Effects of Two-Photon Fluorescence and Polymerization on the First Hyperpolarizability of an Azobenzene Dye

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The technique of hyper-Rayleigh scattering (HRS) has been employed to investigate the first hyperpolarizability (β) of the azo dye Disperse Red 19 and a polymer in which Disperse Red 19 appears as a side-chain moiety. In addition to HRS, these two molecules were found to exhibit substantial two-photon-induced fluorescence (TPF). The TPF spectra for these molecules were measured, and corrected HRS intensities were obtained. Using an external reference method, β values of $(1480 \pm 100) \times 10^{-30}$ and $(1470 \pm 90) \times 10^{-30}$ esu were determined for the dye and polymer systems, respectively, in dimethyl sulfoxide at 1064 nm. The difference between these two values is very small and shows that the effect of polymerization on the HRS intensity, in the dilute concentration limit, is negligible.

Introduction

Nonlinear optics (NLO) holds considerable promise for future advances in high-speed switching technologies.[1,2] Among the materials which have been considered for use in switching devices include inorganic crystals,[3,4] organometallic complexes,[5] and Langmuir−Blodgett films.[6,7] However, organic chromophores hold the most potential by far, due to their possibility for integration with polymers that facilitates processing.

In order to investigate organic chromophores for their potential in future use in NLO devices, the chromophore's molecular first hyperpolarizability (β) must first be accurately determined. The traditional method for measuring β was electric-field-induced second-harmonic generation (EFISH).[8] Recently, a technique based on two-photon light scattering has gained increasing popularity.[9] This technique has been termed hyper-Rayleigh Scattering (HRS), since it involves incoherent scattering of light at double the incident frequency, in contrast to Rayleigh scattering which deals with the scattering of light at the same frequency as the incident radiation. The experimental technique of HRS is rather simple, and it also requires fewer approximations in data analysis, thereby leading to a more direct measurement of β. However, several problems have been identified concerning the HRS experiment. The existence of other nonlinear mechanisms, such as two-photon-induced fluorescence (TPF), has been demonstrated; this TPF contribution to the HRS intensity cannot be separated solely by using the HRS experimental technique. Recently, Flipse et al.[10] obtained a TPF spectrum for DANS (4-(dimethylamino)-4′-nitrostilbene) and suggested that the same mechanism might be present for other similar chromophores which have the donor and acceptor groups separated by a stilbene, azobenzene, or other type of long π-conjugated moiety. Indeed, TPF has been observed from a wide variety of molecules, including laser dyes such as coumarins and rhodamines,[11] aromatic amino acids such as tyrosine,[12,13] and even inorganic semiconductors.[14] In the present work we have measured the TPF spectra and used the results to correct the HRS intensity and thus obtain first molecular hyperpolarizabilities for this important class of NLO molecules.

Furthermore, we are also interested in the effect of polymerization on the measured β value. To examine this effect, we have synthesized a functionalized polymer, attaching the dye Disperse Red 19 as a side-chain NLO moiety. We then carried out the HRS and TPF measurements on the free dye and the functionalized polymer. Shown in Figure 1 are the chemical structures for Disperse Red 19 (DR19) and the synthesized polymer (DR19P). A recent paper[15] has suggested that the effect of polymerization should enhance positive orientational correlation of the chromophores and hence increase the observed HRS intensity. However, considering the fact that HRS is due to fluctuations of chromophore orientation and density, the presence of a polymer would seem to inhibit these fluctuations and thus lead to a decreased HRS intensity. The results presented herein will hopefully help to elucidate a firmer understanding of the polymerization effect on HRS.

Experimental Section

DR19 and DR19P were synthesized in our laboratory according to literature methods[16] and characterized by infrared spectroscopy, UV spectroscopy, and ^{1}H NMR. As described in ref 16, one DR19 chromophore per repeat unit in the polymer chain is guaranteed; otherwise the polymerization step would terminate. After synthesis, the DR19 polymer was repetitively purified in ethanol before the characterization step. The polymer was found to have a weight average molecular weight of 26 500 g/mol, with a dispersity of 1.15, as determined by gel permeation chromatography (GPC). Polystyrene in tetrahydrofuran was used as a standard to calibrate the GPC apparatus.

All solvents used were ACS grade. *p*-Nitroaniline (*p*NA) (Aldrich, 99+% purity), serving as an external reference for the HRS measurements, was used directly from the bottle without further purification. For the HRS experiment, we first prepared concentrated stock solutions of DR19, DR19P, and *p*NA; then by successive dilution, we prepared a number of sample solutions. Each sample was filtered with a 0.1 μm Teflon filter (Whatman) to remove possible undissolved particulates.

Shown in Figure 2 is the experimental setup for the HRS and two-photon fluorescence experiments. The HRS part of this setup is very similar to our previous publications.[17−19] A

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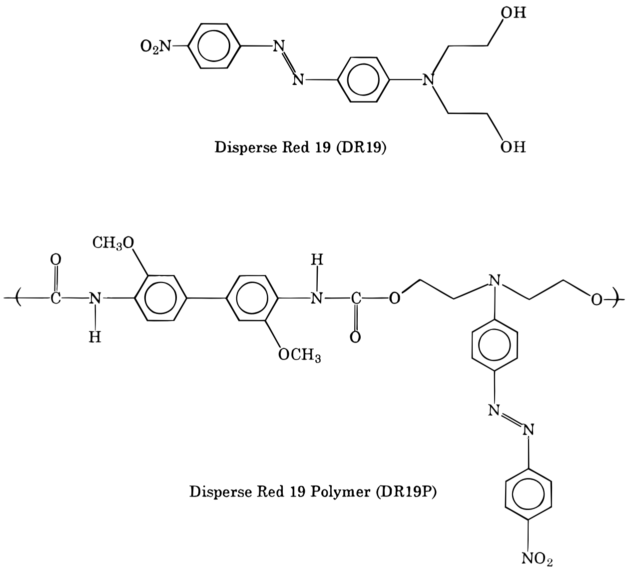

Disperse Red 19 (DR19)

Disperse Red 19 Polymer (DR19P)

Figure 1. Chemical structures of the two chromophores studied in this work.

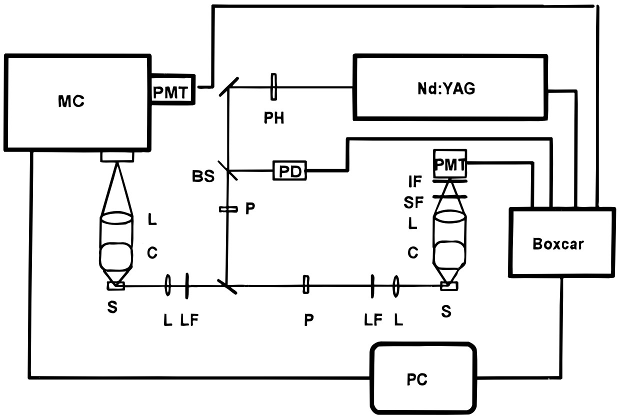

Figure 2. Experimental setup for the HRS and TPF experiments. MC, monochromator; PMT, photomultiplier tube; PH; pinhole; PD, photodiode; P, polarizer; LF, long-pass filter; L, lens; S, sample; C, camera lens; SF, short-pass filter; IF, interference filter; PC, personal computer.

Nd:YAG laser (Spectra-Physics GCR-11, 10 Hz, 8 ns pulse-width, 1064 nm) was used for both experiments. The laser radiation impinging on the sample was filtered using long-pass filters to remove possible SHG from the laser and optical components. The excitation beam passed through a polarizer to orient the polarization perpendicular to the scattering plane ("s" polarization). Part of the beam was split into a photodiode (ET2000, Electro-Optics Technology) to measure the intensity of the fundamental excitation beam. The scattered light was then collected at 90° by a camera lens (*f*/1.3) and a biconvex lens focused onto the detection apparatus. For the HRS experiment, a band-pass filter centered at 532 nm (10 nm width) and a short-pass filter attached in front of an electronically-cooled photomultiplier tube (PMT) served as the detection apparatus. For the TPF experiment, a single-grating monochromator (Spex 1870C, 0.5 m) and the same PMT as in the HRS experiment were used for detection. The PMT was attached to an integrating boxcar; for the TPF experiment, 128 laser pulses (12.8 s × 10 pulse/s) were integrated before a data point was obtained. The boxcar and monochromator were controlled by a personal computer. Absorbance measurements were carried out on a Hewlett-Packard 8452A diode array UV/vis spectrophotometer.

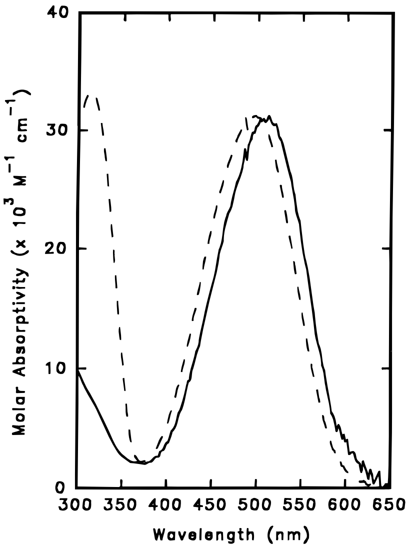

Figure 3. Molar absorptivity spectra for the two chromophores in DMSO: (—) DR19; (- - -) DR19P.

Results and Discussion

The theory of HRS is well established in the literature.[20,21] When light at frequency ω strikes a liquid or amorphous solid sample, at high fundamental intensity, incoherent scattering at the second-harmonic frequency of 2ω can occur. For our Nd:YAG laser, the second harmonic is at a wavelength of 532 nm. For a binary system consisting of a chromophore dissolved in a solvent, in the very dilute concentration limit, the intensity of the second harmonic light $I_{2\omega}$ can be related to the molecular properties of the scattering system in the following manner:

$$\frac{I_{2\omega}}{I_\omega^2} = G(N_c\beta_c^2 + N_s\beta_s^2) \tag{1}$$

Here I_ω is the intensity of the fundamental light, N_s, N_c are the number densities of the solvent and chromophore, respectively, β_s, β_c are the effective molecular first hyperpolarizabilities of the solvent and chromophore, respectively, and G is a proportionality constant depending on the scattering geometry and the solvent environment of the chromophore.

If the scattering medium is capable of absorbing some of the second-harmonic light, the scattering intensity will be attenuated. One must therefore correct for this absorption using the following equation

$$I_{2\omega}(\text{obs}) = I_{2\omega}(\text{true})e^{-\sigma l N} \tag{2}$$

where $I_{2\omega}$(true) is the intensity of the second-harmonic light actually generated, $I_{2\omega}$(obs) is the intensity of the second-harmonic light detected after absorption, l is the path length of the scattering cell, N is the number density of the absorber, and σ is a linear absorption cross section which can be determined from linear absorption measurements according to $\sigma = 1000\epsilon \ln(10)/N_A$ where N_A is Avogadro's number and ϵ is the molar absorptivity expressed in units of M^{-1} cm^{-1}.

Shown in Figure 3 are the molar absorptivity spectra for DR19 and DR19P. The peak near 500 nm arises mainly due to the $\pi \rightarrow \pi^*$ transition and is associated with the charge transfer process. Upon polymerization, the linear absorbance for the dye moiety undergoes a small blue shift: $\lambda_{max}(DR19) = 512$ nm, $\lambda_{max}(DR19P) = 496$ nm. The absorbance peak near 310 nm for DR19P can be attributed to absorption from the biphenyl group in the polymer backbone. Using the concentration values

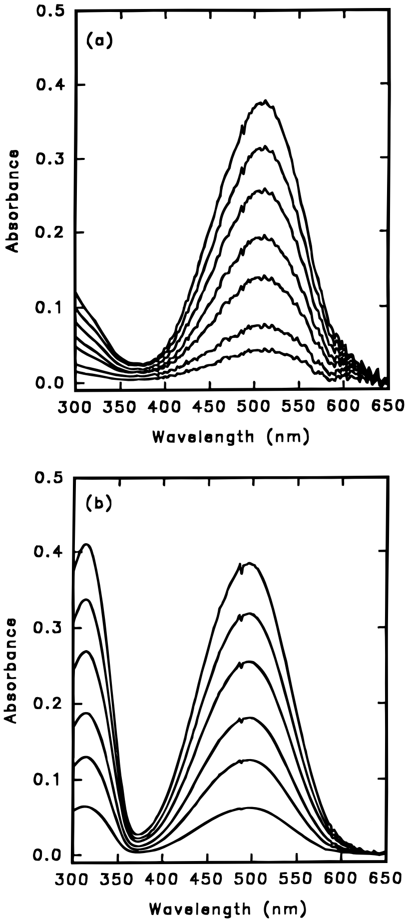

Figure 4. Absorbance spectra for the two chromophores in DMSO: (a) DR19; (b) DR19P.

calculated for the DR19 solutions from successive dilution and employing the assumption that ϵ_{DR19} (512 nm) $\approx$ ϵ_{DR19P} (496 nm), the number density of dye in the DR19P samples can be calculated from Beer's Law. The series of linear absorption spectra used to determine the concentration of the DR19P samples can be seen in parts a and b of Figure 4 for DR19 and DR19P, respectively. For comparison, the number density of dye units in the polymer solutions was calculated using molecular weight data and was found to be in good agreement with the absorbance measurements. Using Figure 4a, b one notes that significant absorption for both molecules at the second-harmonic wavelength is present. From the linear absorption measurements taken, we have calculated linear absorption cross sections of $\sigma = 1.027 \times 10^{-16}$ cm^2 for DR19 and $\sigma = 8.614 \times 10^{-17}$ cm^2 for DR19P at 532 nm. The HRS data herein presented have been corrected using these absorption cross sections.

According to eq 1, $I_{2\omega}$ should be proportional to I_{ω}^2; this quadratic dependence was observed and can be seen in parts a and b of Figure 5 for DR19 and DR19P, respectively. However, as mentioned above, two-photon-induced fluorescence could also be present in these dyes. The intensities from both the HRS and TPF processes are proportional to I_{ω}^2 and cannot be distinguished in an intensity dependence measurement as presented in Figure 5.

In an effort to investigate the TPF contribution to the HRS intensity, we have measured the TPF spectrum for both DR19 and DR19P in DMSO. Shown in parts a and b of Figure 6 are the normalized TPF spectra for DR19 and DR19P, respectively. The overall spectrum can be divided into two regions: a HRS region near 532 nm and a much broader TPF region centered at about 575 nm. The HRS region is sharp and is clearly differentiated from the TPF region. Although few data points are presented in Figure 6a, b, these results are reproducible. To facilitate data analysis, we have fitted each region of both spectra to Gaussian functions of the form

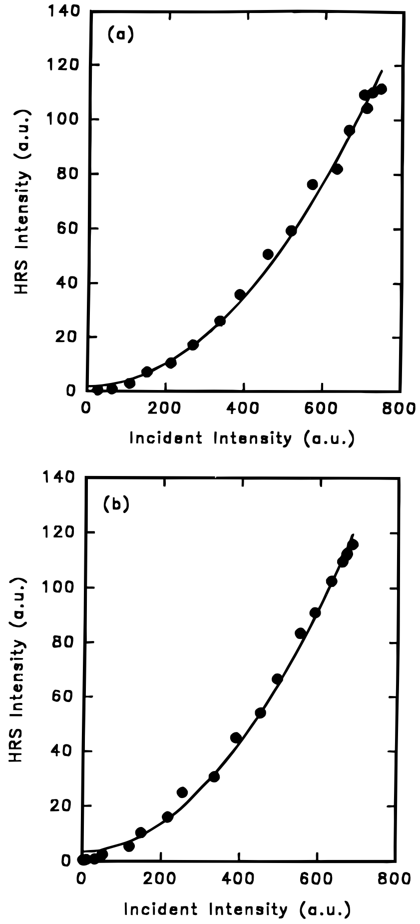

Figure 5. HRS intensity vs incident intensity for the two chromophores in DMSO: (a) DR19; (b) DR19P. The solid lines represent a quadratic least-squares fit through the experimental data. Corrected for background intensity.

$$G(x) = A \exp\left[-0.5\left(\frac{x - x_c}{\sigma}\right)^2\right] + \mathrm{b}(x) \tag{3}$$

where A is the amplitude, x_c is the peak center, σ is the peak width at half-height (fwhm), and b is the background intensity, which decreases slightly with x. Table 1 shows the parameters obtained via least-squares fitting from these spectra. By integrating each Gaussian function at 532 nm for the width of the 2ω band-pass filter (10 nm), the TPF contribution to the $I_{2\omega}$ intensity can be calculated. In this manner, we have found that TPF accounts for 36.2% of the $I_{2\omega}$ intensity for DR19 and 25.0% for DR19P. Clearly, the TPF mechanism has considerable importance for azo dyes in second-order NLO measurements.

In parts a and b of Figure 7 the concentration dependence of the HRS intensity is presented for both DR19 and DR19P before and after correction for TPF, respectively. The experimental points have been corrected for linear absorption. In a concentration-dependence experiment, where the intensity at 2ω is measured as a function of number density of chromophore, eq 1 shows that the dependence should be linear; the slope contains information about the molecular hyperpolarizability of the chromophore, while the intercept is associated with the 2ω intensity from the solvent. This solvent contribution is the basis

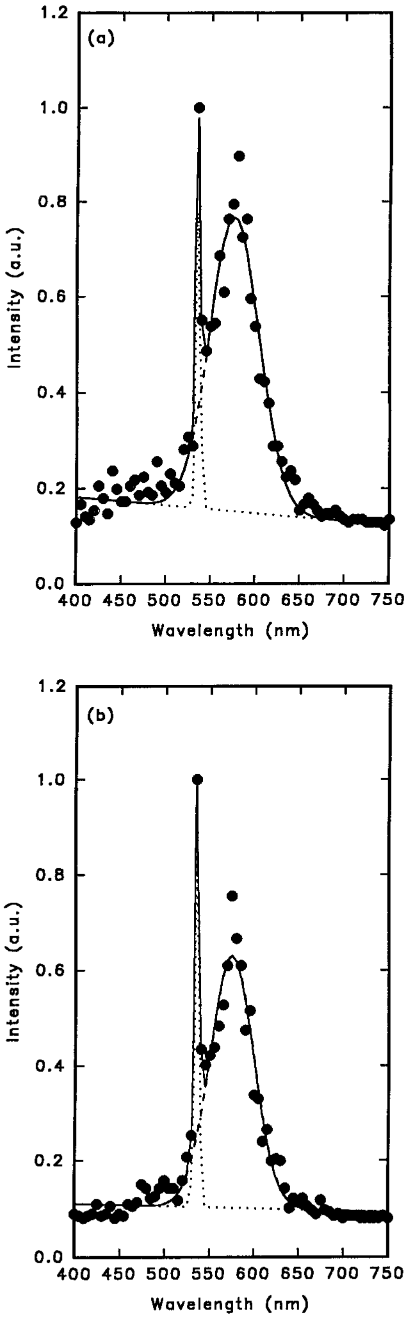

Figure 6. TPF spectra for the two chromophores in DMSO: (a) DR19; (b) DR19P. (●) Experimental data points; (···) Gaussian fit to HRS peak; (- - -) Gaussian fit to TPF peak; (—) sum of the two peaks (total intensity).

TABLE 1: Gaussian Function Parameters Obtained from the Normalized TPF Spectra of DR19 and DR19P Dyes

peak	A (a.u.)	x_c (Å)	σ (Å)	b (a.u.)
DR19 HRS	0.66	5339	22.62	$0.25-(1.69 \times 10^{-5})x$
DR19 TPF	0.61	5744	275.99	
DR19P HRS	0.78	5336	23.79	$0.13-(5.00 \times 10^{-6})x$
DR19P TPF	0.53	5728	244.90	

for the internal reference method. However, since the intercept is typically very small, this leads to large errors in the determination of β for the chromophore compared with the external reference method.[22] For our measurements, we have chosen to use *p*NA as an external reference, and the results are thus more accurate. Simultaneously with the measurement of these two chromophores, the HRS intensity was also measured for *p*NA in DMSO, to be used as an external standard. There is no detectable TPF intensity from *p*NA.[10] According to the external reference method

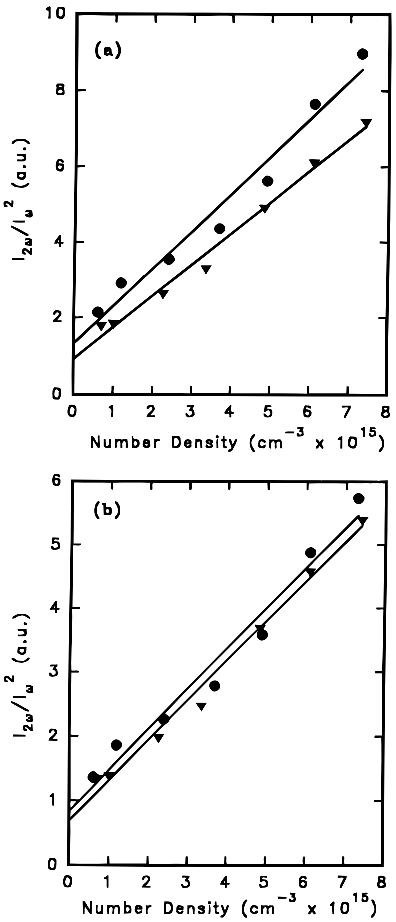

Figure 7. $I_{2\omega}/I_{\omega}^2$ vs number density for the two chromophores in DMSO. Corrected for linear absorption. (●) DR19; (▼) DR19P. (a) Before correction for TPF. (b) After correction for TPF. The solid lines represent a linear least-squares fit through the experimental data.

$$\beta_c = \beta_{st}\sqrt{m_c/m_{st}} \tag{4}$$

where β_c, β_{st} are the effective molecular first hyperpolarizabilities for the chromophore and standard, respectively, and m_c, m_{st} are the slopes, determined from a concentration dependence experiment, for the chromophore and standard, repectively. In our previous work,[23] β_c was measured to be 28.8×10^{-30} esu for *p*NA in DMSO at 1064 nm. Using this value, we have obtained effective molecular first hyperpolarizabilities of $\beta_c = (1480 \pm 100) \times 10^{-30}$ esu for DR19 and $\beta_c = (1470 \pm 90) \times 10^{-30}$ esu for DR19P. It is interesting to note that (as Figure 7a demonstrates) the $I_{2\omega}$ intensity for the DR19 solutions are consistently higher than that of the DR19P solutions, even after correcting for linear absorption, but this difference is due solely to DR19's greater TPF contribution to the $I_{2\omega}$ intensity than to DR19P's contribution. This result is confirmed by repeated experiments.

Due to symmetry requirements, elastic second-order effects are forbidden in centrosymmetric media. Thus the molecular mechanism for HRS in solutions is generally considered to be fluctuations in the chromophore's orientation and density, which serve to create a "pocket" of noncentrosymmetry in an otherwise isotropic solution. The introduction of a polymer into the solution would be expected to retard these fluctuations and hence decrease the HRS intensity compared to the free dye. However, a recent paper by Persoons et al.[15] showed a dramatic *increase* in the HRS intensity of a polymer−dye system compared to the free dye. They have interpreted the HRS intensity enhancement to be due to increased orientational correlation among the side-chain chromophores. The present experiments show no detectable increase in the HRS intensity of DR19 and DR19P. It is possible that the effect might become more significant if the distance between chromophore were reduced. This wouldlead to greater orientational correlation between chromophore units along the side chain and hence an increase in HRS intensity. However, one also expects the HRS intensity to decrease with increasing concentration since at higher chromophore density in an amorphous polymer, the fluctuations in orientation and density would be retarded. In light of these considerations, further investigations into the effect of polymerization on HRS would be well justified.

Since at 532 nm, the first hyperpolarizability is affected by two-photon resonance for these dyes, we can estimate the intrinsic hyperpolarizabilities β_0 using the two-state model[1]

$$\beta_0 = \left(1 - \frac{\omega^2}{\omega_0^2}\right)\left(1 - \frac{4\omega^2}{\omega_0^2}\right)\beta_{2\omega} \qquad (5)$$

where $\beta_{2\omega}$ is the value measured at 2ω with the fundamental beam at ω, and ω_0 is the resonant frequency of the charge transfer transition. Assuming that ω_0 corresponds to $\lambda_{\max}$ in the linear absorption spectrum (Figure 3), we have calculated the β_0 values to be $(84 \pm 6) \times 10^{-30}$ esu for DR19 and $(151 \pm 9) \times 10^{-30}$ esu for DR19P. The larger β_0 value for DR19P is due solely to its blue shift compared to DR19. It can be seen that both DR19 and DR19P exhibit significant resonance enhancement due to the proximity of the $\lambda_{\max}$ from absorption for both systems to 2ω. It should be emphasized though that the two-state model considers only the contribution from the charge transfer state; contributions from other electronic states and the effect due to the environment surrounding the chromophores are not included.

In summary, we have investigated the effect of polymerization on the first hyperpolarizability of an azo dye. We have measured β for both the free dye and the polymer in which the dye was attached as a side-chain moiety and have found the difference between the two hyperpolarizabilities to be negligible. We have also found that these dyes exhibit significant TPF, which enhances the observed intensity at 2ω. We have carried out a quantitative TPF experiment to correct for the fluorescence intensity contribution, thereby obtaining true values for the chromophores' β values.

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