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Invited Paper

The effects of molecular aggregation and isomerization on the fluorescence of "push-pull" hyperpolarizable chromophores☆

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Abstract

Hyperpolarizable organic molecules are attracting interest for use in nonlinear optical devices. Some zwitterionic merocyanine chromophores with exceptionally high first hyperpolarizabilities have been synthesized that possess an electron donor moiety coupled to an electron acceptor through a conjugated double bond system. Aligned arrays of these molecules tethered to a polyurethane backbone and spun onto a substrate to form a thin film, respond to the application of external electric fields with changes to their refractive indices, i.e. the electro-optic effect. This behavior can be capitalized upon to fabricate optical switches and modulators.

High concentrations, or loadings, of these nonlinear optical molecules in thin films are required to produce a usable electro-optic effect, ca. 0.1–0.5 mol L^{-1}, and this promotes molecular aggregation which alters their polarizabilities and also has implications for their photostabilities. The fluorescence spectra of these molecules in polymer films at ambient temperature and in solution in a 9:1 ethanol–water mixture over a range of temperatures down to 80 K show a substantial blue shift as the temperature is lowered. This is attributed to a reduction in the solvating power of the solvent as it becomes increasingly more viscous at lower temperatures. At the lowest temperatures studied a shoulder on the lower energy side of the fluorescence spectral distribution is apparent which is ascribed to the formation of antiparallel dimers/aggregates; a consequence of the highly dipolar character of these molecules. In addition, dual fluorescence is observed in high viscosity environments suggesting the involvement of twisting about the bridging conjugated bond system that links the electron donor to the electron acceptor.

Keywords: Merocyanine; Aggregation; Nonlinear optics; Fluorescence; Hyperpolarizability

1. Introduction

There has been considerable interest recently in fabricating nonlinear optical devices such as electro-optic modulators and switches based on polymers containing extensively conjugated "push-pull" molecules with electron donor and acceptor groups at opposite ends of the molecules. As a consequence of these terminal substituent groups and the bridging conjugated polyene system between them, such molecules have high first-order hyperpolarizabilities, β [1–5]. The organic molecules can be either dissolved and embedded (hosted) in a solid polymer matrix or chemically tethered to the polymer chain. The molecules are highly polar, i.e. have large dipole moments, μ, and thus, by the application of a strong electrical field while the polymer is at a temperature above its second-order phase transition temperature, T_g, the optically nonlinear moieties can be aligned. Then, when the temperature is lowered below T_g; the molecules are locked into this anisotropic spatial arrangement and the bulk material exhibits a second order nonlinear susceptibility, $\chi^{(2)}$, by virtue of the ensemble of aligned hyperpolarizable molecules. It is the product of these molecular electronic properties, μ and β, that provides a measure of a molecule's merit as an electro-optic material.

Although not a sufficient condition, one property a molecule must possess for first-order hyperpolarizablity is a delocalized π-electron system such as that encountered in aromatics and/or conjugated polyenes. In addition, the electronic polarizability must be asymmetric [1–5] and therefore most hyperpolarizable molecules have significant charge transfer character. The electronic states of molecules with extensive charge separation can

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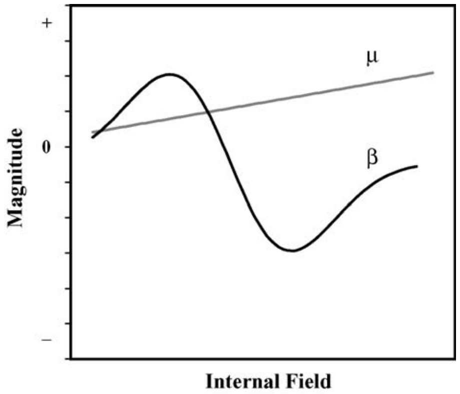
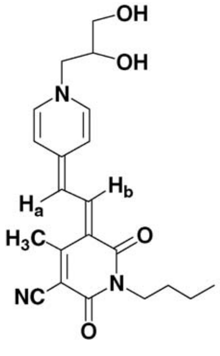


Fig. 1. Dependence of dipole moment, μ, and first-order hyperpolarizability, β, on the internal electric field in "push-pull" molecules.

be regarded as a mixture of both zwitterionic and non-charge-separated resonance forms. The dependence of β on the degree of charge separation, i.e. the contribution made by the zwitterionic resonance form to the electronic structure [6,7] of the π-electron system bridging the donor and acceptor groups, is represented graphically in Fig. 1. Inspection of the diagram shows that for these "push-pull" molecules, $|\beta|$ passes through maxima at two values of the internal electric field, i.e. one on the left-hand side, LHS, and the other on the right-hand side, RHS of the diagram. Given that the figure of merit of a molecule in terms of its bulk nonlinear susceptibility is related to the scalar product, $|\mu{\cdot}\beta|$ [1], highly dipolar, "RHS" molecules are excellent candidates on which to base the design of organic electro-optic materials/devices [7–9].

Many electro-optic modulators make use of the thin film Mach-Zehnder interferometer architecture. The voltage required to drive these modulators is inversely dependent on the electro-optic coefficient, r_{33}, of the material, which is directly proportional to $\mu{\cdot}\beta$ and the number density of the nonlinear chromophores in the polymer matrix. For a desirably small drive voltage of <1 V, r_{33} must be greater than approximately 50 pm V^{-1}. To realize this level of drive voltage with the values of $\mu{\cdot}\beta$ attainable with conjugated organic molecules, the requisite molecular number density must be $\sim 10^{20}$ molecules cm^{-3} [10]. At these very high chromophore concentrations, the solubility of optically nonlinear molecules in the matrix is a major practical issue and, in the case of highly polar RHS molecules, electrostatic interactions with attendant molecular aggregation will compromise the electro-optic effect [10–13]. In recognition of the impact of this behavior on the utility of these molecules as electro-optic device materials, the molecular aggregation of two RHS merocyanine molecules with structures I and II that have been synthesized in this laboratory was examined in solution; in a glassy solvent at temperatures extending down to 80 K and in ambient temperature in polyurethane film. The molecules have large hyperpolarizabilities measured previously in dilute solutions: -61×10^{-30} esu for compound I [12] and -125×10^{-30} esu for compound II [14] (Graph 1).

Another photophysical phenomenon that can affect the magnitude of the first-order hyperpolarizability of these merocyanines is *cis–trans* isomerization about double bonds and/or rotation about the single bonds within the conjugated bridging system between the electron donor and acceptor groups. Twisting about any of these bonds disrupts the alternating single/double bond conjugated system thereby preventing full π-electron delocalization and concomitant electronic decoupling of the resulting non-coplanar terminal donor–acceptor groups [15,16]. In addition, as the bonds twist, charge separation occurs that impacts on the overall dipole of the molecule [16–20]. This phenomenon was evident as dual fluorescence exhibited by the two merocyanine molecules studied in this work.



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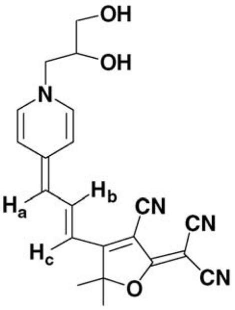

II

Graph 1. Chemical structures.

2. Experimental

2.1. Materials

The syntheses of the two hyperpolarizable merocyanines studied in this work have been described previously [12,14]. They were purified by repeated recrystallization from isopropanol using a Bolton extraction technique and then dried under vacuum. The *N*-dihydroxypropyl substituent on the electron donor pyridinylidene moiety enables the molecules to be tethered within the backbone of a polyurethane, for example, via a condensation with monomeric toluene diisocyanate (∼85:15 mixture of the 2,4 and 2,6 isomers) to give a 1:1 merocyanine–urethane polymer. The 1:1 stoichiometries of the merocyanine-containing polymers were indicated by the appropriate integrals of the proton resonances associated with the merocyanine and the diisocyanate-derived moieties observed in the NMR spectra of the polymers in dimethylsulfoxide, d_6 DMSO, solutions. The resonances attributable to merocyanine I, for example, were the pyridylidene/olefinic interconnect protons, appearing as two discrete, broad multiplets with the same chemical shifts as those of the pure chromophore [δ 8.36 (d, *J* 6.9 Hz, 2H) and δ 7.8 (d, *J* 6.9 Hz, 2H and two overlapping doublets, with only one, *J* 15.0 Hz, assignable)]. Those attributable to the toluene diisocyanate-derived moiety [2,6-:2,4-] were the amide and aromatic protons with broad signals at δ 7.1, 9.0 and 9.7, the latter resonance being exchangeable in D_2O indicating it to be the NH proton.

The solvents were Sigma–Aldrich, highest commercially available grade DMSO, ethanol and methanol and were used as supplied.

2.2. Methods

Thin, optical-quality films of the polymers containing the merocyanines were spun from 0.45 μm filtered DMSO solution onto 25 mm × 25 mm microscope slides to a thickness of approximately 1 μm and the films were heated to 90 °C overnight to remove any residual solvent.

Solutions of the merocyanines were prepared in 9:1 ethanol–methanol mixed solvent or in DMSO at concentrations of $\sim 10^{-5}$ mol L^{-1} to give optical densities of ∼0.8 in a 10 mm cuvette at their absorption maxima of 500 nm for compound I and 575 nm for compound II. The loadings (concentrations) of merocyanines in 1 μm thin films were ∼4 orders greater than in the fluid solutions, i.e. 10^{-1} mol L^{-1} compared to 10^{-5} mol L^{-1}.

The absorption spectra of the merocyanines in the different solvents/matrices were determined using a Hewlett-Packard 8451A diode array or Cary 50B10 UV–vis spectrophotometer. Their fluorescence emission spectra were determined using a Hitachi F-3010 spectrofluorimeter fitted with a red-enhanced Hamamatsu R928 photomultiplier tube.

The temperature dependence of the merocyanine fluorescence spectra was determined in 9:1 ethanol–methanol mixed solvent at a concentration of 1×10^{-5} mol L^{-1} from 295 K to 80 K using an Oxford Instruments DN1704 temperature-controlled, optical sample cryostat. This mixed alcohol solvent was chosen because it forms a glassy matrix at low temperatures. The samples were allowed to thermally equilibrate at each temperature for approximately 30 min before each measurement.

The room temperature absorption and fluorescence spectra of successively purified samples of both the merocyanines are identical. This demonstrates that the spectral features determined for the compounds in solution are not associated with adventitious impurities or unchanged starting materials.

3. Results

3.1. Absorption spectra

In 9:1 ethanol–methanol at concentrations of $\sim 1 \times 10^{-5}$ mol L^{-1} the absorption spectrum of merocyanine I from 300 nm to 700 nm displays a strong absorption band with a maximum at 500 nm (see Fig. 2a). This shifts to 510 nm in DMSO (spectrum not shown), a solvent with a lower solvating power, E_T (30), than ethanol–methanol [20]. Similarly, the maximum in the absorption spectrum of merocyanine II red-shifts from 575 nm in ethanol–methanol (Fig. 2a) to 580 nm in DMSO (spectrum not shown). Both compounds also exhibit weaker absorption bands with maxima at 330–350 nm and extinction coefficients of 0.15 and 0.22 times those of the main bands for compounds I and II, respectively. The positions of these short wavelength absorption bands are the same in DMSO and in alcohol, i.e. insensitive to solvent polarity. At somewhat higher concentrations in the region of 5×10^{-4} mol L^{-1} in fluid solution, a shoulder on the short wavelength side of the main band is apparent. Similarly, when the merocyanines are tethered to the polymer at a 1:1 ratio giving very high chromophore loadings of ∼0.1 mol L^{-1}, the thin film spectra display absorption maxima at 515 nm and 580 nm with shoulders at ∼480 nm and ∼540 nm for I and II respectively as shown in Fig. 2b. The high energy transitions of the merocyanines are obscured by the polymer absorption at wavelengths less than 400 nm, and therefore this spectral region is not shown in the figure.

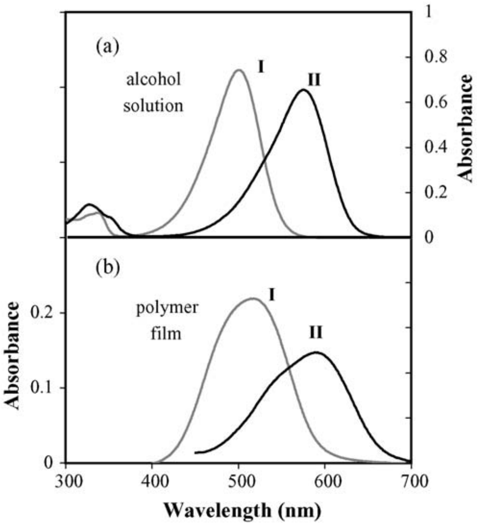

Fig. 2. The absorption spectra of compound I and II in (a) 9:1 ethanol–methanol solvent and (b) polymer film.

3.2. Fluorescence spectra

The emission spectra of dilute solutions of compounds I and II in 9:1 ethanol–methanol solvent at room temperature excited at 340 nm are presented in Fig. 3. The strongest emission bands have maxima at 565 nm and 640 nm, respectively. Identical spectral distributions were observed when exciting in the main absorption bands at 500 nm and 550 nm, respectively. Significantly weaker fluorescence emission with a maximum at 410 nm is apparent from both molecules. The ratios of the flu-

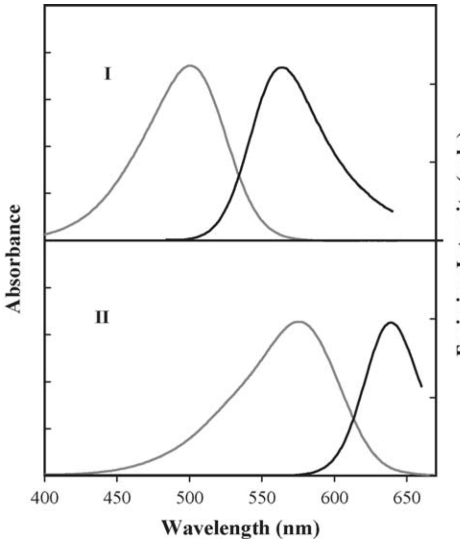

Fig. 3. The normalized fluorescence and absorption spectra of dilute solutions of compounds I and II in 9:1 ethanol–methanol solvent.

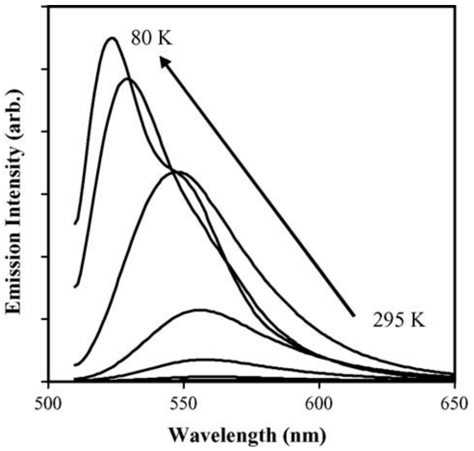

Fig. 4. The fluorescence spectra of compound I in 9:1 ethanol–methanol solvent at temperatures from 295 K to 80 K.

orescence yields of the short to long wavelength emission of compounds I and II are 1:25 and 1:200, respectively.

As the temperature of the ethanol–methanol solutions are lowered, the fluorescence yields of the main fluorescence bands increase and the maxima shift to progressively shorter wavelength as shown in Figs. 4 and 5. The spectral distributions also change; at 80 K a shoulder on the long wavelength side is apparent at 550 nm for I while for II the shoulder is at 630 nm and the maximum at 600 nm. The yield of fluorescence in the short wavelength band, maximum 410 nm, also increases with decreasing temperature though no significant spectral shift occurs in this band.

The fluorescence spectral distribution of both compounds at 300 K at high concentration in the thin polyurethane films is in striking contrast to that in dilute solutions. In solid films the emission from both merocyanines I and II excited in the short wavelength absorption band at 320–350 nm is dominated by emission with maxima at 395 nm and 380 nm, respectively, as shown in Fig. 6. Both compounds I and II exhibit some long wavelength emission with maxima at 600 nm and 715 nm, respectively. These positions are substantially red-shifted relative to the ambient temperature emission in dilute fluid solution. This emission is 2.5–3 times weaker than the short wavelength band; a reversal of the trend in the relative yields of the two bands encountered in dilute fluid solution.

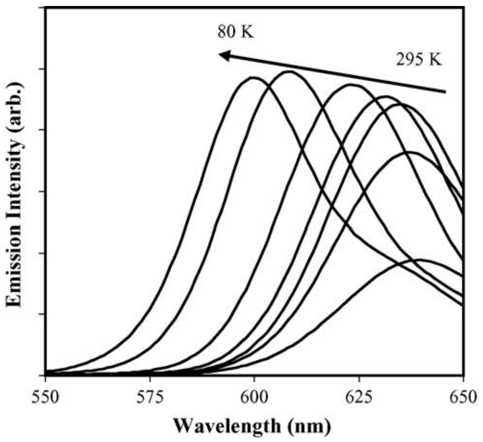

Fig. 5. The fluorescence spectra of compound II in 9:1 ethanol–methanol solvent at temperatures from 295 K to 80 K.

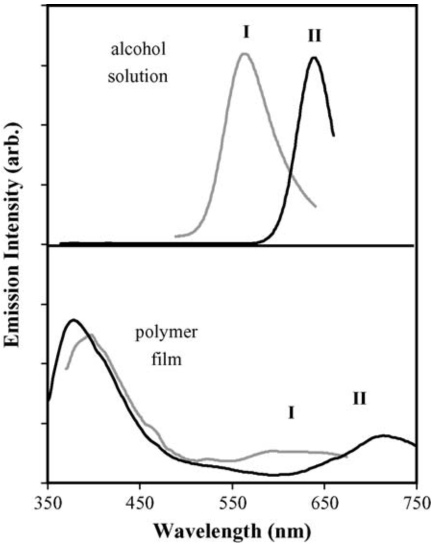

Fig. 6. The fluorescence spectra of compounds I and II in 9:1 ethanol–methanol solvent and in polymer film, excited at 320–350 nm.

4. Discussion

4.1. Ambient temperature absorption and fluorescence spectra

Würthner et al. have published a number of studies of the absorption spectra of “push-pull” merocyanines in fluid solutions [11,12,22–26]. The blue shifts they observed in the absorption spectra at higher concentrations and/or in poorer solvents relative to that in dilute solution are indicative of the formation of H-dimers according to the excitonic coupling model [27]. In such dimers, the individual molecules associate in a stacked arrangement with the high dipole moments of these molecules stabilizing an antiparallel coupling geometry through coulombic interactions. However, there was no longer-wavelength shoulder indicative of J-aggregate formation where the molecules are associated in a “head to tail” arrangement.

Dimer formation, and the attendant exciton interactions of the transition dipole moments, splits the degeneracy of the isolated molecules and the consequence of this for fluorescence is a reduction in the energy of the lowest excited singlet state and a concomitant red-shift in the emission spectra [27].

In dilute (10^{-5} mol L^{-1}) solutions at ambient temperature, the absorption spectra of both merocyanines studied in this work show no evidence of either H-dimer (blue-shift) or J-dimer (red-shift) formation. Further, the fluorescence spectra associated with the lowest excited singlet states display mirror image relationships to the corresponding absorption bands with Stokes shifts of between 55 nm and 70 nm which are typical of fluorescence of dipolar, monomeric molecules in polar solvents [28,29]. The absorption spectral shift of both com-

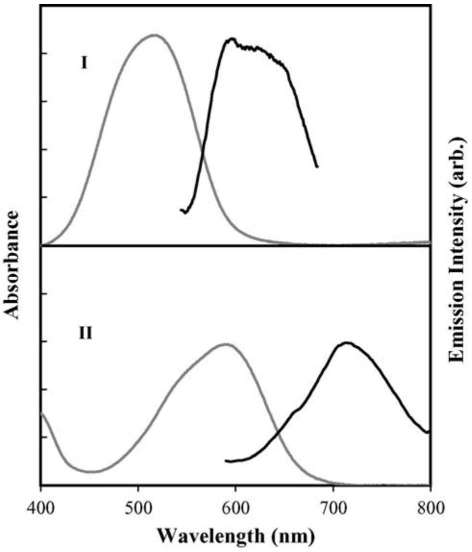

Fig. 7. The normalized absorption and fluorescence spectra of compounds I and II at high number densities in polymer film.

pounds towards shorter wavelengths in the 9:1 ethanol–methanol mixture (solvating power, $E_T(30) \sim 53$) relative to DMSO ($E_T(30) = 45$) [21] is indicative of the highly dipolar (zwitterionic) character of the ground states of these molecules and the differences between the dipole moments of the lowest excited singlet states and the ground states [22–26]. The mirror–image relationship between the absorption and fluorescence spectra contrasts with that of compounds I and II at very high concentrations in a polymer matrix (Fig. 7). The absorption spectra of merocyanine I and II in polymer films display minor shoulders at 480 nm and 540 nm, respectively, indicating the formation of dimers. However, the tendency for dimer formation was not as pronounced as that reported previously for merocyanines in several fluid solvents at lower concentrations [22] suggesting that tethering the merocyanines to the polymer is effective in holding them apart. There is some extension of the spectral distribution of the absorption band to longer wavelengths which suggests the presence of either some J-dimer formation or electronic interaction with the polymer chain. Pronounced emission is apparent at considerably longer wavelengths than the fluorescence originating from the monomer, Fig. 7, and this is attributed to emission from the lowest excited singlet state of the dimer, i.e. the lower energy level state resulting from exciton splitting. Emission with large Stokes shifts has been reported previously from “face to face” dimers of merocyanines [28].

A recent theoretical study has described and highlighted the consequences of merocyanine aggregation on the hyperpolarizability of these compounds. It also examined the impact of solvent dielectric by determining the extent and orientation of the aggregation [13].

4.2. *Effect of temperature on fluorescence*

When dilute solutions of merocyanines I and II in the 9:1 ethanol–methanol solvent are cooled, the fluorescence emission maxima shift to progressively shorter wavelengths, i.e. higher energy. This behavior is consistent with the reduction in the solvating power of the solvent with the increasing viscosity that accompanies a lowering of the temperature, hence restricting solvent dipole reorientation during the excited-state lifetime [30]. This dependence of spectral position on the polarity or solvating power of the matrix is indicative of a difference between the dipole moments of the ground and lowest excited states associated with these “RHS” molecules [29]. At the lowest temperatures investigated, i.e. less than ~100 K, second fluorescence bands for both compounds I and II appear at longer wavelengths than the main monomeric emission maxima. The appearance of these lower energy bands is ascribed to emission originating from dimers/aggregates (excimers).

4.3. *Dual fluorescence*

In all the matrix/solvent systems employed in this study, a short wavelength fluorescence band is observed that is the mirror image of the absorption spectrum corresponding to emission from an upper singlet state, S_2. For both molecules this absorption band is located in approximately the same spectral position and because the only moiety common to these molecules is the 1,4-dihydroxypyridinylidene nucleus, the short wavelength absorption/fluorescence is assigned to this part of the molecules. This is consistent with departures from a planar geometry of the ground state molecule by twisting about the conjugated bond, π-electron system bridging the donor and acceptor [15,16] that reduce the overlap between the localized p orbitals on adjacent C atoms. Such an impediment to π-electron delocalization causes a diminution of the coupling between the donor and acceptor groups and therefore, the effect of a non-planar molecular configuration is to introduce some 1,4-dihydroxpyridinylidene zeroth-order character into the ground-state wavefunction. One factor that favors twisting within the bridge will be the relief it provides from the steric interaction/interference between the central olefinic hydrogen atom, H_a, or the vinylidene hydrogen atom, H_b, and the *o*-methyl or cyano substituents on the acceptor groups of merocyanines I and II, respectively (see structures I and II). At least in the case of merocyanine II, such an interaction is evident from the through-space interactions and the chemical shifts in the NMR spectrum [14]. In addition, twisting about the bonds of the bridge results in a redistribution of intramolecular charge and therefore various twisted configurations will be stabilized or destabilized to different extents by coulombic interactions with the immediate molecular environment/dielectric.

In these molecules, traversing the reaction coordinate from the Franck-Condon vibrational level of the upper excited state, S_2, to the lowest excited singlet state, S_1, requires elongation (weakening) of the double bond in the donor–acceptor bridge followed by twisting of the bridge system to effect the internal conversion to S_1. This transition is accompanied by a very substantial intramolecular redistribution of charge [15–20]. Therefore, not only must the energy barriers associated with intramolecular translational and rotational diffusion be surmounted, substantial reorganization of the surrounding dielectric medium must occur to accommodate the changes in charge distribution that attend the internal conversion, $S_2 \rightarrow S_1$.

The activation energies for such electron transfers are proportional to $(\lambda + \Delta G^\circ)^2$, where ΔG° is the standard free energy change of the process and λ is the reorganization energy associated with the movement and reorientation of polar solvent molecules surrounding the charge-separated solute entity [31]. Because of the parabolic dependence of the activation energy on $(\lambda + \Delta G^\circ)$, even though ΔG° may be negative, if the reorganization energy is sufficient, i.e. $-\Delta G^\circ > \lambda$, the kinetics is consigned to the "Marcus inverted region" with a reduction in the rate of electron transfer from the donor to the acceptor as ΔG° becomes more negative [31]. Because λ depends on the microviscosity of the solvent/matrix, in a semi-rigid environment it may be sufficiently high that the rate of the $S_2 \rightarrow S_1$ transition is reduced to such an extent that radiative relaxation (fluorescence) directly from S_2 to the ground state competes with internal conversion and subsequent emission from S_1. For compounds I and II in the polymer matrix, it is proposed that λ is so large that it is responsible for the fluorescence from S_2 (maxima at 380–395 nm) being more intense than the usual, longer wavelength fluorescence from the S_1 state.

5. Conclusions

Most "push-pull" merocyanines exhibit a high degree of asymmetric polarizability making them candidates for use in nonlinear optical materials and applications. However, this attribute is partially negated by dimerization in an antiparallel arrangement (H-dimer) at the high concentrations required for utilization in electro-optic devices. This is, at least in part, because the first-order hyperpolarizability tensors of the merocyanine molecules are opposed in this dimer configuration. Further, a recent theoretical study has described the significant changes to the hyperpolarizabilty of these compounds caused by aggregation as a result of absorption spectral shifts away from, or towards, resonance as well as changes to the transition dipole moments [13]. The fluorescence spectra of merocyanines I and II studied in this work corroborated the absorption spectral evidence for H-dimer formation for a number of merocyanines reported previously [11,12,22–26]. However, when compounds I and II were incorporated into a polyurethane matrix at high concentrations, the tendency for H-dimer formation was not as pronounced as that reported previously for merocyanines in fluid solvents [23]. It is concluded that the polymeric matrix exerts some spacer effect that holds the solute merocyanine molecules apart.

When merocyanines I and II are excited into one of their upper singlet states, direct radiative relaxation (fluorescence) to their ground states competes with internal conversion to their lowest excited singlet states. It is proposed that the large change in the transition dipole moment between the states which is attended by substantial reorganization energy of the surrounding dielectric medium contributes to this atypical photophysical behavior.

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