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Self-Aggregation and Optical Absorption of Stilbazolium Merocyanine in Chloroform

Daniel L. Silva,*[,†,‡] N. Arul Murugan,[§] Jacob Kongsted,[∥] Hans Ågren,[§] and Sylvio Canuto[†]

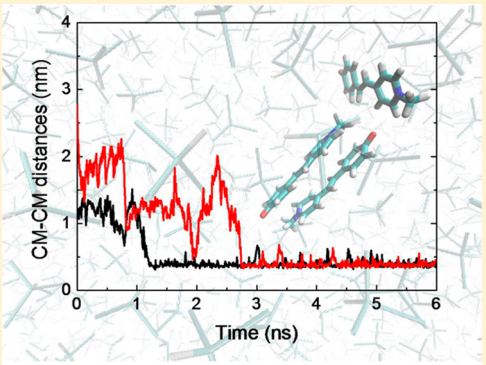
[†]Instituto de Física, Universidade de São Paulo, Caixa Postal 66318, 05314-970 São Paulo, SP, Brazil

[‡]Departamento de Ciências da Natureza, Matemática e Educação, Universidade Federal de São Carlos, Rod. Anhanguera – Km 174, 13600-970 Araras, SP, Brazil

[§]Department of Theoretical Chemistry and Biology, School of Biotechnology, Royal Institute of Technology, SE-106 91 Stockholm, Sweden

[∥]Department of Physics, Chemistry and Pharmacy, University of Southern Denmark, Campusvej 55, DK-5230 Odense M, Denmark

ABSTRACT: Dipolar aggregation is in many cases detrimental for the functioning of optical materials. In this study we investigate self-aggregation and optical absorption of stilbazolium merocyanine (SM) in chloroform solution by performing classical Molecular Dynamics (MD) simulations under ambient conditions. The reversal solvatochromic shift, the large bathochromic shift, and the structured absorption band presented by SM in chloroform solution are all aspects of its optical absorption behavior for which the existence of self-aggregation is yet not completely understood. Moreover, the spectroscopic properties of SM oligomers and their occurrence in solvent of low polarity remain a relevant topic that deserves to be investigated. Our analysis of the aggregation behavior of SM in chloroform verified that the majority of the chromophores are involved in the formation of oligomers in solution, where the whole dimer and part of the trimer populations present a stable π-stacking structure. The optical properties of the monomers and oligomers in solution were evaluated by means of a discrete polarizable embedding quantum mechanical/molecular mechanical (PE-QM/MM) response scheme where the quantum part is described at the level of density functional theory. The visible absorption spectrum of SM in chloroform is simulated using time average values obtained for the monomeric and oligomeric forms of SM from the PE-QM/MM calculations performed on uncorrelated configurations extracted from the classical MD simulations. This study shows that the self-aggregation of SM in chloroform may exist, but it is not essential for reproducing the reversal solvatochromic shift in chloroform and that the process does not contribute to enhance the bathochromic shift nor explain the structure observed in its absorption band. Moreover, it is verified that since the electronic transitions of the monomer and oligomers are close together, changes in the interplane separation between the monomeric units of the stacked oligomers substantially affect the spectral resolution of their contribution to the optical absorption spectrum.



1. INTRODUCTION

In recent years, an intense worldwide effort has been focused on research dealing with the design and development of organic conjugated materials with suitable optical properties for applications in various optical devices.[1−3] This broad effort comprises works conducted by both experimentalists and theoreticians. In the vast majority of applications these materials are in a condensed phase environment, either a liquid or a solid. Therefore, it is evident that obtaining a better understanding regarding the optical behavior of these materials in condensed phase is an important goal.

The tunability of merocyanines from weakly dipolar (polyene-like) to highly dipolar (zwitterionic) chromophores depends on the polarity of the liquid environment. This fact makes them among the most interesting molecules to study in regard to the effect of the environment on the molecular figures-of-merit of organic chromophores for many applications. Within this class of materials, stilbazolium merocyanine (SM) has caught special attention because, in addition to exhibit a large solvatochromic shift due to a change in solvent polarity, it also exhibits a reversal solvatochromic shift in solvents of low polarity.[4−6]

Two hypotheses have been suggested in order to explain the solvatochromic reversal of the SM molecule. The first hypothesis assumes a change in the ground-state molecular structure of SM induced by the solvent environment. Such a solvent-induced structural modification has been supported by experimental studies employing spectroscopic techniques for example NMR, X-ray, and Raman.[7] Moreover, the findings of recent theoretical studies support that the solvatochromic reversal of SM should be attributed to a change in its π-electron distribution from a neutral quinonoid form to a zwitterionic

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form following the change in solvent polarity from nonpolar to polar.[8,9] The second hypothesis attributes the solvatochromic reversal to the self-aggregation of SM in nonpolar solvents.[10] Despite this, it is important to note that one hypothesis does not exclude the other since, while the change of the charge form of SM occurs in a polar solvent, the self-aggregation of SM is assumed to occur only in a nonpolar solvent.

The UV−vis absorption spectrum of SM in chloroform is found to possess a structured and broad band. The UV−vis absorption spectrum of SM in chloroform, with the dye concentration in the $2 - 8 \times 10^{-4}$ mol/L range, is shown in Figure 1. The experimental spectrum was digitized from the work reported by Tsukada and co-workers.[11]

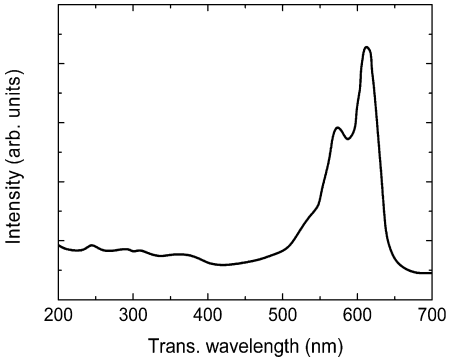

Figure 1. UV−vis absorption spectrum of SM in chloroform at low concentration ($2-8 \times 10^{-4}$ mol/L range). The experimental spectrum was digitized from the work reported by Tsukada and co-workers.[11]

There are several possibilities for the origin of such a structured band: (i) the oscillator strength of the transition associated with the lowest energy excited state is distributed among its 0−0 and vibronic states; (ii) it may be ascribed to the existence of both cis and trans isomers of SM in solution; and (iii) it may be due to self-aggregation of SM molecules. Tsukada and co-workers argued that the first possibility can be excluded by the fact that the shoulder, which is observed only in aprotic solvents of low polarity, is observed at a fixed wavelength (578 nm), while the solvent change shifts the main peak.[11] In addition, they argue that no vibrational mode corresponding to the gap between the shoulder and main peak can be observed. Moreover, Catalán and co-workers showed that SM has an intrinsically structured absorption spectrum and that this structure (shoulder plus main peak) disappears when its oxygen atom (basic center) is solvated.[12] Tsukada and co-workers further reported measurements of the absorption spectrum of SM in chloroform with a wide range of concentration and clearly proved that both the main peak at 618 nm and the shoulder at 578 nm obey the Lambert−Beer law.[11] Therefore, they concluded that the third possibility should be excluded. Based on these facts, Tsukada and co-workers concluded that a contribution coming from the *cis* isomeric form is the most plausible possibility in order to justify the structured absorption spectrum of SM in the Vis region. However, Catalán and co-workers argued that such a conclusion is not convincing at least for two reasons: first, for other merocyanines the structured spectrum is observed in all kinds of solvents; second, the emission of such systems maintains its spectral shape and quantum yield when different peaks of the absorption band are excited.[12] Due to these reasons, it is evident that the origin of the structure observed in the absorption band of SM in solvent of low polarity remains unclear.

In the present context, the aim of this study is to shed light on this issue by investigating the absorption behavior of the neutral quinonoid form of SM in chloroform solution taking into account the effects of the self-aggregation process on its Vis absorption spectrum. Although Tsukada and co-workers exclude the self-aggregation of SM as a possibility to explain the structured absorption band of SM in chloroform based on experimental evidence, the findings from the simulations performed in the present study indicate that it is plausible to consider the existence of SM oligomers in chloroform solution. In fact, the self-aggregation of merocyanine dyes in solvent of low polarity has already been reported in some works.[10,12−14] Therefore, it is evident that the optical behavior of SM oligomers is essential in order to understand the absorption spectrum of this dye in a wide spectral region. Nevertheless, it is important to emphasize that, as it was already shown in previous works considering only the monomeric form of SM,[8,9,15,16] the results obtained and presented here for the SM monomer explicitly indicate that the self-aggregation process of SM is not essential to explain the reversal solvatochromic shift of this dye in nonpolar solvents. However, it is important to point out that the amplitude of the solvatochromic shift in chloroform was not well reproduced,[8,9] and this motivates us to undertake a study that would explicitly account for the contributions coming from the self-aggregation process. Moreover, if the self-aggregation and the change in ground state molecular structure contribute to the optical property in a combined way, then those results based just on the monomers are not sufficient, and it is important to explore the changes in absorption properties due to the possible oligomerization.

Merocyanine dyes possess a large hyperpolarizability, which makes them quite useful for nonlinear optical applications. However, the self-aggregation of merocyanine dyes has been identified as an important problem in the fabrication of materials for technological applications. For example, such organic materials for nonlinear optical and photorefractive applications rely on a noncentrosymmetric arrangement of the dye molecules. In this sense one can immediately realize that if the dimeric form of SM has a centrosymmetrical structure, then the SM dimer is detrimental for the potential application of the dye in second-order nonlinear optical devices. Therefore, in addition to the presented study addressing fundamental issues, we expect that the findings and conclusions may be relevant to the application of merocyanine dyes.

In this study we performed classical Molecular Dynamic (MD) simulations for a system representing a 3×10^{-2} M solution (25 SM in 10545 chloroform molecules). For practical reasons, the concentration of the simulated solution is higher than the ones ($10^{-4} - 10^{-3}$ M) usually used in experimental studies concerning the self-aggregation and absorption behavior of merocyanine dyes in solvent. We monitored the formation of oligomers in solvent based on these classical MD simulations. We understand that, although the rate of occurrence of oligomers formation in solution, which is closely related to solution concentration, is an important issue, the optical properties of the oligomers themselves are independent of the rate at which they are formed and are, in turn, essential to observe any effect of the oligomerization process on the optical behavior of the dye in solution. By simulating a solution with higher concentration than a more realistic solution, we are able to reduce the oligomer formation time and obtain a reasonable

amount of oligomers to efficiently investigate and report the structures and structural fluctuation of the SM oligomers in solution. Moreover, although the concentration directly affects the rate of occurrence of oligomers, i.e., the amount of trimers, dimers, and remaining monomers in solution, it is important to clarify that the main purpose of this study is to seek some evidence about the contribution of self-aggregation process of SM dye to its large bathochromic shift and the structured absorption band presented by SM in chloroform solution. For this purpose an accurate description of the oligomers population (or the rate of occurrence of oligomers) is not crucial.

To evaluate the optical properties of monomers and oligomers in chloroform, we employed a sophisticated quantum mechanical/molecular mechanical (QM/MM) scheme. The visible (Vis) absorption spectrum of SM in chloroform was simulated using the time average values obtained for the monomeric and oligomeric forms of SM from QM/MM calculations performed for statistically uncorrelated configurations systematically sampled from the classical MD simulations.

2. COMPUTATIONAL DETAILS

We adopt a sequential molecular dynamics and hybrid QM/MM response procedure.[17] First, classical MD simulations were performed for a system composed of 25 SM molecules and 10454 chloroform molecules. The simulations were performed under ambient conditions (T = 25 °C, P = 1 atm) and adopting the NPT ensemble. In the MD simulations, the leapfrog integrator was used to solve the equation of motion. To control the temperature and pressure of the simulated system, the Berendsen thermostat and barostat were adopted with a coupling constant of 0.2 ps for the temperature and 1.0 ps for the pressure. A cubic box with periodic boundary conditions and a cut-off radius of 14.0 Å for non-bonded interactions were used. Long-range corrections were calculated for interactions and forces beyond the cut-off radius. The Coulomb term of the non-bonded interactions was corrected by the Particle Mesh Ewald (PME) approach. All MD simulations were performed using the GROMACS molecular modeling package.[18,19]

The intermolecular interactions were defined by a Lennard-Jones (LJ) plus Coulomb potential. The intramolecular and LJ parameters were based on the General AMBER Force Field (GAFF),[20] as implemented in the Amber 8 program,[21] adopted to describe both the solute and the solvent molecules. One important aspect prior to the MD simulations is the consideration of the electronic polarization of the solute and solvent molecules due to the solvent environment. To consider this polarization, the initial molecular geometries of the SM and chloroform molecules were obtained from geometry optimization calculations performed at the Density Functional Theory (DFT)[22,23] level with implicit inclusion of solvent effects using the integral equation formalism of the polarizable continuum model (IEF-PCM).[24,25] These DFT/IEF-PCM calculations were performed using the hybrid B3LYP exchange-correlation functional[26,27] and the 6-311++G(d,p) basis set. The atomic charges of the Coulomb part of the potential of SM and chloroform molecules were obtained using an electrostatic CHELPG mapping[28] based on the DFT/IEF-PCM calculations performed using the equilibrium/optimized geometry of SM and chloroform molecules. These DFT/IEF-PCM calculations were in turn performed using the hybrid B3LYP functional[26,27] and the aug-cc-pVDZ basis set. All the DFT/IEF-PCM calculations were performed using the Gaussian 09 package.[29]

Assuming that the dynamics of the self-aggregation process of SM in solution is sensitive to the initial conditions of the system, defined by the initial velocity, coordinates, and spatial orientation of all its constituent molecules, we perform three simulations differing from each other by a distinct initial condition. The distinct initial conditions were obtained by random translational and rotational movement performed over half of the SM molecules before the thermalization stage and by using distinct seeds to generate the initial velocities distribution of the system. The total time of each MD run (with 1 fs time step) was 6 ns, and a total of 6×10^6 configurations were collected. After computing the energy autocorrelation function of the configurations based on each simulation, 50 statistically uncorrelated configurations were extracted from each one. Therefore, in total 150 configurations were selected to perform the *a posteriori* spectroscopic calculations.

Using the distance between the centers of mass (CM) as criterion, we monitored the self-aggregation behavior of SM in chloroform and analyzed the evolution of the oligomers population. To evaluate the optical properties of the monomers and oligomers in solution, we employed a discrete polarizable embedding quantum mechanical/molecular mechanical (PE-QM/MM) response scheme[30,31] where the quantum mechanical part is described at the DFT level. For a specific monomer/oligomer of the system (QM region), the scheme considers its conformational and polarization changes and the dynamical average of the solute−solvent and solute−solute interactions, while still adopting a granular representation of the polarization and electrostatic interactions with the solvent and remaining solute molecules in the system, which are classically described (the MM region). Through a self-consistent reaction field procedure between the QM and MM regions, the mutual polarization between the specific monomer/oligomer and all the remaining molecules in the system is reproduced by the PE-QM/MM scheme.

The Vis absorption spectrum of SM in chloroform was simulated using time average values obtained for the monomeric and oligomeric forms of SM from PE-QM/MM calculations performed over the uncorrelated configurations extracted from the simulations. QM calculations considering only the monomeric and oligomeric forms of SM, i.e., the solvent molecules were removed from the selected configurations, were also performed in order to analyze the role of solvent effects on their optical properties. The QM and PE-QM/MM calculations were performed using a development version of the DALTON program.[32]

Electronic interactions between monomer units induce delocalized excited states (or Frenkel excitons), creating a red-shift or blue-shift of the main absorption peaks in aggregates compared to the monomer in solution. The excitonic coupling can be shown to be composed of two dominant contributions: $V^{\text{exciton}} = V^{\text{Coulomb}} + V^{\text{Exchange}}$. The first term, V^{Coulomb}, shows a long-range dependence which dominates the coupling between singlet excited states; the second term, V^{Exchange}, is a short-range contribution that only becomes relevant at short intermolecular distances. In the case of π-stacked aromatic systems, it is well-known that the typical intermolecular separation distances in self-aggregation is in the range of 3−6 Å.

Under the assumption that the excited states of molecular aggregates are only weakly influenced by intermolecular forces,

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they can be approximated by a linear combination of the excited states localized on each monomer. In such case, the intermolecular charge transfer, between the monomer units, is neglected, and the π-stacked aromatic systems can be described using a truncated description of the intermolecular Hamiltonian that is often referred to as the Frenkel Hamiltonian (or Frenkel exciton model). However, in principle it is difficult to fully justify that the excited states of molecular aggregates are weakly influenced by intermolecular forces. Therefore, in this study we did not neglect this issue and instead of treating the electronic coupling perturbatively, we performed DFT calculations on the whole oligomers, the so-called supramolecular approach, where we intrinsically take into account the full intermolecular Hamiltonian of the coupled chromophores system.

Electronic transitions with significant charge transfer (CT) character are likely to be present in π-stacked oligomers and the reliability of TD-DFT calculations in treating this kind of transitions has often been questioned. On the other hand, the traditional failures of TD-DFT methods are met in the study of CT transitions between donor−acceptor pairs with vanishing overlap, and this is not the case for the molecular orbitals of two stacked monomers at the typical intermolecular separation distances of 3−6 Å. Therefore, to properly handle intramolecular and intermolecular charge transfer processes we employed in this work the CAM-B3LYP functional[33] that combines the hybrid quality of B3LYP functional and the long-range correction (Coulomb-attenuating method) proposed by Hirao and co-workers. Moreover, since an accurate description of dispersion can be critical for a reliable determination of ground state geometries and thereby for vertical excited state energies in the π-stacked aromatic systems, the wB97XD functional[34] was also used in this work. wB97XD is a long-range corrected functional which adopts a dispersion correction to the energy and thereby to molecular gradients. All the QM and PE-QM/MM calculations were performed using these DFT functionals and the Turbomole-TZVP basis set.[35]

3. RESULTS AND DISCUSSION

The CM−CM distances between all the SM molecules were monitored along the whole simulation sequence. For all three MD simulations it was observed that, after a time interval of 2−3 ns, the population of oligomers formed had reached a stable and well-defined distribution. The oligomers population is composed by dimers and trimers, and, in the case of the trimer, stable and unstable structures were observed. Figure 2 illustrates the typical dynamics of formation of the oligomers. The dynamics are described by the CM−CM distances between the chromophores as a function of time. Figures 2a and 2b, where the CM−CM distances between the chromophores basically do not change after a few nanoseconds of simulation, illustrate the formation of SM dimers and trimers with stable structures in solution. Moreover, Figure 2c illustrates the formation of SM trimers with unstable structures.

The formation of the stable dimers and trimers is ascribed to π-stacking interactions. As it can be observed by the oligomer structures (Figure 3), in chloroform the SM molecule tends to form ladder-type H-aggregates. Such structure is a compromise between the maximum overlap of the $\pi-\pi$ systems and the repulsive electrostatic forces. For such stable and stacked oligomers, the interplane separation between their monomeric units is about 4.0 Å. Moreover, although no hydrogen bond involving the carbonyl and methyl imido groups of the monomer units is observed, the existence of such groups

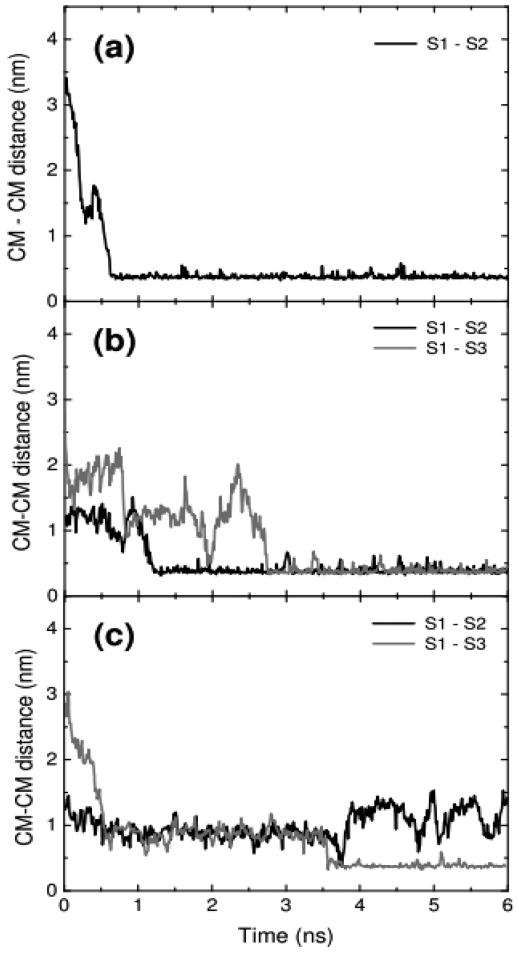

Figure 2. CM−CM distance between chromophores as a function of time is plotted to illustrate the typical dynamics of formation of a SM dimer (a), a stable SM trimer (b), and an unstable SM trimer (c) during the classical MD simulations.

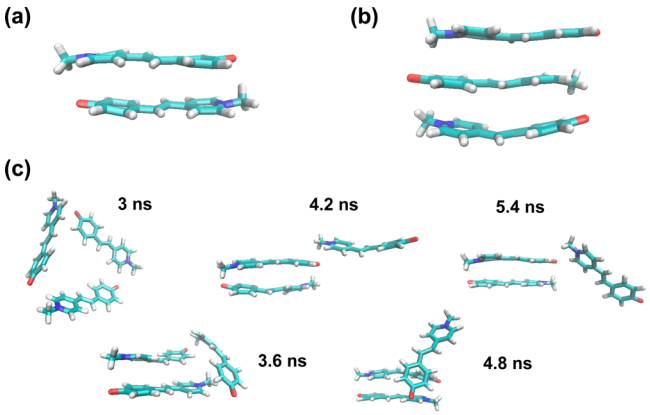

Figure 3. The structure of the stable dimer (a) and stable trimer (b) of SM formed in chloroform solution, and some of the conformations accessed by the unstable trimer (c) during the classical MD simulations.

induces a slight higher approximation of the peripheral parts of the chromophores in comparison with the central parts. Figure 3c shows some of the accessible conformations of a typical unstable SM trimer and the instant of time of the dynamics (Figure 2c) they appear. As it can be seen, the typical unstable trimer of SM identified in this work is basically described by a

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stable and stacked dimer plus a third monomer that preferentially interacts with the peripheral part of the dimer and does not stack to it.

Figure 4 illustrates the occurrence of oligomers formation and the contribution of stable and unstable structures in the case of the trimeric form. Considering all the simulations performed it was found that respectively 43% and 44% of the chromophores have being involved in the formation of dimers and trimers. Therefore, from a total of 75 SM molecules (25 SM molecules in each of the three simulations), only 13% of the SM molecules remained in the monomeric form during the simulations.

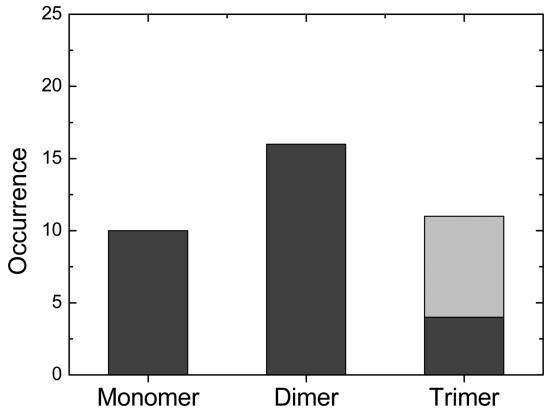

Figure 4. Occurrence of oligomers formation considering all the three classical MD simulations performed. For the trimer, the part of the stacked bar in light gray represents the contribution of the unstable oligomers.

Given the large oligomers population, it is evident that the determination of the optical properties of these oligomers is essential to describe and shed light on the optical behavior of a high concentration solution of SM in chloroform. Table 1 presents the time average wavelength and oscillator strength determined by QM and PE-QM/MM calculations for the six lowest energy transitions of SM in its monomeric form and geometries in chloroform, as described by the structures from the MD simulations. In the case of QM calculations, the solvent molecules were stripped from the structures for performing the *a posteriori* calculations. The calculations were carried out by selecting a single SM monomer present in each simulation performed and using the statistically uncorrelated configurations extracted from each simulation.

Table 1. Time Averaged Wavelength (λ) and Oscillator Strength (f) Determined by the QM and PE-QM/MM Calculations for the Six Lowest Energy Transitions of SM in Its Monomeric Form and Geometries in Chloroform[a]

	vacuum (QM calculations)		in chloroform (PE-QM/MM calculations)	
transition	λ (nm)	f	λ (nm)	f
1	431	1.31	496	1.51
2	382	0.05	337	0.02
3	366	0.04	315	0.01
4	287	0.02	283	0.03
5	273	0.09	270	0.07
6	261	0.03	262	0.06

[a]The values are the average of the calculations carried out on 150 uncorrelated configurations.

The results gathered in Table 1 show that the lowest energy and most intense transition of the SM monomer exhibits a bathochromic shift when it is solvated in chloroform. Moreover, the results indicate that the Vis absorption spectrum of SM in chloroform for a solution with very low concentration should basically be ascribed to this single transition. These results, the transition wavelength and solvatochromic shift (i.e., 65 nm for the first transition), are in fair agreement with the results of recent works in which Car−Parrinello mixed quantum mechanics/molecular mechanics (CP-QM/MM) simulations and PE-QM/MM calculations were employed to study the absorption behavior of the SM molecule in polar and nonpolar solvents.[8,9] However, it is important to note that the average value determined in the present study and in numerous previous theoretical studies for the wavelength of this intense transition of the SM monomer is much smaller than the wavelength at which the peak of the absorption band of SM in chloroform appears in the experimental spectrum (620 nm).[11,12,15,36] The large difference between theoretical and experimental values for the transition wavelength stands as a challenge for quantum chemical methods. According to a previous work employing semiempirical calculations an intermediate mesomeric structure with equal contribution from both quinonoid and mesomeric forms should have the longest transition wavelength.[37] However, such a structure has not been obtained through any *ab initio* quantum chemical method so far.

Table 2 presents the time averaged wavelength and oscillator strength determined for the six lowest energy transitions of SM in its oligomeric forms in chloroform from QM and PE-QM/MM calculations. The calculations were carried out by selecting

Table 2. Time Average Wavelength (λ) and Oscillator Strength (f) Determined by the QM and PE-QM/MM Calculations for the Six Lowest Energy Transitions of SM in Its Oligomeric Forms and Geometries in Chloroform[a]

		vacuum (QM calculations)		in chloroform (PE-QM/MM calculations)	
oligomers	trans.	λ (nm)	f	λ (nm)	f
dimer	1	535	0.04	560	0.03
	2	461	0.09	471	0.57
	3	429	0.54	448	1.61
	4	405	1.52	424	0.44
	5	365	0.08	348	0.05
	6	355	0.06	332	0.03
stable trimer	1	575	0.02	581	0.05
	2	491	0.04	509	0.12
	3	469	0.09	474	0.17
	4	456	0.04	453	0.60
	5	433	0.15	437	1.26
	6	415	0.84	423	1.14
unstable trimer	1	512	0.06	530	0.09
	2	452	0.94	478	1.79
	3	436	1.55	464	2.05
	4	404	0.28	398	0.09
	5	393	0.44	382	0.12
	6	381	0.16	374	0.00

[a]The values are the average of the calculations carried out on 150 uncorrelated configurations.

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a single dimer, a single and stable trimer and a single and unstable trimer formed in each simulation performed and using the uncorrelated configurations extracted from them.

Inspecting the results gathered in Table 2, it is evident that intermolecular interactions are strong enough for the optical properties of the SM oligomers to differ considerably from those of the corresponding monomer. The distinct properties of the oligomers arise from the fact that their monomer units are excitonically (dipole) coupled. As a consequence of this excitonic coupling between neighboring units, the intensity of the lowest-energy electronic transition observed in the SM monomer splits into a band of states in the case of SM oligomers.

In general, the interaction of two monomer units in a dimer may be understood within an excitonic coupling model based on the point dipole approximation.[38,39] This model predicts a splitting of the two lowest energy excited levels and that the transition to the energetically higher level is intense, with the integrated absorption being twice as large as the one of the monomer band. The transition to the lowest-energy level, on the other hand, should be forbidden in the case of an ideal antiparallel arrangement, since in this case the system has a centrosymmetric structure. As seen from the results in Table 2, a substantial splitting between the two-lowest energy transitions of the SM dimer is verified. However, the predictions of the excitonic coupling model concerning the intensities are not satisfied, although the SM dimers have a highly antiparallel arrangement (Figure 3a).

In the case of DFT calculations using the CAM-B3LYP functional, the oscillator strength of the second-lowest energy transition of the SM dimer is much smaller than twice the oscillator strength of the SM monomer. The intensity lost by such transition appears in other two higher-energy transitions shifted about 1100 cm^{-1} and 2350 cm^{-1} in the case that the SM dimer is solvated. This indicates that for the average interplane separation determined by the MD simulations an excitonically coupled monomer picture is not appropriate, most probably because the orbital overlap between two monomers cannot be totally neglected. This should be the case for both the SM dimers and trimers, since the intermolecular distances between the monomer units are quite similar in both oligomers. This fact corroborates a previous work by Sainudeen and Ray, where the nonlinear optical properties of aggregates of a series of zwitterionic merocyanine dyes, including SM, were studied employing the TD-DFT/SOS method.[40] In this work the authors concluded that for such systems an excitonically coupled monomer picture is not appropriate for interplane separations smaller than around 4.2 Å. Nevertheless, it is important to mention that the trends observed in the present study concerning the distribution of intensity among the lowest-energy transitions of the SM oligomers due to excitonic coupling can somehow be sensitive to the choice of the DFT functional.

Aiming to detail the role of monomers and oligomers in the absorption spectrum of SM in chloroform solution, we simulated the absorption band of each species in the Vis region by adopting a standard Gaussian line shape to mimic the distribution of each transition.

One can use the transition energies computed by the PE-QM/MM calculations performed over the uncorrelated configurations of the system/solution to estimate the line width of each electronic transition of the monomeric, dimeric, and trimeric forms of SM dye. However, by doing this one must to remember that only the contribution from the inhomogeneous broadening to the linewidths is consistently taken into account. Moreover, because in the classical MD the time evolution of structural parameters such as bonds, bond-angles, and torsional (dihedral) angles are modeled using harmonic potentials, the molecular vibrations and conformational changes of the chromophore are treated and, therefore, at least a part of the homogeneous broadening is also taken into account intrinsically (in an inconsistent way).

The spectral line width (Γ_{fwhm}, full-width at half-maximum) is directly calculated based on the results of the linear response PE-QM/MM calculations as $\Gamma_{fwhm} = 2[2\ln(2)]^{1/2}\sigma_f$, where σ_f is the standard deviation of the transition energies. The values of the line width obtained by employing this procedure for the SM monomer and stable oligomers varied in the 0.15−0.29 eV range. If we take into account only transitions with an average oscillator strength higher than 0.1, this variation becomes a bit narrowed, i.e., in the 0.15−0.26 eV range.

Taking into account an additional and minor contribution coming from the homogeneous broadening, typically around 0.05 eV for organic molecules, and based on the above information, one can conclude that the value of 0.25 eV adopted for the line width of all transitions in our work is reasonable to simulate the absorption spectrum of the SM monomer and oligomers. In particular, it is a good value for most important/intense transitions taken into account to simulate the absorption spectra. Experimentally, the line width of electronic transitions are known to usually vary in the range of 0.15−0.40 eV for organic molecules.[41] However, it is worth mentioning that although, for convenience, the simulated spectra shown herein were obtained assuming a common line width of 0.25 eV for all transitions, we initially considered this issue and adopted distinct linewidths for the different transitions. By the spectra obtained in this way we realized that the variation of the line width values does not critically affect the spectral profile of the simulated spectra and, therefore, does not affect in any way the conclusions of this work.

By considering the occurrence of oligomer formation (Figure 4) we were able to illustrate the contribution of monomers and oligomers to the absorption spectrum of SM in chloroform and obtain a simulated absorption spectrum by the superposition of these contributions. The absorption spectrum was simulated assuming three distinct equilibrium populations for discussion purpose. The first one assumes the exact oligomers population provided by the MD simulations performed. The second and third conditions assume new equilibrium populations that either eventually would be reached if longer simulations were performed or if a system/solution with slightly different composition/concentration was simulated. The second condition assumes that the population/contribution of unstable SM trimers disappears due to the breaking of such species in a SM monomer plus a stable SM dimer. The third condition assumes that the population/contribution of unstable SM trimers disappears due the stabilization of such structures after the permanent stacking of their third unit occurs. The simulated spectra are presented in Figure 5.

It proved valuable to consider that the additional oligomers populations used here can be assumed as a possible equilibrium population for systems with higher or lower concentrations than the system (25 SMs + 10454 chloroform molecules) simulated in the present work, since the percentage contribution of each species is what really matters. In this

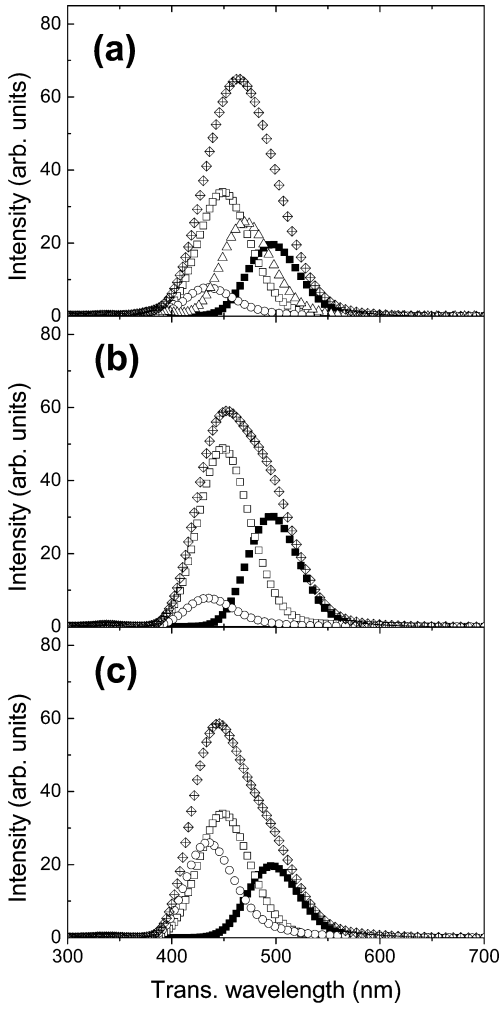

Figure 5. Absorption spectrum of SM in chloroform solution simulated using the results of the PE-QM/MM calculations using the CAM-B3LYP functional and three distinct equilibrium populations: (a) adopting the exact oligomers population provided by the MD simulations performed, (b) assuming that the population/contribution of unstable SM trimers disappears due to the breaking of such species in a SM monomer plus a stable SM dimer, and (c) assuming that the population/contribution of unstable SM trimers disappears due to the stabilization of such structures after the permanent stacking of their third unit occurs. The contribution of monomeric, dimeric, and stable and unstable trimeric species to the absorption spectrum are described respectively by the filled squares, empty squares, empty circles, and empty triangles. The absorption spectrum of SM in chloroform solution is described by the diamonds.

sense, it is reasonable to expect that the case in which the population of unstable SM trimers disappears due to their breaking in a SM monomer plus a stable SM dimer would represent a solution with lower concentration, where the existence of SM in its stable trimeric form should be scarcer. On the other hand, the case in which the population of unstable SM trimers disappears due to their stabilization after the permanent stacking of the third monomer unit would represent a solution with higher concentration, where the existence of SM in its stable trimeric form would be more likely. However, it is worth noting that in making such analogy we are neglecting the dissociation of SM dimers into monomers or the formation of SM dimers by the remaining monomers that should also happen at some rate when the solution concentration decreases or increases, respectively.

The simulated Vis absorption spectrum obtained using the exact oligomers population provided by the MD simulations is given by a broad and structureless band centered at 464 nm. Considering the spectra obtained in the case of the other two equilibrium populations adopted (Figures 5b and 5c), one can conclude that there is very low correlation between the profile of the absorption spectrum and the equilibrium population of the system/solution. The changes in the wavelength and the amplitude of the peak of the simulated spectra with the fluctuation of the equilibrium population are about 16 nm and 9%, respectively.

Figure 5 shows that the maximum of the monomer and dimer contributions are separated in energy by about 0.26 eV. This value is about two times larger than the energy separation between the peak and shoulder observed in the absorption spectrum of SM in chloroform (Figure 1) and, therefore, it supports the idea that the shoulder should not be ascribed to the self-aggregation process of SM. Nevertheless, based on experimental studies in which the changes on the spectral profile of the absorption spectrum of merocyanine dyes as a function of the solution concentration were monitored and discussed in terms of the formation of dimers,[13,14] we preferentially expected to somehow observe a correlation between the wide range profile of the absorption spectrum of SM in chloroform (not the shoulder in particular) and the distribution of the oligomers population of the system/solution.

As already shown, using our theoretical approach, the accuracy in determining the peak of the absorption spectrum of the SM monomer was about ∼0.5 eV. An important issue is whether the accuracy in determining the peak of the absorption spectrum of the SM oligomers is similar to the case of the SM monomer. Through the study conducted by Würthner and coworkers,[13,14] one can verify that an energy separation of ∼0.30 eV between the absorption maximum of monomeric and dimeric forms of merocyanine dyes in chloroform is typically observed experimentally. Therefore, the theoretical value determined here for the energy separation between the absorption maximum of the monomeric and dimeric forms of SM in chloroform is reasonable and evidence that the accuracy in determining the peak of the absorption spectrum of the SM monomer and SM oligomers is reasonably similar.

As already mentioned, it has been anticipated that the optical properties of the SM oligomers can be affected by the interplane separation between their monomer units, and therefore, it is important to address this issue more closely. The equilibrium distances determined through MD simulations are strongly dependent on the parametrized intermolecular potential adopted. In order to verify if the average interplane separations determined through the simulations are reasonable and analyze how strongly they affect the contribution of the oligomers to the absorption spectrum of SM in chloroform, the initial structures of a stable SM dimer and a SM trimer were optimized through geometry optimization calculations at the DFT level with implicit inclusion of solvent effects using the IEF-PCM method. It is well-known that DFT methods suffer from an incomplete treatment of dispersion that can adversely affect its accuracy. However, in recent years many DFT functionals designed to overcome this problem have been developed, and wB97XD[34] is a functional among them. Therefore, the geometry optimization DFT/IEF-PCM calculations were performed using the wB97XD functional and the

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Table 3. Wavelength (λ) and Oscillator Strength (f) Determined by TD-DFT and TD-DFT/IEF-PCM Calculations for the Eight Lowest Energy Transitions of SM Dimer and Trimer in Their Optimized Geometry

		vacuum (TD-DFT calculations)				in chloroform (TD-DFT/IEF-PCM calculations)			
		CAM-B3LYP		wB97XD		CAM-B3LYP		wB97XD	
oligomer	trans.	λ (nm)	f	λ (nm)	f	λ (nm)	f	λ (nm)	f
dimer	1	540	0.04	532	0.05	518	0.07	511	0.08
	2	492	0.04	477	0.06	468	0.37	455	0.62
	3	479	0.02	467	0.02	460	0.01	445	0.01
	4	406	2.24	404	2.23	430	2.28	425	2.03
	5	337	0.06	326	0.04	317	0.03	308	0.03
	6	335	0.01	325	0.00	311	0.01	303	0.00
	7	332	0.00	325	0.00	310	0.00	299	0.01
	8	332	0.00	323	0.00	303	0.01	296	0.00
trimer	1	556	0.06	542	0.09	543	0.11	530	0.16
	2	516	0.01	503	0.01	502	0.00	494	0.00
	3	484	0.00	468	0.01	463	0.02	443	0.03
	4	459	0.03	443	0.04	448	0.68	434	1.46
	5	450	0.04	434	0.03	447	0.22	430	0.07
	6	422	0.35	410	0.67	420	1.51	410	1.48
	7	388	2.71	383	2.41	406	1.42	395	0.76
	8	376	0.02	357	0.00	359	0.00	322	0.00

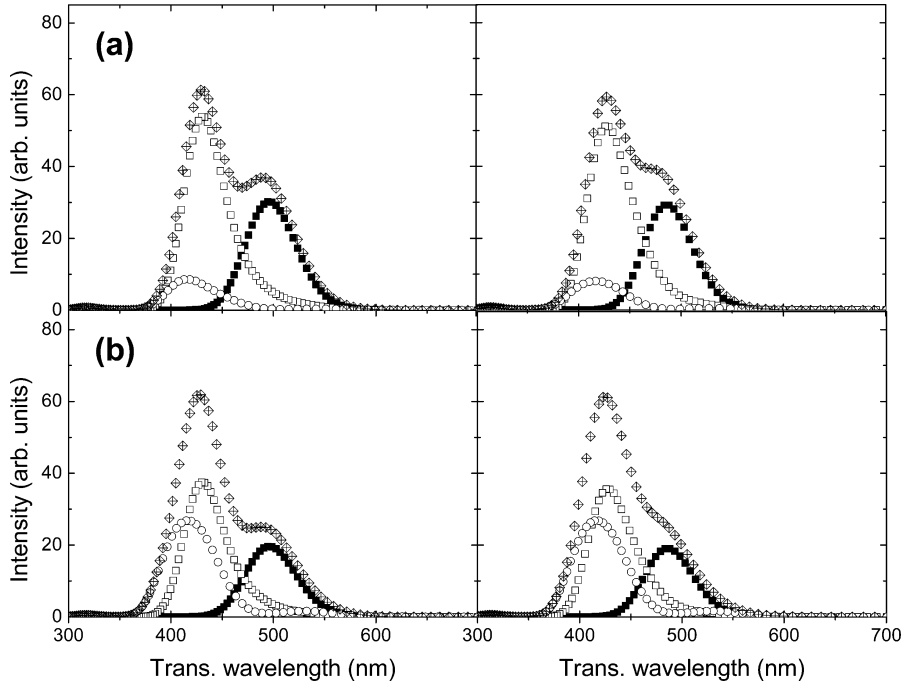

Figure 6. Absorption spectrum of SM in chloroform simulated based on the results of the TD-DFT/PCM calculations employing the CAM-B3LYP (on the left) and wB97XD (on the right) functionals and assuming two distinct equilibrium populations: (a) assuming that the population of unstable SM trimers provided by the MD simulations disappears due to the breaking of such species in a SM monomer plus a stable SM dimer, and (b) assuming that the population of unstable SM trimers disappears due to the stabilization of such structures after the permanent stacking of their third unit occurs. The contribution of monomeric, dimeric, and stable and trimeric species to the absorption spectrum are respectively described by the filled squares, empty squares and empty circles. The absorption spectrum of SM in chloroform solution is described by the diamonds.

6-311G(d,p) basis set. After the geometry optimization the interplane separation between the monomer units diminished to 3.6 Å and 3.5 Å in the cases of the SM dimer and trimer respectively (remember the corresponding interplanar distance for stable oligomers as obtained from force-field MD was 4.0 Å). The changes in the internal molecular geometry of each monomer units were negligible.

Table 3 presents the wavelength and oscillator strength for the eight lowest energy transitions of SM dimer and trimer in their optimized geometry. The transitions were determined by TD-DFT and TD-DFT/IEF-PCM calculations using both the CAM-B3LYP and the wB97XD exchange-correlation functionals. It is important to mention that the TD-DFT/IEF-PCM calculations performed for the SM monomer, in the non-equilibrium geometries provided by the MD simulation or in the optimized geometry determined by a DFT calculation, provided results (not shown) very similar to the one provided by the PE-QM/MM calculations. Based on this, we expect that

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TD-DFT/IEF-PCM calculations would also provide reasonable results for the SM oligomers.

Comparing the results gathered in Tables 2 and 3 one can note that the reduction of the interplane separation in the SM dimer reduces the oscillator strength of its second-lowest energy transition, and therefore, it remains much smaller than twice the oscillator strength of the SM monomer in the case of both functionals. Thus, we again verify that, for a small interplane separation, an excitonic coupling model based on the point dipole approximation is not appropriate to interpret the optical properties of the SM dimer, since the orbital overlap between its monomer units cannot be totally neglected. Moreover, based on the results shown in Table 3, one can note that when compared with the results from vacuum calculations, the results from IEF-PCM calculations for the lowest energy transition show a blue shift, which is just the opposite of what we see in Tables 1 and 2. As already mentioned such a solvatochromic reversal is observed for SM molecule with the change in solvent polarity from nonpolar to polar and it should be ascribed to its change from a neutral quinonoid form to a zwitterionic form.[9] However, here we verified that the changes in the C═O, N−CH3, and three central bonds of the monomeric units of the geometry optimized oligomers are negligible, what indicates that SM oligomers remain as neutral−neutral H aggregates. In addition, it is important to take into consideration that such transition has very low intensity.

Using the results gathered in Table 3, we again simulated the absorption band of the SM monomer and SM oligomers in the Vis region by adopting a standard Gaussian line shape to mimic the distribution of each transition. For comparison purposes, we again assumed a line width of 0.25 eV (full-width at half-maximum) for all the transitions. By considering the occurrence of oligomers formation as given by the MD simulations (Figure 4), we verify the contribution of monomer and oligomers to the absorption spectrum of SM in chloroform and obtain a simulated absorption spectrum by the superposition of these contributions. In such a procedure, we are not able to take into account the existence of unstable SM trimers. Therefore, the exact oligomer population provided by the MD simulations could not be adopted, and the SM absorption spectrum was simulated assuming only the two remaining equilibrium populations already described. The simulated spectra are presented in Figure 6.

As one can see, in the case of CAM-B3LYP in particular, it is now possible to identify along the Vis absorption spectrum of SM a band related to the optical behavior of its monomers and another one related to the optical behavior of its oligomers. Based on this observation we concluded that the role of the interplane separation between the monomer units of the SM oligomers should not be underestimated when the aim is to simulate the Vis absorption spectrum of SM in nonpolar solvents.

Figure 6 shows that by using the optical properties of the SM oligomers in a molecular equilibrium geometry determined by quantum chemical calculations to simulate the absorption spectrum of SM in chloroform, the maximum of monomer and dimer contributions are separated in energy by about 0.37 eV (CAM-B3LYP results) and 0.35 eV (wB97xD results). This value is even higher than the one (0.26 eV) observed when the spectrum was simulated using the properties of the SM oligomers based on nonequilibrium geometries provided by the MD simulations. This observation further supports the idea that the shoulder in the absorption spectrum of SM in chloroform should not be ascribed to its self-aggregation.

Finally, the relative amplitude between the bands ascribed to the monomeric and dimeric forms of some merocyanines have been reported in the literature.[13,14] In those cases, the amplitude of the band ascribed to the dimeric form of such merocynianes is larger than the amplitude of the band ascribed to its monomeric form starting from solutions with concentration higher than 10^{-4} M. The present study corroborates these previous works, but here, besides merocyanine dimers, we also consider the existence of trimers in solution based on the findings from the MD simulations. Moreover, although the population of SM trimers in solution with concentrations of about 10^{-4}−10^{-3} M would perhaps be negligible, our results show that, due to the substantial overlap between the absorption band related to the SM dimers and trimers, it would be difficult to identify the existence of SM trimers in solution through experimental data.

4. CONCLUSIONS

The solvatochromic reversal behavior observed in stilbazolium merocyanine dye in nonpolar solvents has mostly been attributed either to a solvent polarity-dependence of the ground state geometry or to self-aggregation of dye molecules. While there are many theoretical reports that have addressed the former issue, the exploration into the second aspect has largely remained open. As these two hypothesis are not exclusive, there is a need for explicitly studying the contributions to the optical property due to the possible self-aggregation. Here, we present the first direct theoretical modeling of self-aggregation of the stilbazolium merocyanine molecule in solution and the effect of that for the optical properties. Our study shows that stilbazolium merocyanine in chloroform may form oligomers, and we find that respectively 43% and 44% of the chromophores have been involved in the formation of dimer and trimer populations, in the equilibrated situation. However, at this level we find no evidence that this aggregation promotes any significant shift in the absorption spectrum. The reason is that the formation of H-aggregates (head-to-tail interaction mode of the monomers) yield centrosymmetric forms of the dimers and trimers. From calculations based on geometry optimized structures, we have found that the interplanar distance of the dimer and trimer units can alter the intensity of their energy transitions, however this only affects the spectral shape of the absorption spectrum. The main message of this study is that, while self-aggregation of stilbazolium merocyanine dye molecules in chloroform is found to occur, this does not seem to influence the optical absorption properties to any appreciable extent.

AUTHOR INFORMATION

Corresponding Author

*E-mail: dlsilva.physics@gmail.com.

Notes

The authors declare no competing financial interest.

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