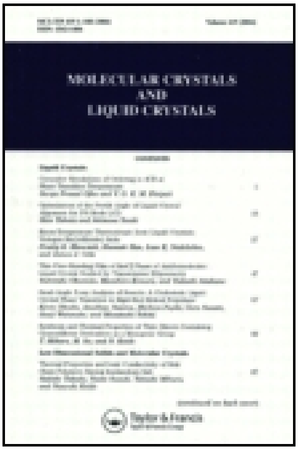

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Large Optical Torque Enhancement By Oligothiophene Dye In A Nematic Liquid Crystal Host

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LARGE OPTICAL TORQUE ENHANCEMENT BY OLIGOTHIOPHENE DYE IN A NEMATIC LIQUID CRYSTAL HOST

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We have studied the nonlinear optical response of the nematic liquid crystal E7 doped with the oligothiophene dye TR5. Z-scan measurements showed a large positive (self-focusing) nonlinearity, originating in director reorientation. The oligothiophene dye enhances the nonlinearity of the host, in a similar manner to that of azo- and anthraquinone dyes in guest-host systems which exhibit the Janossy effect. The enhancement factor is unusually large; our TR5-E7 system showed as large a dye-induced optical torque enhancement factor as any observed in a guest-host system. Here we present our experimental results, determine the enhancement factor, and hypothesize that the dominant mechanism involves a photo-induced decrease in the orientational mobility of the dye molecules.

Keywords: dye doped nematics; janossy effect; nonlinear optical response; oligothiophene dyes

INTRODUCTION

The oligothiophene family of dyes has been studied and used in many areas of condensed matter physics. Due to their photonic and electronic properties, oligothiophenes show potential for applications in a variety of areas, from nonlinear optics, organic LEDs and organic lasers to LCDs [1–5].

Liquid crystals are known to posses a large nonlinear optical response. The torque exerted by the optical field can easily reorient the 'soft' anisotropic liquid crystal, giving rise to the so called 'giant' optical nonlinearity [6]. The Janossy effect is the enhancement of optical torque in dye-liquid

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crystal guest-host mixtures due to the presence of an absorbing dye dopant at a low concentration [7]. In this case, the torque is not due to angular momentum transfer form the optical field, but originates in a Brownian ratchet mechanism [8,9]. A wide variety of anthraquinone and azo dyes have been characterized from the optical torque enhancement point of view [10–12].

New dyes of the oligothiophene family have been developed recently that promised to be effective as optical torque enhancement agents [13]. Preliminary measurements showed a large positive effect in 5CB doped with a small amount of the TR5 oligothiophene dye [2]. In this paper we present results of measurements carried out to determine the dye induced enhancement factor in the TR5-E7 system.

EXPERIMENTAL

The synthesis of the TR5 oligothiophene dye, 5,5″-bis-(5-butyl-2-thienylethynyl)-2,2′:5′2″-terthiophene has been described previously [13]. The chemical structure of TR5 is shown in Figure 1. In our samples, 0.46 wt% of TR5 dye was dissolved in the nematic host E7 (MERCK). Instead of the pure nematic liquid crystal 5CB, we used the commercial nematic mixture E7, which has a higher nematic-isotropic transition temperature, in order to reduce thermal contributions to the NLO response. Cells were constructed using glass plates with transparent ITO electrodes which were coated with the polyimide JALS-688-R11 (JSR Microelectronics) which produces homeotropic anchoring. Pieces of Mylar foil with 36 μm thickness were used as spacers. The cells were filled with the guest-host mixture using capillary action and were subsequently sealed.

To determine the nonlinear optical response, the Z-scan technique was used [14]. A plane polarized Gaussian beam from CW argon laser tuned to $\lambda = 475\,\text{nm}$ was focused to a 55 μm beam waist (FW@1/e). The aperture ratio was 20%. Z-scan measurements were performed with and without the application of a low frequency electric external field to the sample, which suppresses reorientation and enables the separation of thermal and reorientational contributions to the NLO response. The p-polarized pump beam was incident at 45° to the cell normal. In this geometry, instead

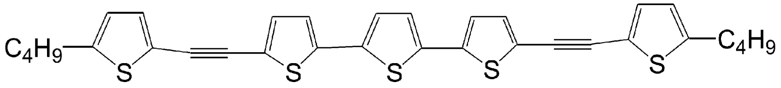

FIGURE 1 Chemical structure of oligothiophene dye TR5.

of a first-order Freedericksz transition, there is a continuous reorientation of the director as function of the pump intensity, which allows simple analysis of the response. The procedure for analyzing the data and determination of the dye induced enhancement factor are described [10]. All measurements were carried out at room temperature. Linear absorption and fluorescence spectra were measured with a fiber optic spectrometer (Ocean Optics).

RESULTS AND DISCUSSION

We have studied the linear optical properties of the TR5-E7 guest-host mixture. Linear absorption is shown in Figure 2. The system shows an absorption maximum at 439 nm. The dichroic ratio at this wavelength is $DR_{\lambda\max} = 9.38$, which corresponds to an order parameter (of the transition dipole of the dye) of $S_{dye} = 0.736$. Our data is in accord with the findings of Ref. [5], where it was found that increasing the number of thiophene rings results in a higher order parameter, presumably due to the increased length of the dye molecule. Also shown in Figure 2 is the fluorescence spectrum of

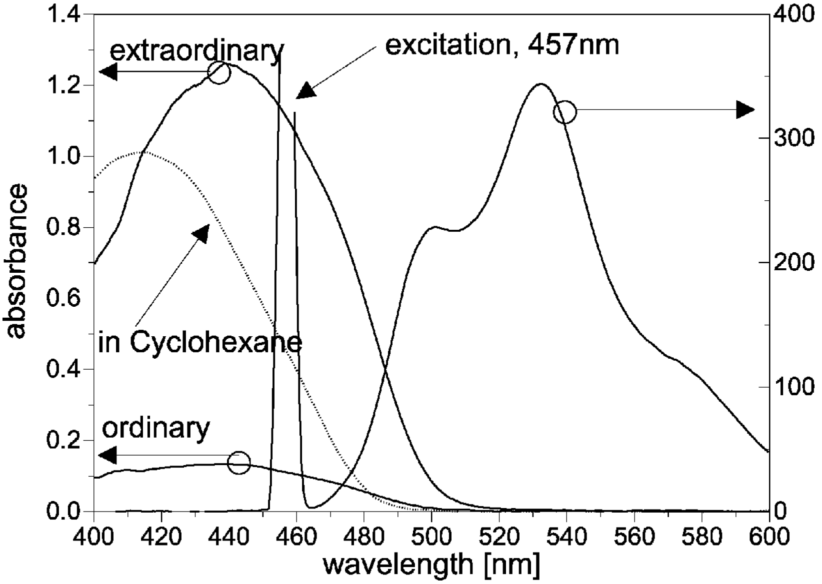

FIGURE 2 The linear absorption and dichroism of TR5; fluorescence spectrum when excited at 457 nm.

TR5. Visual observations suggest that the dye is strongly fluorescent; however, the quantum efficiency has not yet been determined.

The Z-scan technique is a powerful method to determine the effective third order nonlinear optical coefficients of materials in a wide variety of phases. At low intensities, the amplitude of the modulation in the normalized closed and open aperture curves is proportional to the intensity dependent refraction and absorption coefficients, respectively. The relative position of the peak and valley in the closed aperture curve allows the determination of the sign of the nonlinear index. We show below only closed aperture curves, since the open aperture curves are constant within experimental error, indicating that the nonlinear absorption is negligible. Figures 3 and 4 show the closed aperture curves for the pure E7 host and for TR5 doped E7, respectively, both with and without an applied low frequency electric field. The external electric field can orient the director normal to the cell walls, and suppress the reorientational contribution to the nonlinear optical response. The thermal nonlinearities, however, are essentially unaffected by the external field. As shown in Figure 3, the

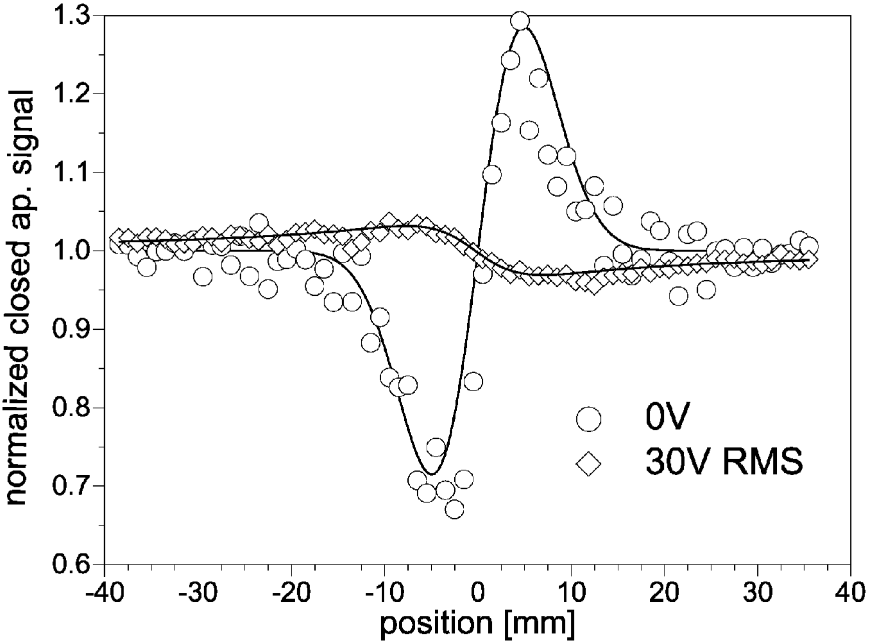

FIGURE 3 Z-scan signal from the undoped E7 host, P = 7.2 mW. The positive reorientational component is suppressed by the external field and only the negative thermal component remains.

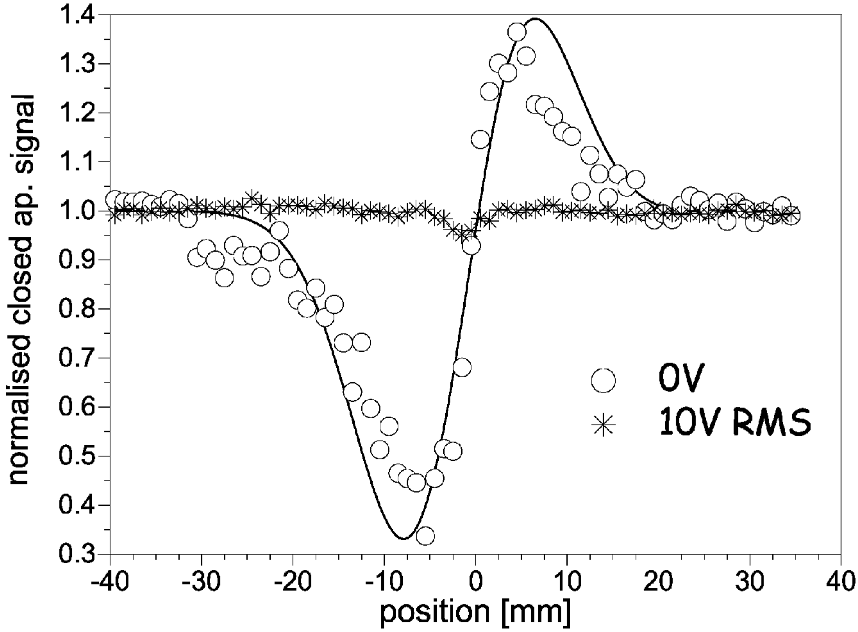

FIGURE 4 Z-scan signal from the TR5-E7 guest-host mixture, P = 34 μW. The large positive component can be completely suppressed by the application of an external field and the thermal contribution is negligible.

pure host exhibits a positive nonlinear index. This is due to the direct optical torque which rotates the director towards the direction of electric field of the pump beam. The optical torque density is

$$\mathbf{\Gamma}_{opt} = \varepsilon_0 \varepsilon_a (\hat{\mathbf{n}} \times \mathbf{E})(\hat{\mathbf{n}} \times \mathbf{E})$$

where $\hat{\mathbf{n}}$ is the director, **E** is the electric vector of the optical field and ε_a is the dielectric anisotropy. The optical torque always results in a positive (focusing) nonlinear response for calamitic liquid crystal molecules. When an external electric field is applied, the peak-valley positions reverse and the modulation amplitude decreases. Once the director reorientation is suppressed, the thermal nonlinearity becomes manifest. If the contribution is negative, the position of the peak and valley become reversed. The dominant thermal contribution is laser heating of the ITO electrodes.

Next, we consider the response of the dye doped sample. Again, a large positive nonlinearity is observed without the external field. In this case, the pump power was 200 times smaller than that used for the undoped sample. The closed aperture curve, measured with the external field applied, is a constant, indicating that laser heating at this power is negligible.

It has been argued that the dye induced torque, $\mathbf{\Gamma}_{\text{dye}}$, is proportional to the optical torque, $\mathbf{\Gamma}_{\text{opt}}$ [15]. In this case, the light induced torque can be written as

$$\mathbf{\Gamma}_{light} = (1+\eta)\mathbf{\Gamma}_{opt}$$

where η is the enhancement factor. In the limit of small attenuation, the optical torque is proportional to the input power. Furthermore, in the case of low input power, the modulation amplitude in the normalized closed aperture curve is proportional to the input power. In this case, we can write for η

$$\eta = \frac{\Delta\nu_{dye}/P_{dye}^{av}}{\Delta\nu_{host}/P_{host}} - 1$$

where $\Delta\nu$ is the modulation amplitude (peak-valley difference) in the closed aperture z-scan curve; these values were corrected to eliminate thermal contributions. For the dye-doped case, we use the expression $P_{dye}^{av} = P_{dye}\frac{1-e^{-\alpha d}}{\alpha d}$ for the average power to compensate for light attenuation in the sample. Here α is the absorption coefficient for the appropriate polarization and d is the path length. We find that in our experiment the enhancement factor $\eta = 440$. Since η is expected to be proportional to the dye concentration, a more appropriate measure of the enhancement is the quantity η/α, which is independent of concentration. For our system, $\eta/\alpha = 3.4\,\text{cm}$. For comparison, the quantities η and η/α for other dyes with a high enhancement factor are presented in Table 1. The dye AQ2, first reported in 1992 [10], had the largest normalized enhancement factor η/α in the literature for some time. More recently, Kreuzer *et al.* showed that partial deuteration of the dye HK271 increases

TABLE 1

Dye	Enhancement factor η	Normalized enhancement factor η/α (cm)	Pump wave-length λ (nm)	Host	Cell thickness d (μm)	Dye concen-tration (wt. %)	Ref.
TR5	440	3.4	457	E7	36	0.46	This work
AQ2	238	1.7	633	E63	35	0.50	10
D4	−95	−0.35	633	E63	35	0.50	10
deuterated HK271	‘about a factor of 2’ that of AQ2 ‘∼1.4’ times that of AQ2		633	5CB E63	100	0.10	16

the enhancement factor, when the dye is dissolved in the host 5CB, by "about a factor of two" [16]. (HK271 from Nematel and AQ2 from BDH have the same composition (see Refs. [16] and [18].). Unfortunately the value of enhancement factor of HK271 is not provided in Reference [16], but if it is comparable to that of AQ2 measured in Reference [10], and if the effect of deuteration of the dye in the host E7 is the same as in 5CB, an increase of "about a factor of 2" , then one would expect the normalized enhancement factor for deuterated HK271 to be also $\eta/\alpha = 3.47\,\mathrm{cm}$. Although exact comparisons are difficult, due to incomplete data as well as to differences in the experimental parameters involved, we nonetheless conclude from our experimental results that the optical torque enhancement for the oligothiophene TR5 is as great as any that has been observed to date in guest host systems.

Janossy demonstrated [15] that a change of the interaction potential of liquid crystal and dye molecules on photo excitation can give rise to the enhancement. This model was later extended by Marrucci *et al.* [17] who also considered the change of the orientational mobility of the dye molecules on excitation. According to their model, the expression for the optical nonlinearity, which is proportional to $1+\eta$, is [16]

$$\zeta = K\left\{\frac{\tau_e D_e}{1+6D_e\tau_e}\right\}\left(\frac{u_e}{D_e}-\frac{u_g}{D_g}\right)$$

where K is a constant proportional to the dye concentration. This expression indicates that if the strength of interaction between the liquid crystal and dye molecules in the excited state, u_e, is greater than that in the ground state, u_g, a positive enhancement is expected. In the opposite case, when $u_g > u_e$, a negative enhancement is expected, as has been observed in the case of some anthraquinone dyes [10]. Another mechanism contributing to enhancement originates from the difference between the orientational mobilities D_e, in the excited, and D_g, in the ground states. For certain anthraquinone dyes this latter effect was found to dominate. Marrucci *et al.* [12] argued that enhanced intermolecular hydrogen bonding between dye and liquid crystal host molecules on photoexitation results in a decrease in the orientational mobility of excited dye molecules. This can explain the large positive enhancement observed in the case of AQ2. Since the enhancement mechanism is operational while the dye is in the excited state, the magnitude of the enhancement is proportional to the excited state lifetime, τ_e. Krauzer *et al.* [16] demonstrated with time resolved fluorescence measurements that the increase in the enhancement factor of deuterated HK271 directly correlates with the increase in the excited state lifetime. Deuteration suppresses nonradiative relaxation channels thus increases the lifetime of the excited state.

Since data on interaction strengths, mobilities and lifetimes of the dye TR5 has not yet been obtained, we merely speculate here about the mechanism underlying the observed high enhancement factor. We note that the interaction strength parameters u_e and u_g describe anisotropic dispersion interactions which orient the molecules. It seems unlikely that the photo-induced change in these interactions is large enough to account for the observed strong enhancement. On the other hand, it has been argued [12] that even a modest change in isotropic interaction strength can contribute significantly to the enhancement through the resulting change in the orientational mobility of the excited dye molecules. We speculate that the optical torque enhancement in TR5 originates primarily from a photo-induced changes in orientational mobility. We envision two plausible mechanisms. Figure 2 indicates that TR5 shows a strong solvatochromic red shift in the polar solvent of E7, suggesting the possibility of the increase in the polar interaction between host and excited dye molecules. This could result in a decrease of orientational mobility, similar to the case of enhanced hydrogen bonding [12]. Another plausible mechanism is as follows. The E7 host is a eutectic mixture of cyano-biphenyls and terphenyls. The cyano-group in the liquid crystal molecules is an acceptor, while the TR5 molecules are strong donors. Since the molecular core is symmetrically substituted with apolar alkyl groups, the electronic excitations occur predominantly in the core. This is in contrast to the first excitation of a push-pull substituted azo-dye, for example, where due to asymmetry, low energy excitations involving intramolecular charge transfer play an important role. It seems plausible to us that on excitation, intermolecular charge transfer takes place between the donor TR5 and an accepting bi- or terphenyl liquid crystal host molecule. As a result, complexation occurs, where the orientational mobility of the complex containing the excited dye molecule is reduced. This change in mobility results in a positive enhancement factor.

Since TR5 is a fluorescent dye (see Fig. 2), time resolved pump-probe, fluorescence lifetime and fluorescence depolarization measurements are possible. We plan to carry out such measurements in the near future and look for verification of the proposed mechanism.

SUMMARY

We have studied dye induced enhancement of the optical torque in the nematic liquid crystal E7 dye doped with the oligothiophene dye TR5. We have found that TR5 exhibits a very large positive enhancement in E7, as large as any that has been observed in any guest host system to date. We propose that the mechanism underlying the enhancement is the decrease of the orientational mobility of the dye on photoexcitation. Reasons for this decrease might be the increase of polar interaction between host and dye or charge transfer complex formation on photoexcitation.

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