J. Phys. Chem. A **2006,** *110,* 8963−8969

Effect of Conjugation Path Length on Quadratic Nonlinear Optical Properties of Monomer and Aggregates of Zwitterionic Merocyanine Dyes

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Received: February 23, 2006; In Final Form: May 24, 2006

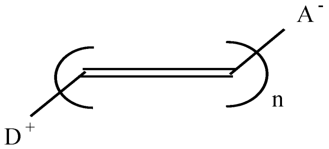
We present a quantum-chemical analysis of the conjugation path length effect on first hyperpolarizabilities of a series of zwitterionic merocyanine dyes whose synthesis has been reported earlier (*J. Am. Chem. Soc.* **2002**, *124*, 9431, *J. Am. Chem. Soc.* **1997**, *119*, 3144). The effect of the conjugation path lengths is evaluated to demonstrate the engineering guidelines for enhancing molecular optical nonlinearity. The first hyperpolarizabilities are calculated for extended conjugated monomer and H and J type aggregates of merocyanine dyes, to provide insight into the intermolecular interactions and the relationship between structural and collective nonlinear optical properties. The molecular geometries for monomers are obtained via B3LYP/6-31G(d,p) level optimization including the SCRF/PCM approach, and the dynamic nonlinear optical (NLO) properties for monomer and aggregates are calculated with the ZINDO/CV method, including solvent effects. It is found that the chain length dependence of the first nonlinearity peaks at $n = 6$ and then it starts changing slowly for monomer and aggregates of zwitterionic merocyanine dyes. It is concluded that an excellent NLO response in solution might vanish when the active chromophore forms higher H aggregates. The importance of our results on the design of electrooptic materials has been discussed.

Introduction

In recent years an intense worldwide effort has been focused on the research of design and development of organic conjugated materials with large optical nonlinearities due to their potential applications in various optical devices.[1−5] A large number of organic π-conjugated molecules have been investigated[1−8] in the last twenty years. The outcome of the results has helped to establish certain guidelines for molecular design to get good second-order nonlinear optical (NLO) materials. However, roughly more than 80% of all π-conjugated organic molecules crystallize in centrosymmetric space groups, therefore producing materials with no second-order bulk susceptibility $\chi(2)$. To overcome this problem, ionic and zwitterionic organic chromophores are considered to be an important class of materials for application in second-order NLO.[5−12]

In polar solvents merocyanines have zwitterionic structure in the ground state, containing two oppositely charged heteroaromatic rings (Chart 1) linked directly or linked through a vinyl unit and have been reported as second-order NLO chromophore theoretically and experimentally by Abe et al.[13−15] Lambert et al.[16] have studied a new family of zwitterionic NLO chromophores in which a polyene bridge is capped by phenyl rings substituted by NR_3^+ in one end and at the other end by BR_3^-. Abbotto et al.[17,18] have reported the synthesis and NLO properties of a series of novel zwitterionic chromophores. Their measured $\mu\beta$ values are negative and some of the highest values reported till now in the literature. Zwitterionic merocyanine dyes are very interesting especially for electrooptic applications due to the large nonlinear optical susceptibilities and the good alignment of the chromophores in the cocrystals.[12] Merocyanine dyes can switch from zwitterionic to quinoid character in the ground state (Chart 1) with solvent polarity. Recently[23,24] we have demonstrated that solvents play a remarkable role on the structure and first hyperpolarizabilities of zwitterionic dyes. Changing the solvent from low to high dielectric causes not only an increase in magnitude of β but also a change in sign, therefore passing through zero at intermediate dielectric. Bublitz et al.[25] have has already shown experimentally (using electric field induced second harmonic generation) that one can change the sign of β for donor/acceptor polyenes, from positive to negative by changing the solvents.

CHART 1: Schematic Diagram of Extended Conjugated Merocynine Dyes Used in This Manuscript[a]

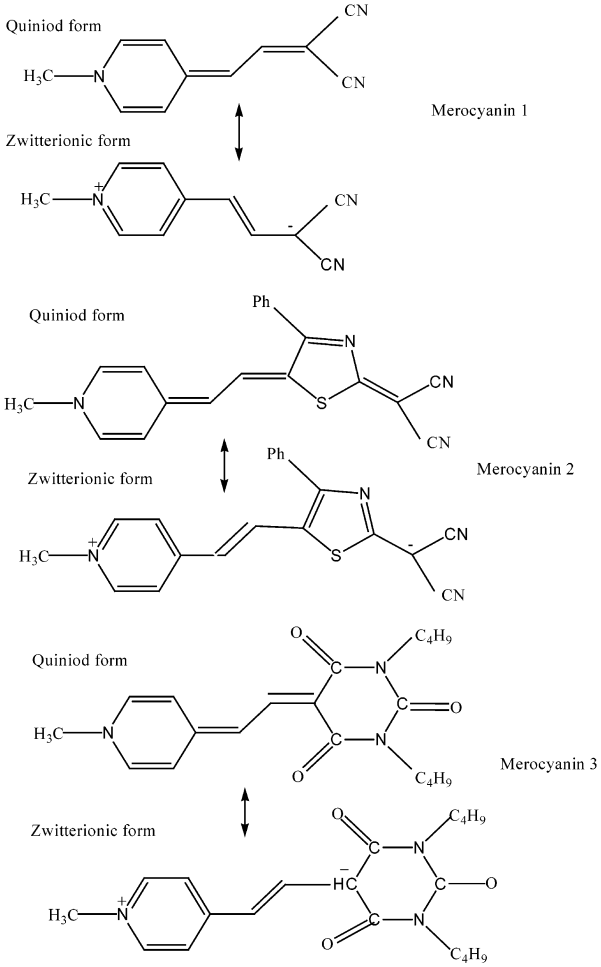


[a] n Denotes Number of Double Bonds.

For device applications, the chromophore must be present in high concentration (>5% by mass) in the polymer, where interchromophore interactions can modify their properties substantially. In the process of device development, materials based on well-designed chromophores having large dipole moments and excellent molecular hyperpolarizabilities often failed to provide the expected electrooptic response.[26,27] The intermolecular interactions are sufficiently strong enough to change the optical properties of the aggregates significantly compared with those of the corresponding monomer. Many aggregates contain a large number of randomly or semirandomly positioned monomers encompassing a wide variety of different local interaction geometries, which makes it challenging to understand the details of the role intermolecular interaction for the predicting of linear and nonlinear optical properties of the aggregates. Recently we have reported[24,28] that the first hyperpolarizability changes tremendously as the monomer undergoes aggregation and the magnitude of first hyperpolarizabilities are highly dependent on the nature of the aggregates.

10.1021/jp061176b CCC: $33.50

SCHEME 1: Structures of Merocyanine Monomers Used in This Manuscript



To understand the effect of conjugation path length and solvent polarity on the NLO properties of the zwitterionic molecules, in this paper, we report a systematic study of the structure of a series of merocyanine dyes (Chart 1 and Scheme 1) using density functional theoretical (DFT)[29,30] calculations with a fairly extensive basis set (6-31G**) and the dynamic NLO properties using the ZINDO/CV approach[24,28,31−33] including solvent effect. In this manuscript, we also present the dynamic first hyperpolarizabilities of merocyanine aggregates aiming to investigate the intermolecular interactions and understanding the relationship between structural and collective optical properties. The primary reasons for the choice of merocyanine aggregates are as follows: (1) Merocyanine dyes are reported[34] to form only H aggregates in dioxane solvent even at 1 μM concentration and J aggregates have been shown to form when merocyanine dyes are incorporated in Langmuir Blodgett films.[35] Measurement of first hyperpolarizabilities of J and H aggregate separately for merocyanine dyes using hyper-Rayleigh scattering[36,37] method are highly visible. (2) Due to the tunability of the π-system of merocyanines from weakly dipolar (polyene-like) to highly dipolar (zwitterionic) chromophores, merocyanines are identified as the most promising chromophores for NLO applications.[38,39] To design NLO devices, one must not only find simple molecules having large hyperpolarizabilities but also combine these molecules to form noncentrosymmetric macroscopic structures. This cannot be done without understanding the intermolecular interactions between these merocyanine chromophores. To understand how the solvent polarity affects the structure of the zwitterionic dyes we have used self-consistent reaction field (SCRF) approach with polarizable continium model (PCM),[40,41] as implemented in Gaussian 03.[42] Recently Cammi[20] et al. and others[21,22,43,44] have used polarizable continuum model to calculate the solvent effects on the hyperpolarizabilities of different chromophores. They have shown that the PCM model allows obtaining complex NLO properties that can be directly compared with the outcome of the experimental measurements. To account for both solvent and dispersion effects, we have adapted the ZINDO/CV technique with SCRF method for the calculation of dynamic β's.

Computational Method

All the molecules reported in this paper have been fully optimized with the density functional theory (DFT) B3LYP methodwith the 6-31G** basis set using the Gaussian 03 program. Synthesis of all the merocyanine dyes investigated in this work has been reported before by Wurthner et. al.[34] It is now well-known that the solvent polarity exerts an important influence on the structure as well as the first NLO coefficients in neutral and ionic molecules.[1−8] To explicitly take into account the solvent polarity effects, we have adapted SCRF approach with the polarizable continuum model (PCM)[40,41] as implemented in Gaussian 03. The PCM model is one of the most frequently used continuum solvation methods and has seen numerous variations over the years. The radius of the molecular-shape cavity used for this DFT/PCM calculation was determined from the molecular length + van der Waals radius of the outermost atoms.

To calculate dynamic β values, we have adapted the ZINDO/CV technique combined with SCRF method. The primary code for the ZINDO algorithm was developed by Zerner and coworkers,[45] whereas the ZINDO/SOS technique has been extensively used by several authors to compute β for different molecules.[31−33,46,47] Recently, the ZINDO methods have been combined with the correction vector techniques (CV) to obtain dynamic NLO coefficients in which the sum over all the eigenstates of the chosen configuration interaction (CI) Hamiltonian is exactly included.[31−33] We have used this technique to calculate β for the ionic and neutral weak organic acids[32] and the theoretical values match very well with the experimental data obtained via the HRS technique. To reliably estimate the NLO properties, excited-state energies, state dipoles, and transition dipole moments we have used a multireference double CI (MRDCI) formalism, where single and all higher (double, triple and quadruple) excitations have been incorporated. The MRDCI approach includes a larger part of electronic correlation and therefore is more appropriate to calculate the NLO response of conjugated molecules. Several publications[48−50] have reported that MRDCI provide excitation energies and dipole matrix elements which are comparable with experimental data, but unfortunately it is not size consistent and we can thus expect less accurate results compare to experimental values for aggregates. The self-consistent field determinant, the HOMO → LUMO, HOMO → LUMO+1, HOMO−1 → LUMO, HOMO−1 → LUMO+1, HOMO−2 → LUMO, HOMO → LUMO+2, singly excited determinants and the (HOMO, HOMO) → (LUMO, LUMO) doubly excited determinants have been taken care of as reference determinants in the MRDCI formalism. The choice is based on the finding that these transitions dominate for one- and two-photon allowed transition. For single excitation, the CI active space consists of 20 occupied and 20 unoccupied orbitals. For MRDCI we have used 4 reference determinants and for each reference determinant we

TABLE 1: Theoretical (T) and Experimental (E) Absorption Maximum (λ_{max}, in nm) for Monomer (M) and H Aggregates (D) for Marocyanines 1−3[a]

compound	λ^E_M	λ^T_M	λ^E_D	λ^T_D
1	494	478	448	433
2	671	686	554	571
3	515	528	476	488

[a] Experimental data have been taken from ref 34.

have used 5 occupied and 5 unoccupied molecular orbitals to construct a CI space with configuration dimension 1000−1100.

To test the validity of the theoretical methodology used in this work, we have calculated linear optical properties (λ_{max}) for monomer and H dimer. Table 1 shows good agreement between reported experimental values with MRDCI calculation values. Absorption spectra for higher aggregates are not known in the literature, and as a result, we cannot compare our theoretical results with experimental values. Similarly, due to unavailability of the literature data, we cannot compare the calculated β properties with the experimental values for the dimer, though it is known in the literature that ZINDO/MRDCI first hyperpolarizability data for monomer are comparable with experimental data. Because we see fairly good agreements between experimental and MRDCI absorption maxima (λ_{max}) for dimers, we believe that for higher aggregates, if direct comparison of theoretical results with experiment is not possible, this comparison can be used for experimental guidelines.

To account for the solvent polarity effect in the ZINDO/CV approach, we have used expanded self-consistent reaction field (SCRF) theory[19] where self-consistent solute/solvent interactions are described by dipolar and multipolar terms up to $l = 1-12$. The cavity radius, as used in this ZINDO/CV/SCRF calculation, was obtained from the Gaussian 03 code by calculating the molecular volume first, and then adding 0.5 Å to account for the nearest approach of the solvent molecules. The calculation involves the determination of molecular volume inside the cavity of electron density 0.001 electrons/bohr^3. We have increased the radius further by 0.5−1.5 Å and the results remain unchanged. Thus it could be assumed that the radius calculated through Gaussian is sufficient enough to encapsulate the molecule inside the cavity. To avoid dispersion effect, we have used a photon wavelength corresponding to 1907 nm for computing β tensors. Kanis et al. have shown[46,47] that ZINDO/SCRF can reproduce experimental results in donor−acceptor organic molecules reasonably well. In the above case, we first optimized the geometry at the DFT/PCM level in the presence of appropriate dielectric for different solvents using the Gaussian-03 package. The optimized DFT level geometry is then used as an input for ZINDO/SCRF/CV calculation at a photon wavelength corresponding to 1907 nm.

Results and Discussion

Our results indicate that the structure of all merocyanine monomers are dramatically affected by the polarity of the surrounding media (as shown in Figure 1), they are predominantly quinoid in the gas phase, and the zwitterionic character is strongly predominant in good polar solvents. An intermediate situation has been found for less polar solvents, such as chloroform. We have reported a similar trend for different series of merocyanine dyes.[23]

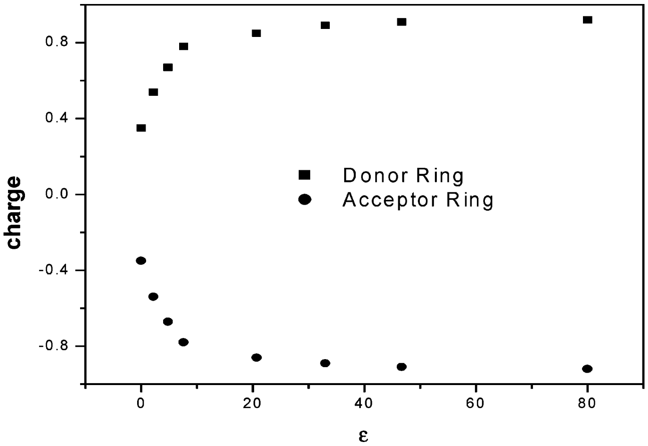


Figure 1. Plot of charge distribution vs ϵ for merocyanine **3** (ring 1 is the pyridine ring and ring 2 is the styryl ring).

TABLE 2: First Hyperpolarizabilities (in 10^{-30} esu) of Merocyanine Monomers in Different Solvents

ϵ	β^{M1}	β^{M2}	β^{M3}
1	170	210	158
1.43	200	250	190
1.92	215	260	200
2.02	234	270	205
2.22	240	280	210
4.33	360	380	280
4.9	−220	−302	−185
5.62	−380	−480	−220
7.58	−480	−640	−260
8.93	−450	−620	−280
10.36	−410	−560	−320
20.7	−380	−502	−290
24.55	−340	−480	−250
32.63	−298	−388	−220
36.84	−280	−350	−210
46.7	−265	−320	−200
78.39	−245	−301	−185

Computed β values are listed in Table 2. We find that the solvent effects are really impressive for merocyanine monomers. First-order NLO responses are low and positive in the gas phase and then increase slowly with solvent polarity. Then it started to decrease with the solvent polarity. The β values remain negative in all the polar solvents and have the highest values at a moderate ϵ (6−8) and then again decrease slowly with the increase of ϵ. This behavior is mainly due to the change of the structure from quinoid to zwitterionic form. Once it is in mostly zwitterionic form, β values decrease with the increase of solvent polarity. An excellent NLO response in solution might vanish when the active chromophore is dispersed in a matrix with suitable ϵ. The commonly established procedure for the NLO compound to report β values in one solvent may in certain cases be insufficient to draw definite conclusions on the overall chromophore performance and the prospect for different design strategies.

To understand the origin of the remarkable solvent effects in zwitterionic molecules, we calculated the change in dipole moment between ground and charge-transfer excited state ($\Delta\mu_{eg}$). According to the two-state model,[51]

$$\beta^{\text{two state}} = \underset{\text{static factor}}{\frac{3\mu_{eg}{}^2\Delta\mu_{eg}}{E_{eg}{}^2}} \; \underset{\text{dispersion factor}}{\frac{\omega_{eg}{}^2}{(1-4\omega^2/\omega_{eg}{}^2)(\omega_{eg}{}^2-\omega^2)}} \qquad (1)$$

where μ_{eg} is the transition dipole moment between the ground state $|g\rangle$ and the charge-transfer excited state $|e\rangle$, $\Delta\mu_{eg}$ is the difference in dipole moment and E_{eg} is the transition energy. Because $\mu_{eg}{}^2$ and $E_{eg}{}^2$ cannot be negative, β will be negative only if $\Delta\mu_{eg}$ is negative. Table 3 lists the $\Delta\mu_{eg}$ vales for compounds **1**−**3** in different mediums. This confirms that $\Delta\mu_{eg}$

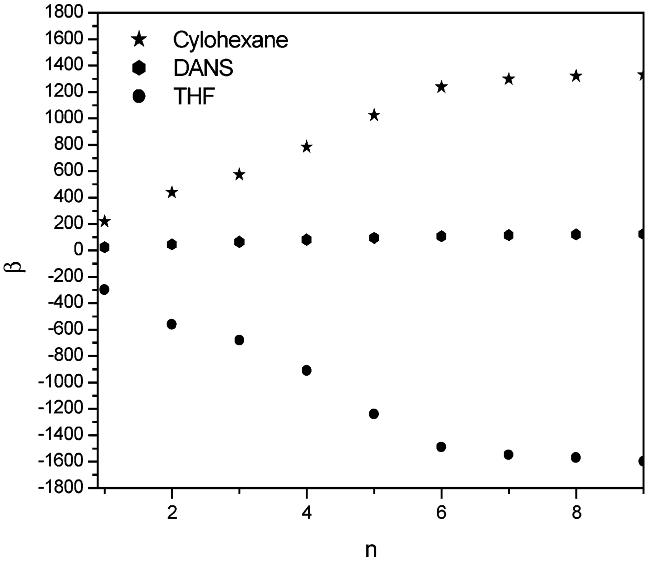


Figure 2. Plot of β (in 10^{-30} esu) vs *n* for compound **2** in cyclohexane and THF solvents and DANS in THF solvent.

TABLE 3: Change of Permanent Dipole Moments ($\Delta\mu_{eg}$) (in Debye) of Merocyanine Monomers in Different Solvents

ϵ	$\Delta\mu_{eg}^{M1}$	$\Delta\mu_{eg}^{M2}$	$\Delta\mu_{eg}^{M3}$
1	8	8.7	9
1.43	8.8	8.9	9.7
1.92	9	9	9.9
2.02	9.1	9.2	10
2.22	9.3	9.4	10.2
4.33	10.2	10.6	11.9
4.9	−7.6	−8.1	−8.8
5.62	−9.1	−9.4	−10.1
7.58	−11.8	−12.5	−13.1
8.93	−11.1	−12.2	−13
10.36	−10.9	−11.9	−12.6
20.7	−10.6	−11.6	−12.4
24.55	−10.4	−11.1	−12
32.63	−10.2	−10.8	−11.8
36.84	−9.9	−10.5	−11.7
46.7	−9.7	−10.4	−11.6
78.39	−9.1	−9.8	−10.4

could be the main factor for the remarkable solvent effect on the first hyperpolarizabilities of the zwitterionic molecules.

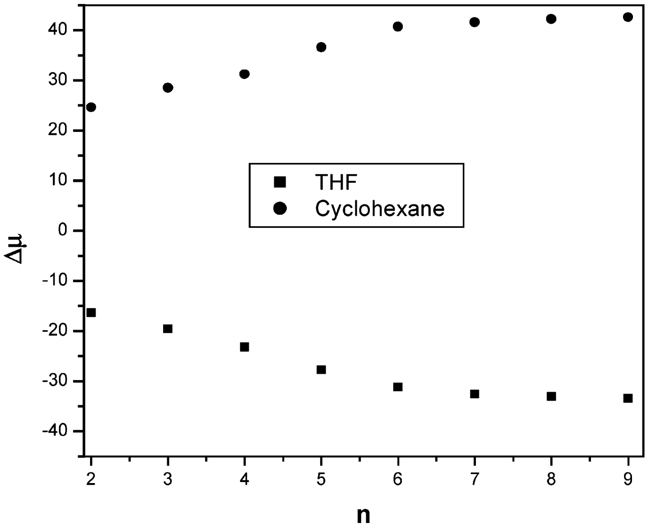
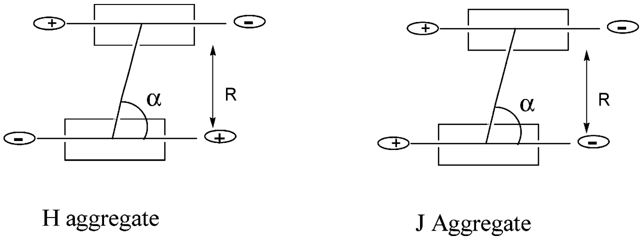


Figure 3. Plot of $\Delta\mu$ (in Debye) vs *n* for compound **2** in cyclohexane and THF solvents and DANS in THF solvent.

SCHEME 2: Model Structure of J and H Dimers of Merocyanines, Where R Is the Distance between Two Monomer Centers and α Is the Slip Angle



Elongation of the conjugation pathway is one of the primary design steps for increasing β values of neutral organic molecules, and several studies have been performed in this direction.[1−4] But only very recently[16] has investigation been started for the study of first hyperpolarizabilities of zwitterionic molecules in that direction. The elongation effect of the conjugation path length is established here to demonstrate the engineering guidelines for enhancing molecular optical nonlinearities. We have computed β's for conjugated zwitterions by extending *n* (number of conjugated double bonds between donor and acceptor groups as shown in Chart 1 and Scheme 1) from 1 to 9 for compound **2** in cyclohexane ($\epsilon = 2.02$) and THF ($\epsilon = 7.52$) solvents. β_{vec} vs *n* plots are shown in Figure 2. To compare with the neutral compounds, we also included β_{vec} for extended conjugated DANS (neutral) molecules in THF. The most interesting aspect of this plot is β_{vec} is negative in THF, whereas it is positive in cyclohexane. Our data indicate a significant increase in the first hyperpolarizability on elongation of the conjugation pathway. β increases 2 times as the number of conjugated double bonds increases from 1 to 2. The rates of increase of β_{vec} with *n* are much higher for zwitterionic molecules than for the corresponding neutral molecules. It is interesting to note that β for zwitterionic merocyanine dyes peaks at $n = 6$ and then it starts changing slowly. To understand the origin of negative β_{vec} in THF solvents and positive β_{vec} in cyclohexane, we have plotted $\Delta\mu_{eg}$ vs *n* as shown in Figure 3. $\Delta\mu_{eg}$ increases with *n* in both solvents but the main difference arises due to negative $\Delta\mu_{eg}$ in THF, whereas it is positive in cyclohexane. It is interesting to note that $\Delta\mu_{eg}$ for zwitterionic merocyanine dyes peaks at $n = 6$ and then it starts changing slowly. Figure 3 indicates that the $\Delta\mu_{eg}$ follow the same trend as we have noted for the β.

In the case of the dimer we have taken the optimized monomer structure as the optimized structure and we varied only intermolecular distance and the slip angle (the angle between the dipole direction and line connecting the two centers). The interaction between two monomers in the dimers may be understood using the excitonic coupling model[17,18] based on the point dipole approximation. According to this model, due to the dipolar interaction there will be a splitting of the excited energy levels in the magnitude of

$$\Delta E = 2\mu_{DM}^2/4\pi\epsilon_0 R^3(1 - 3\cos^2\alpha)\sin^3\alpha \qquad (2)$$

where μ_{DM} is the transition dipole-moment, *R* is the distance between two monomer centers as shown in Scheme 2 and α is the slip angle. To evaluate whether the excitonically coupled monomer model, is applicable for merocyanine dimers or not, that is, whether the electrons remain associated with a single monomer and orbital overlap between monomers can be neglected, we carried out ZINDO/CV calculation of the electronic transition energies, oscillator strength of the dimer for merocyanine **3**. We varied *R* from 3.5 Å to 8.5 Å without changing the monomer geometries. At large intermolecular

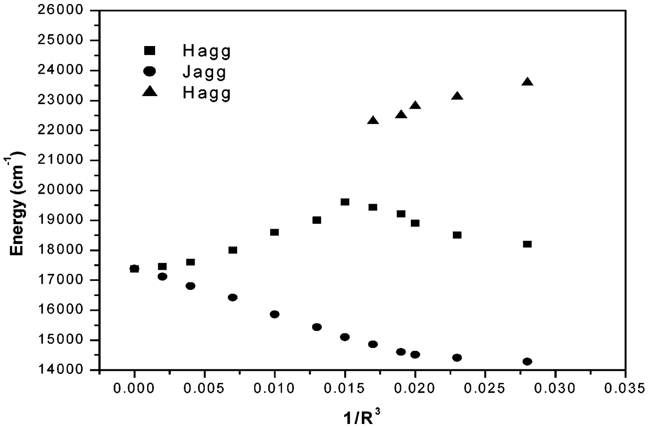


Figure 4. Energies of J and H dimers as a function of the inverse cube of separation (in Å) between the intermolecular planes.

separations, two nearly degenerate electronic transitions are found (as shown in Figure 4) and these are (1) a forbidden one corresponding to J transition and (2) a strongly allowed one corresponding to H transition. The next transition with significant oscillator strength is more than 18 900 cm^{-1} higher in energy. As the monomers are brought closer together, the splitting between the forbidden and allowed transitions increases rapidly while the oscillator strength remains nearly unchanged. At distances of 4.3 Å or less, however, the splitting between the two lowest transitions ceases to increase, and the oscillator strength of the H-band begins to decrease from $f = 3.6$ at $R \approx 4.4$ to $f = 2.1$ at 3.6 Å. The intensity lost from the H-band appears in a new transition shifted more than 2900 cm^{-1} to the blue. This indicates that an excitonically coupled monomer picture is reasonable for interplane separations greater than about 4.2 Å but breaks down for shorter distances. We cannot neglect totally the orbital overlap between two monomers at distances below 4.2 Å.

To calculate the first hyperpolarizabilities of H and J type-dimers (as shown in Scheme 2) in different solvents by the ZINDO/CV/SCRF method using solvent parameters and 1907 nm as the excitation source, we have used the monomer structure in different solvents as optimized structure and the monomers are separated by 4.45 Å. We have used a slit angle of 60° and the angle between the dipoles of 120° for H type-dimers as measured by 2D NMR.[34] In the case of the J-type dimer we have used same intermolecular separation and slit angle of 30°, as measured in LB films.[35] Computed β values in cyclohexane ($\epsilon = 2.02$) and THF ($\epsilon = 7.52$) solvents are shown in Figure 5. For a given chain length, the first hyperpolarizability of the J-type dimer is 1.3−1.7 times higher than that for the corresponding monomer, whereas β for the H-type dimer is 2.7−3.2 times lower than that for the corresponding monomer.

The origin of the change in hyperpolarizabilities of zwitterionic monomers to J- and H-type dimers can be explained using a two-state model. Our calculations indicate that in the case of J-type dimers, the increment of first hyperpolarizability is due to two factors and these are (1) the red shift of the absorption maxima brings it closer to the peak of the two-photon resonance wavelength and (2) $\Delta\mu_{eg}$ values are about 1.1−1.4 times that of the corresponding monomer. Similarly, in the case of the H-type dimer, due to the antiparallel dipoles, the hyperpolarizabilities are greatly reduced and this can be due to several factors including (1) the blue shift of absorption maximum and (2) $\Delta\mu_{eg}$ values being 2−3 times lower than the values for the corresponding monomer. Though in J aggregates the first hyperpolarizability increases by a factor of 1.3−1.7, β per molecule decreases about 0.65−0.85 times. Our calculations indicate that the electrostatic aggregation of merocyanine dyes is very important for the limiting performance of the EO properties at higher dye level loading.

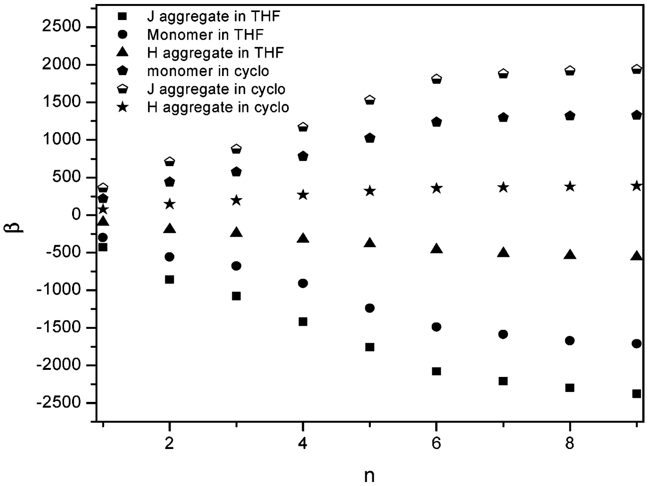


Figure 5. Plot of β (in 10^{-30} esu) vs n for monomer, J and H aggregates for compound **1** in cyclohexane and THF solvents.

The first-order NLO responses are always positive in cyclohexane and always negative in THF for a given n. The same picture is valid for compounds **1** and **3**. So there are clearly important consequences from this in the choice of molecular environment when NLO molecules of merocyanine aggregates are evaluated. The commonly established procedure for the NLO compound to report β values in one solvent may in certain cases be insufficient to draw definite conclusions on the overall chromophore performance and the prospect for different design strategies. It is interesting to note that β for zwitterionic merocyanine aggregates peaks at $n = 6$ and then it starts changing slowly. Our calculation indicates that the $\Delta\mu_{eg}$ values follow the same trend as we have noted for the β.

Dimers are only a first approximation to the aggregates present in real materials. In a real chromophore−polymer system at higher chromophore loading, the chromophore may exist in a wide range of forms including monomers, various types of dimers, higher aggregates and large nano- or microcrystalline states. Higher aggregates of highly dipolar push−pull chromophores are recognized to limit the performance of EO and other NLO effects that require loading of a higher concentration chromophore into a polymer. Here we have investigated the dynamic hyperpolarizabilities of extended conjugated higher aggregates at $\epsilon = 10.36$, using the ZINDO/CV/SCRF method and 1907 nm as the excitation source. In the case of higher aggregates, we have taken the DFT optimized monomer structure using a solvent dielectric constant of $\epsilon = 10.36$, as the optimized structure and the monomers are separated by 4.45 Å from each other. The slit angle was kept as 60° between two consecutive monomer for H-type aggregates and 30° for J-type aggregates. Figure 6 shows how the first hyperpolarizabilities change for higher aggregates with the path lengths for compound 1.

Our calculations indicate that the β values for J-type aggregates increase tremendously from −810 (for dimer) to −2640 for hexamer in the case of compound **1**, whereas the first hyperpolarizabilities decrease to −11 for the hexamer in the case of H-type aggregates. The same trend has been observed for compounds **2** and **3**. This can explain the recent observation of drastic change in first hyperpolarizabilities with concentration by Cross et al.[52] Cross et al.[52] have performed the EFISHG

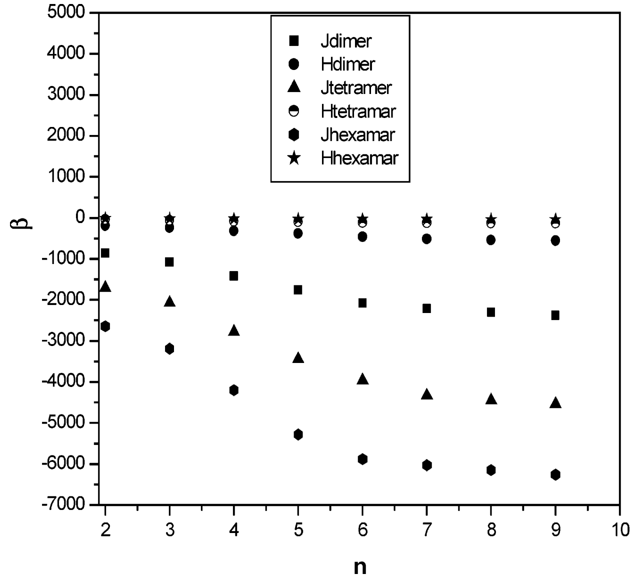


Figure 6. Plot of β (in 10^{-30} esu) vs n for dimer, tetramer and hexamer J and H aggregates for compound **1**.

experiment in the concentration range 10^{-3} to 10^{-1} M. Because merocyanine dyes are known to form H-type aggregates mainly in nonpolar solvents, with the increase in concentration from 10^{-3} to 10^{-1} M, one can expect the formation of higher H-type aggregates. Because the β values decrease tremendously with the increase in the number of monomers in the aggregates, one can expect the total β values to be near zero at higher concentrations. Our calculations indicate that for higher aggregates β peaks at $n = 5-6$ and then changes slowly.

Conclusion

In this paper, we have reported the first hyperpolarizabilities of monomer and aggregates of zwitterionic merocyanine chromophores. We have analyzed the effect of the conjugation path length on the β values for zwitterionic monomers and aggregates. It is found that the chain length dependence of the first nonlinearity peaks at $n = 6$ and then it changes slowly for zwitterionic merocyanine dyes. We have found that $\Delta\mu_{\mathrm{eg}}$ is largely responsible for the saturation behavior. We have demonstrated that the dynamic hyperpolarizabilities of J-type aggregates are several times higher than that of monomers and it is due to the fact that (1) the red shift of the absorption maxima brings it closer to the peak of the two-photon resonance wavelength and (2) $\Delta\mu_{\mathrm{eg}}$ values for dimers are about 1.1−1.4 times lower than that of corresponding monomer. However, the hyperpolarizability reduces tremendously for H-type of aggregates due to the antiparallel dipoles and this can be due fact that (1) the blue shift of the absorption maximum and (2) $\Delta\mu_{\mathrm{eg}}$ values for dimers are 2−3 times lower than those for the corresponding monomer. Our calculation indicates that β for zwitterionic aggregates peaks at $n = 6$ and then it changes slowly. We have found that $\Delta\mu_{\mathrm{eg}}$ values follow the same trend as we have noted for β. Our calculations indicate that if the monomer has a tendency to form H aggregates, the total β is near zero for higher aggregates, which implies that the EO properties can vanish at higher dye level loadings.

Acknowledgment. We thank the NSF-CREST grant HRD-0318519 and ONR grant no. N00014-03-1-116 for generous funding. We also thank the Mississippi Center for Super Computer Resource (MCSR), University of Mississippi, Oxford, MS, for the generous use of their computational facilities. P.B. thanks the C.R.I center of Le Mans university for the access to linux computer for connection from France to the MCSR Center and in particular F. Calvayrac, P. Delage and S. Bourdais. We also thank reviewers whose valuable suggestion improved the quality of the manuscript.

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