants found in the kinetics show the same viscosity dependence, which reduces the chance of misinterpreting the kinetics measured by time-resolved SSHG.

Surface Second Harmonic Generation. *Concentration Dependence of SSHG Kinetics.* A typical transient SSHG signal recorded at a water/alkane (dodecane) interface is shown in Figure 7a. Prior to further analysis, the square root of SH intensities was calculated, and the kinetics were normalized so that the signal was 0 for negative time delays and equal to 1 at its maximum (Figure 7b). The resulting time-dependent quantity, $S(t)$, is proportional to the difference between the initial

population of molecules contributing to the enhancement of SH generation and the population at time delay t after excitation.

In previous studies, both single[21] and biexponential[24,26,48] decays of the SSHG signal have been observed with MG at various interfaces. The faster component is always identified with the decay of the S_1 state of monomeric MG molecules. The longer component of the decay observed for molecules adsorbed at the silica surface has been attributed to the deactivation of excited aggregates. On the other hand, its origin was not clear in the case of an air/liquid interface because the kinetics were not affected by a change of MG concentration by a factor of 2 at concentrations around 1.5×10^{-4} M.[24] Alternatively, the slower decay component could be due to the $S_x \rightarrow S_0$ relaxation if the S_x state does not contribute to SHG enhancement and the molecules have to relax to the S_0 state for the enhancement to occur.

The intensity of the second harmonics generated at liquid/liquid interfaces is much stronger than in case of an air/water interface, therefore our present measurements could be carried out at lower MG concentrations than the previous studies.[24] They show a clear dependence of the SSHG signal kinetics on the dye concentration (Figure 8a), the decay being slower at higher concentrations.

In order to study the influence of the concentration on the presence of the slower decay component, the time profiles $S(t)$ obtained at several MG concentrations in the 2×10^{-6} M to 2.1×10^{-4} M range were analyzed with biexponential functions convolved with a Gaussian instrument response function (IRF):

$$S(t) \sim f(t) \otimes \left[A_1 \exp\left(-\frac{t}{\tau_1^{\mathrm{SH}}}\right) + A_2 \exp\left(-\frac{t}{\tau_2^{\mathrm{SH}}}\right)\right] \quad (2)$$

where $f(t)$ denotes the IRF, τ_1^{SH} and τ_2^{SH} are the time constants (we assume that $\tau_1^{\mathrm{SH}} < \tau_2^{\mathrm{SH}}$), A_1 and A_2 are their relative amplitudes normalized so that $A_1 + A_2 = 1$. All temporal profiles were analyzed simultaneously, and the decay times were kept equal for all of them and were found to be $\tau_1^{\mathrm{SH}} = (2.5 \pm 0.1)$ ps and $\tau_2^{\mathrm{SH}} = (22 \pm 1)$ ps. The best-fit curves at the three lowest concentrations are shown together with the experimental data in Figure 8a. The small deviations of the residuals from the straight line seen in Figure 8b may suggest that either the two
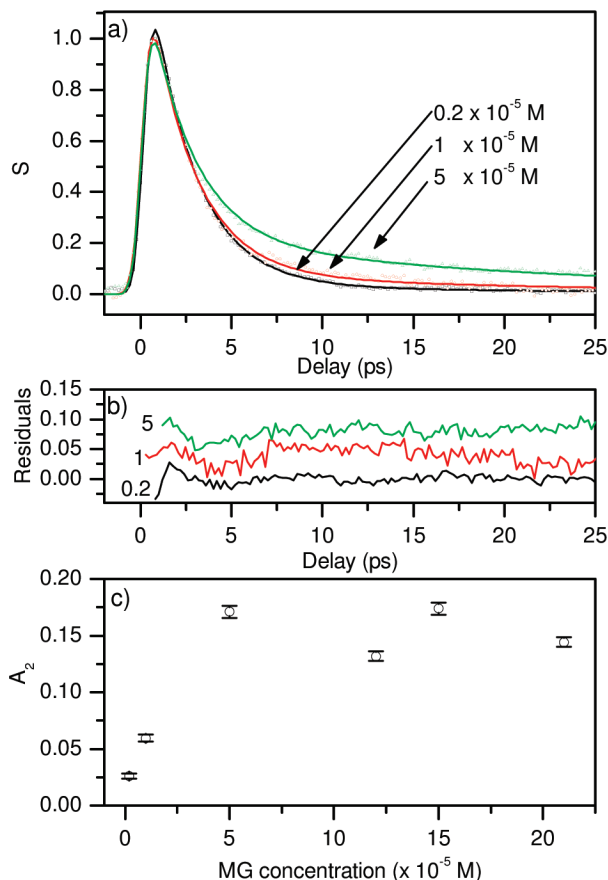
Figure 8. (a) Time profiles of the SSHG signal measured with MG at a water/dodecane interface at selected dye concentrations. (b) Residuals of the biexponential fits; the curves are displaced vertically by 0.04 in order to distinguish them. (c) Relative amplitude of the slower component of the biexponential function fitted to the SSHG data at various MG concentrations.

components are not enough to reproduce the measured data, or the decay times are weakly changing with increasing concentrations. Nevertheless, the contribution of this neglected factor is relatively small, and the quality of the fits is sufficient to analyze the concentration dependence of the amplitude of the slower decay component, A_2. As it can be seen in Figure 8c, A_2 is less than 0.03 at 2×10^{-6} M, and increases up to approximately 0.15 at 5×10^{-5} M MG, above which it remains approximately constant. This observation supports the identification of the slower component as the decay of the excited state of aggregates adsorbed at the surface and indicates that, above a certain dye concentration, a saturation regime is reached: the increase of the bulk concentration does not cause the increase of the relative concentration of aggregates at the interface. The concentration dependence was not revealed by the previous studies[24] of air/water interfaces, either because this effect is intrinsic to liquid/liquid interfaces, or because those measurements were carried out at concentrations above the saturation threshold.

The interpretation of the slower decay time as the relaxation of excited aggregates means that the SSHG signals originating from monomeric molecules decay monoexponentially, whereas for the ground state recovery biexponential kinetics are expected (the first step of the excited state deactivation, corresponding to the shortest time constant τ_1 seen in the transient absorption measurements would not be resolved with the temporal resolution of our SSHG setup). Although it cannot be excluded that for MG at a water/dodecane interface, only the slower component of the relaxation (the back-twist of the rings in the

electronic ground state) has been observed, and the faster component (the twist in the excited state) has been missed as a result of insufficient temporal resolution, the IRF is short enough to allow observation of both components for BG, especially in more viscous water+glycerol mixtures. Because this is not the case and no faster component has been revealed in any of the systems under study, it has to be assumed that only the second step (rings twisting) of the excited state deactivation is reflected by the kinetics of the SSHG signal, and there is no experimental evidence for biexponential decay of the SSHG signal originating from monomeric dye molecules.

This observation can be only understood if we assume that the dye molecules in both isomers of the ground state, the stable planar and the transient twisted form, contribute to the enhancement of the second harmonic generation to a similar extent. Because of this similarity, the back-twist of the rings and planarization of the geometry is not reflected in SSHG kinetics. Therefore the decay time of SSHG signal, τ_1^{SH}, corresponds to the lifetime of the electronic excited state of the dye, τ_2 measured by transient absorption spectroscopy and these two time constants will be compared in the further analysis.

Viscosity Dependence of SSHG Kinetics. The studies of the local interfacial viscosity were carried out with solutions of MG and BG in water+glycerol mixtures constituting the lower layer of the samples. The amount of glycerol in the mixture has been varied from 0 (pure water) to 47 wt %, with the resulting viscosity varying from 1 to approximately 5 cP. Dodecane was used as the upper, nonpolar phase.
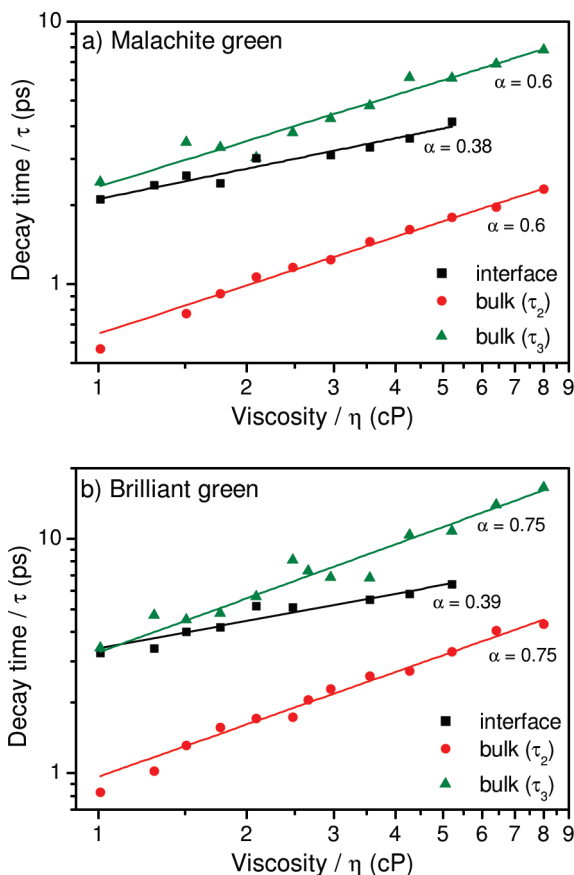
For the sake of reliability, the SSHG kinetics with MG at water+glycerol/alkane interfaces were analyzed with a monoexponential function:

$$S(t) \sim f(t) \otimes \left[A_1 \exp\left(-\frac{t}{\tau_1^{SH}}\right) + A_0 \right] \qquad (3)$$

where only the faster, predominating component of the decay was taken into account, whereas the slower component was treated as a constant offset A_0. This procedure was well justified because the relative contribution of the slower component at the MG concentration used in the experiments (10^{-5} M) amounted to only a few percent, and the time window in which the data were analyzed was comparable to the longer decay time, and was thus too short for τ_2^{SH} to significantly contribute to the decay. For BG, which was used at twice higher concentration than MG because of its lower extinction coefficient, the data were analyzed with biexponential curves convolved with the IRF (eq 2), but only the shorter decay time was analyzed.

The decay times obtained with both dyes in various water+glycerol mixtures are shown as a function of the mixture's viscosity in Figure 9. The decay times at the water/dodecane interface are almost 4 times larger than the shortest viscosity-dependent decay time measured in bulk solutions and are very similar to those reported before.[21,24] This slow-down has been attributed to the increase of water viscosity in the interfacial region because the decay time of MG at water/alkane interfaces was found to be relatively independent of the viscosity of the alkane constituting the upper phase.[21,20]

When comparing bulk water and the water/dodecane interface, one can recognize that, for both MG and BG, the slow-down of the excited state decay when going from bulk to interface is identical, namely, it amounts to a factor of approximately 4. The ratio between the corresponding decay times of both dyes stays practically constant (for bulk $\tau_{2(BG)}/\tau_{2(MG)} = 1.45$ and $\tau_{3(BG)}/$

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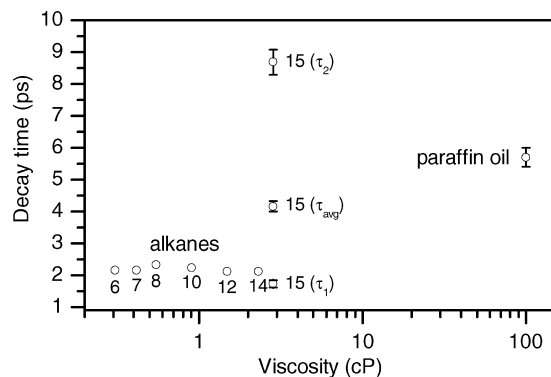*J. Phys. Chem. C, Vol. 113, No. 48, 2009* **20711**

Figure 9. Decay times of the SSHG signals measured at the interfaces between water+glycerol mixtures (lower layer) and dodecane (upper layer) and of transient absorption in bulk solutions of MG (a) and BG (b). The solid lines are the best-fits of eq 1.

Figure 10. Decay times of the SSHG signal measured at water/alkanes interfaces (the numbers next to the data points indicate the length of the alkane chain; for pentadecane both time constants of the biexponential decay as well as their amplitude-weighted average are shown) and at a water/paraffin oil interface.

$\tau_{3(MG)} = 1.41$, and for the interface $\tau_{BG}^{SH}/\tau_{MG}^{SH} = 1.55$). If we assume that the frictional forces exerted by the solvent on different parts of the molecule have a cumulative effect, this result can be interpreted as an indication that the layer of water that exhibits a higher viscosity encompasses entirely the aniline groups of BG, including the ethyl substituents. If this layer was thinner and interacted only with parts of the aniline groups close to the central carbon atom, the difference between the decay times of MG and BG measured at the interfaces would be less pronounced than that measured in bulk solutions. Because this difference is very similar in both media, it can be inferred that the structural modification of water, which leads to the increase of local viscosity, spans several molecular layers below the interface.

The viscosity dependence of the decay time at interfaces can also be reproduced with eq 1, but the values of the exponent α are smaller for interface than for bulk, namely, $\alpha = 0.38 \pm 0.03$ for MG and $\alpha = 0.39 \pm 0.04$ for BG. Clearly the relaxation of the excited dyes is less affected by the addition of glycerol at interfaces than in bulk solutions, which suggests that the local structure of the liquids plays a major role in the increase of the frictional resistance in the interfacial layer, and that the addition of glycerol contributes only to a lesser extent. It cannot be excluded that the number of glycerol molecules is reduced close to the interface compared to the bulk liquid (because of a reduced solubility of glycerol in the interfacial layer).

The very weak dependence of the SSHG decay time on the viscosity of the nonpolar phase has been previously interpreted as evidence that the rotation of the phenyl ring (projecting into the alkane phase) is not involved in the deactivation of the excited state of MG.[21,20] It must be noted, however, that the volume of the phenyl ring is smaller than that of dimethylaniline substituents. Therefore, its rotation even in the most viscous alkane used in those experiments (pentadecane) might be faster then the rotation of the larger substituted aniline groups in water. Moreover, the boundary conditions for the rotation of a nonpolar phenyl ring in a nonpolar alkane should be close to the pure slip limit, whereas, for the rotation of polar aniline groups in polar phase, the boundary conditions would be shifted toward the stick limit.[49] This effect further increases the difference in the rotation rates of phenyl and aniline groups in favor of the former.

If this was the case, the effect of the upper phase's viscosity would be seen only for highly viscous alkanes. In order to verify this hypothesis, we carried out a series of time-resolved SSHG measurements at interfaces between water and various alkanes (with 6, 7, 8, 10, 12, 14, and 15 carbon atoms in the chain) as well as at the water/paraffin oil (which is a solution of long solid alkanes in shorter ones) interface. For all alkanes except pentadecane, we obtained very similar, almost monoexponential decays (with only a small contribution of the slower component as described above) with a decay time around 2.2 ps. For pentadecane, on the other hand, the decays were clearly biexponential and slower than for other alkanes, with an average amplitude weighted decay time of 4.2 ± 0.1 ps. The decays measured with paraffin oil as the upper phase were again monoexponential but with a decay time of 5.7 ± 0.3 ps, clearly distinct from those found with the short alkanes (Figure 10).

Therefore, the relaxation of MG at the interface remains unaffected by frictional forces in the upper layer only with short alkanes of low viscosity. When the viscosity of the upper phase reaches very high values as for paraffin oil, the relaxation becomes significantly slower. This contradicts the image of the relaxation in which the phenyl ring does not play any role and leads to the following conclusion: the rotation of all three rings of the dye is involved in the radiationless deactivation; however, because of the smaller molecular volume of the phenyl ring, its rotation rapidly follows the motion of aniline groups when the phenyl ring is surrounded by a low-viscosity medium. The rotation of the phenyl ring becomes a bottleneck for the relaxation only in highly viscous liquids, and the effect of the increased viscosity of the upper phase can be seen. Still, as the case of water/pentadecane interface shows, the influence of the alkane on the relaxation cannot be described exclusively by its viscosity, and some structure-specific effects might appear.

Conclusions

We have studied the dependence of the relaxation rate of two triphenylmethane dyes, MG and BG, on the macroscopic viscosity of the solvent in bulk solutions and at water/alkane interfaces. The viscosity of the solvent was varied by mixing glycerol and water in various proportions in both bulk and interface experiments. For the former, we used femtosecond transient absorption spectroscopy and verified that both dyes are suitable viscosity probes in water+glycerol mixtures.

Three distinct processes following optical excitation have been revealed, and the two slower of them were described by the same power function of viscosity, which leads us to the conclusion that they can be identified with a twist and twist-back of the aromatic rings attached to the central carbon atom. Therefore, we provide additional evidence supporting the identification of the intermediate state appearing in the relaxation pathway of MG and BG with the twisted form of the molecule.

The relaxation of the excited dyes at interfaces has been studied by time-resolved SSHG. We have shown that the kinetics of the second harmonic signal may be described by monoexponetial decays at low dye concentrations (below 10^{-5} M) and by biexponential functions at higher concentrations, therefore we attribute the faster component present in the decays to the relaxation of monomeric molecules, and the slower one to the relaxation of dye aggregates adsorbed at the interface. For dye concentrations above 5×10^{-5} M, the amplitude of the slower component does not change with the increase of the concentration.

The excited state decay times at the interfaces increase with the macroscopic viscosity of the water+glycerol phase according to a power function that is similar to that found in bulk solutions. However, the exponent of the function is lower for interfaces than for bulk. This means that the viscosity at the interface is not affected by the addition of glycerol in the same manner as bulk solution and is to a large extent determined by structural modification of the water layer underlying the interface. The similar magnitude of the relaxation slow-down for MG and BG observed at water/dodecane interfaces suggests that the thickness of the structurally modified, highly viscous interfacial liquid is enough to encompass the whole dye molecule. Therefore, it should span at least several molecular layers beneath the interface.

Finally, we have verified the influence of the alkane viscosity on the dye relaxation and showed that the relaxation is slowed down with highly viscous liquids constituting the upper phase of the sample. This contradicts the earlier statement that the phenyl ring does not play a role in the relaxation of MG excited state. As a result of the smaller molecular volume of the phenyl ring and different hydrodynamic boundary conditions, its rotation in short alkanes (up to 14 carbon atoms in the chain) is faster than the rotation of the aniline groups submerged in the water phase, which accounts for the hidden alkane viscosity dependence of the decay time. The frictional resistance experienced by the phenyl ring only becomes the bottleneck for the relaxation in highly viscous alkanes.

Supporting Information Available: Values of time constants of MG and BG excited-state deactivation found by transient absorption in bulk solution and by SSHG at liquid/liquid interfaces. This material is available free of charge via the Internet at http://pubs.acs.org.

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