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Conformational Switching and Exciton Interactions in Hemicyanine-Based Bichromophores

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Abstract: Conformational changes in two hemicyanine-based bichromophores were demonstrated by varying the polarity as well as temperature of the medium. Dramatic changes in the ground and excited singlet state properties were observed upon folding of the bichromophores, due to the formation of intramolecular aggregates of H-type. These aspects were studied, in detail, using steady-state absorption and time-resolved fluorescence spectroscopy. Time-resolved fluorescence studies indicate that both the bichromophores exhibit a monoexponential decay, with a short lifetime, in mixed toluene−CH_2Cl_2 solvents having lower proportions of toluene. Interestingly, biexponential decay with short and long-lived species was observed at higher proportions of toluene, due to the presence of unfolded and folded forms. Folding results in the intramolecular stacking of the chromophores which restrict their torsional dynamics, leading to a longer lifetime. Upon laser excitation, the folded form of the bichromophore undergoes rapid conformational changes, due to photoinduced thermal dissociation.

Introduction

The design and study of molecular as well as supramolecular photoactive systems have been actively pursued in recent years, due to their potential applications in optoelectronic devices[1−6] (for e.g., molecular switches,[2−4] sensors,[3] transducers,[5] and information processing and storage devices[6]). Of particular interest is the design of molecular systems which undergo conformational changes,[7−9] analogous to the folding of proteins.[10] Synthetic molecular systems and polymers which can fold into well-defined conformation in solution (foldamers[11]), through noncovalent interactions, have been reported. These include (i) solvophobically driven conformational folding of phenylacetylene-based oligomers into ordered helical structures[7] and (ii) the donor−acceptor interaction of aromatic groups, leading to pleated structures.[8] Conformational changes and molecular motions in photoactive molecular and supramolecular systems can be modulated by chemical, photochemical, or electrochemical methods.[1,2] Such changes when translated to optical as well as electronic properties can form the basis of switching devices.[1] We have now designed two nonconjugated bichromophores (1 and 2 in Scheme 1), which can fold and unfold by varying the solvent polarity or by the application of external stimuli such as heat or light.

Earlier studies on nonconjugated bichromophores of cyanines,[12] squaraines,[13] and porphyrins[14] mainly deal with the interaction between the chromophores. In contrast with aromatic compounds which form molecular associates in their excited states (e.g., pyrene[15]), chromophoric dyes have a unique ability to self-organize into aggregates in their ground state. Interaction between the chromophores in their ground state has been fairly well explained by McRae and Kasha[16a] in terms of exciton coupling theory, in which the excited state of the dye aggregate splits into two energy levels (Davydov splitting). The transition to the upper excited state is allowed in the case of face-to-face

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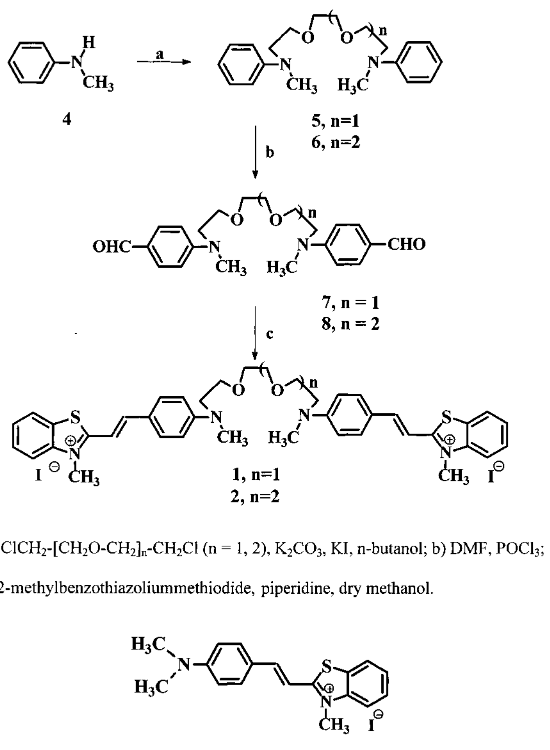
Scheme 1. Synthesis of the Bichromophores **1** and **2**



a) $ClCH_2$-$[CH_2O$-$CH_2]_n$-CH_2Cl (n = 1, 2), K_2CO_3, KI, n-butanol; b) DMF, $POCl_3$;

c) 2-methylbenzothiazoliummethiodide, piperidine, dry methanol.

(parallel) dimers and to the lower state for head-to-tail (linear) dimers.[16] The former type of dimer is characterized by a hypsochromically shifted absorption band (H-aggregate) and the latter one by a bathochromically shifted absorption band (J-aggregate), as compared to the isolated monomer. Recently, some interesting observations have been made in the case of nonconjugated dimers of a few merocyanines[12a] and squaraines,[13] tethered by methylene groups. For both these systems, an extended conformation is preferred in nonpolar solvents and a folded one in polar solvents, leading to J- and H-aggregates, respectively. In contrast to the squaraine dimers, which do not fluoresce, an excimer-type fluorescence was observed from the folded form of merocyanine dimers. The studies on bichromophores, reported so far, deal mainly with chromophoric interactions, and it is possible to design bistable systems by modulating their optical properties. In the present study, we report the dynamics of folding–unfolding processes of two nonconjugated bichromophores containing hemicyanine units (hemicyanines are polymethines containing heterocyclic and nonheterocyclic groups on either end) linked together by a poly(ethylene glycol) chain (Scheme 1). The conformational switching in these molecular systems led to substantial changes in their singlet excited-state properties, due to the formation of intramolecular aggregates.

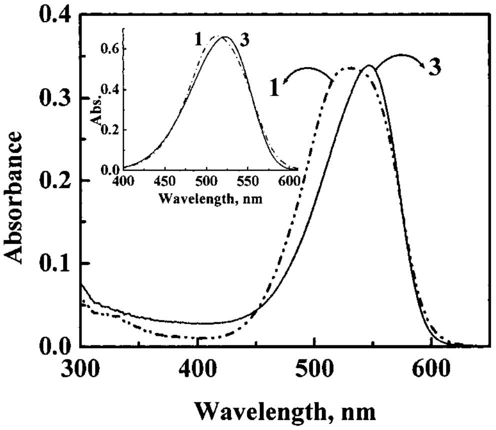


Figure 1. Absorption spectra of bichromophore **1** and model compound **3** in dichloromethane. Inset shows the absorption spectra of **1** and **3** in methanol.

Table 1. Absorption and Emission Properties of Compounds **1**–**3** in Dichloromethane

	absorption		fluorescence	
compd	λ_{max}, nm (ϵ, $M^{-1}cm^{-1}$)	$\Delta\nu_{1/2}$, cm^{-1}	λ_{max}(em.)[a]	Φ_f[b]
1	540 (104940)	2979	600	0.01
2	540 (107000)	2979	600	0.0098
3	553 (89563)	2283	597	0.018

[a] Solutions were excited at 500 nm and emission monitored in the region 520–700 nm for estimating ϕ_f; [b] error limit ± 5%.

Results and Discussion

Synthesis. Bichromophores **1** and **2**, containing two units of hemicyanines ((aminostyryl)benzothiazolium chromophores), were synthesized through the pathways shown in Scheme 1. Synthesis and spectroscopic characterization of the bichromophores are given in the Experimental Section and the details of the intermediate compounds are included in the Supporting Information. The model compound **3** (Scheme 1) was prepared by following a reported procedure.[17] On the basis of the ^1H NMR studies, it is concluded that **1** and **2** adopt an "all-trans" geometry, which minimizes the steric interactions in the bichromophores.

UV/Vis Absorption and Conformational Switching. The absorption spectra of bichromophore **1** and model compound **3** in dichloromethane and methanol are presented in Figure 1. The spectral properties of **1**–**3** in dichloromethane are summarized in Table 1. Both the bichromophores exhibit a broad band centered around 540 nm in CH_2Cl_2. The absorbance of this band follows Beer Lambert law and the spectral shape remains unaffected with concentration, ruling out the possibility of strong intra- or intermolecular interactions. Thus, the broad band, absorbing around 540 nm, may correspond to the monomeric form of the bichromophores. Similar results were obtained for model compound **3** and bichromophores, in polar solvents such as $CHCl_3$, CH_3CN, CH_3OH, etc. The origin of this structureless absorption band is attributed to a donor–acceptor charge-transfer (CT) transition (Supporting Information). Recent X-ray diffraction studies[18] as well as absorption spectral studies[19a] have also suggested an intramolecular charge-transfer resonance between

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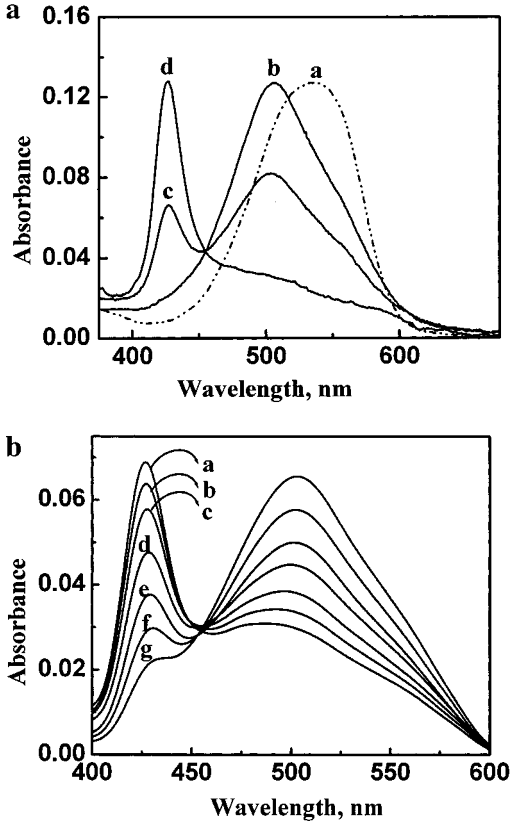
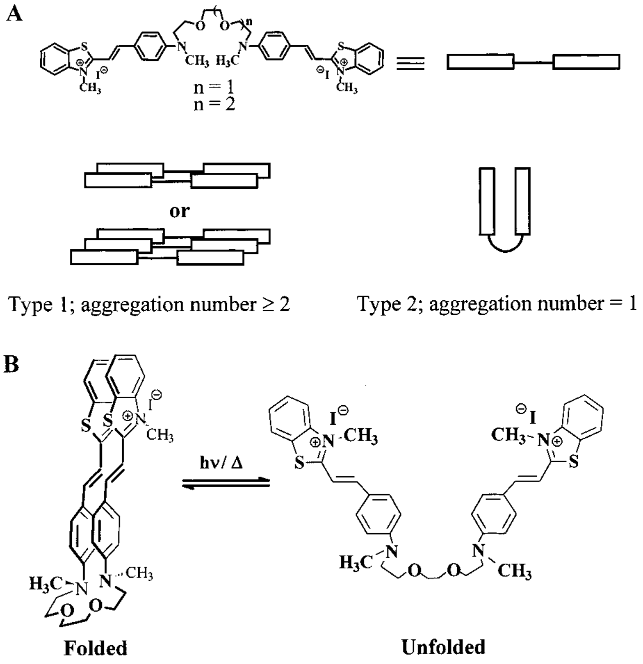


Figure 2. (a) Visible absorption spectra of **1** at 25 °C in mixed toluene−CH_2Cl_2 solvents of the following proportions (toluene:CH_2Cl_2): (a) 0:100, (b) 70:30, (c) 75:25, and (d) 95:5. (b) Visible absorption spectra of **1** at various temperatures in a (4:1) mixture of toluene and CH_2Cl_2 (a) 15, (b) 20, (c) 24, (d) 28, (e) 32, (f) 36, and (g) 38 °C.

the nitrogen atoms in hemicyanine dyes. The half-width of the absorption band ($\upsilon_{1/2}$) of **3** in CH_2Cl_2 is 2200 cm^{-1} and a spectral broadening was observed with increase in polarity of the solvent (Supporting Information). There are several bonds in hemicyanines, which may undergo torsional motions. It is suggested that the torsional motions, coupled with solvent reorganization may lead to spectral broadening of hemicyanines, in polar solvents.[19b] Compared to **3**, both the bichromophores **1** and **2** exhibit a broad absorption band and $\upsilon_{1/2}$ is not influenced by solvent polarity ($\upsilon_{1/2} \sim 3000$ cm^{-1}). The chromophoric units in **1** and **2** are linked together by a flexible poly(oxoethylene) chain. Depending on the nature of the solvent, the poly(oxoethylene) bridging unit can adopt various conformations,[9c] which may result in weak through-space interactions between the two hemicyanine units, in **1** and **2**. These factors along with the torsional motions of the hemicyanines may lead to the broadening of the absorption spectrum.

Addition of varying amounts of toluene to a solution of **1** in CH_2Cl_2 led to a gradual hypsochromic shift in its absorption band (Figure 2a). Interestingly, on increasing the toluene content in a solution of **1** in CH_2Cl_2 (25 °C), a decrease in the intensity of the monomer band was observed, accompanied by the formation of a sharp band at 420 nm (traces "c" and "d" in Figure 2a). The intensity of the 420 nm band is markedly higher at lower temperatures (Figure 2b). A complete reversal to the monomeric form was observed with an increase in temperature,

Scheme 2. (A) Pictorial Representation of the Aggregation of Bichromophore (Type 1, card pack arrangement; Type 2, intramolecular folding) and (B) an Illustration of the Folding−Unfolding Process of Bichromophores Based on the Photophysical Studies



indicating that an equilibrium process is involved. Similar results are observed for the bichromophore **2** (Supporting Information).

Cyanines and squaraines derived from benzothiazolium units are known to form face to face or parallel dimers (H-aggregates), characterized by the appearance of a blue-shifted absorption band.[20] In the present case, the new high-energy band, observed at 420 nm, may be assigned to an H-aggregate, arising from the parallel stacking of the hemicyanine chromophores, on the basis of analogy. Parallel stacking is possible in two different ways: (i) through an intermolecular interaction between two or more bichromophores (aggregation number ≥2) in a card pack arrangement or (ii) through an intramolecular interaction between two hemicyanine units of the bichromophore, as a result of folding of the molecule (aggregation number = 1). A simplified representation of these possibilities is shown in Scheme 2A. Additional information concerning the nature of stacking was obtained by investigating the aggregation properties of the bichromophores. The aggregation numbers of **1** (Figure 3) and **2** were determined by studying the effect of concentration of the bichromophores on the absorption spectrum. Monomer and aggregate bands are well separated and the spectral overlap at the absorption maximum is negligible (Figures 2 and 3). The extinction coefficients of **1** and **2** were estimated at their peak maxima in a 7:3 mixture of toluene and CH_2Cl_2 (aggregation is not observed in this solvent composition at 25 °C). The concentrations of the monomer and aggregate were estimated[21] and they followed a linear dependence for both the bichromophores. The plot of log[monomer] versus log[aggregate] was found to be linear and the aggregation number was estimated

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(21) The equilibrium constants (K = [F]/[UF]) were estimated from the concentrations of the unfolded form ([UF] = absorbance of UF/ϵ of UF) and the folded form ([F] = total concentration − [UF]).

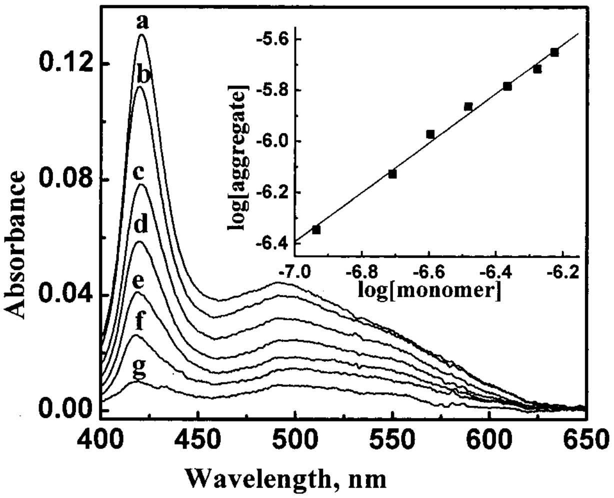

Figure 3. Visible absorption spectra of **1** at different concentrations (0.56−2.84 μM) in a 17:3 mixture of toluene and CH_2Cl_2 at 25 °C. The inset shows the plot of log [aggregate] vs log [monomer].

as 1, from the slope. A representative example is shown in the inset of Figure 3. These results indicate the formation of intramolecular aggregates of Type II (Scheme 2A), wherein the bichromophoric system undergoes a folding process. Thus, as shown in Scheme 2B the bichromophores can exist in two extreme conformations, folded and unfolded, depending on the polarity and temperature. The sharp band with absorption at 420 nm probably corresponds to a folded conformation. The long wavelength band observed in the 450−600 nm region corresponds to an unfolded geometry where the bichromophores can exist in several disordered conformations.

Solvent-dependent conformational changes in poly(oxoethylene) linkers were investigated by theoretical as well as experimental methods.[9c,22] It is reported that the carbon−carbon bond of the $-OCH_2CH_2O-$ unit exists predominantly in the gauche conformation in a high polar medium, but shifts to the trans conformation in a low polar medium.[22] Solvent-dependent conformational changes in poly(oxoethylene)-linked binuclear complexes were investigated recently by probing the photoinduced energy transfer.[9c] In polar solvents, the unfolded conformation of bichromophores may be more stable due to the presence of the gauche conformation. The polarity-dependent conformational changes of the bridging unit and the solvophobicity of the dye in nonpolar medium help in the folding of **1** and **2**, overcoming the Coulombic repulsion between the chromophores. Solvophobically driven folding processes were recently reported for substituted phenylacetylene oligomers[7] and merocyanine dimers.[12a,20b] In the present case, both the molecular systems prefer a well-ordered folded conformation in nonpolar medium with parallel stacking of the chromophores (Scheme 2B), since such an arrangement can minimize the polar chromophoric surface exposed to the nonpolar solvent.

One of the interesting features of these bichromophores is their ability to undergo temperature-dependent conformational changes. The folding−unfolding process in bichromophores is highly sensitive to the temperature of the medium (for e.g., Figure 2b) and the interconversions are possible in a smaller temperature range. The equilibrium constants ($K_{24°C}$) for the formation of intramolecular aggregates of **1** and **2** through the folding are estimated as 1.2 and 3.5, respectively. These values are orders of magnitude lower than those reported for the intermolecular dimerization constants of merocyanines, which are mainly driven by electrostatic dipole−dipole interactions.[23a] The free energy for the formation[23b] ($-\Delta G_{24°C}$) of the intramolecular aggregates of **1** and **2** was estimated as 0.35 and 3.1 kJ mol^{-1}, respectively. The low value of the equilibrium constant and free energy of formation of the homoaggregates are advantageous in the present case, since they permit the interconversion in a smaller temperature range (15−35 °C). Formation of intermolecular aggregates of **3** was not observed under identical conditions.

Steady-State Emission Properties. Recent investigations[24] of the excited state properties of hemicyanine dyes suggest that (i) the singlet excited state of the chromophore deactivates mainly through bond twisting (rotamerism[24a,b]) and rigidization by structural modifications[24c] prevent the nonradiative deactivation and (ii) the substitution of the dialkylamino group in hemicyanines markedly reduces the trans−cis isomerization.[24d] The model compound **3** in CH_2Cl_2 has a broad emission spectrum with a maximum centered around 597 nm. The quantum yield of fluorescence (0.018 in CH_2Cl_2 at 25 °C) was found to be independent of the excitation wavelength. Viscosity-dependent studies of **3** indicate that the singlet excited state of the chromophore deactivates through competing radiative and nonradiative channels (Supporting Information). In the present case an enhancement in the fluorescence quantum yield (Φ_f) and lifetime (τ_s) was observed for **3** in viscous medium. Rigidization of the molecule in viscous medium may retard the nonradiative decay channels such as bond twisting in the excited state.

Conformational switching of **1** and **2** was studied by steady state and time-resolved fluorescence techniques. The unfolded forms of both bichromophores in CH_2Cl_2 emit around 600 nm (Table 1), with almost identical quantum yields ($\Phi_f \sim 0.01$). A substantial lowering of emission yield was observed for both bichromophores on increasing the toluene content. The relative emission intensities of **1** (excited at the isosbestic point) in mixtures of dichloromethane and toluene are shown in Figure 4. Lowering of the emission yield is attributed to the formation of intramolecular aggregates, resulting from the folding of the bichromophores. The folded form of the bichromophores (in a 19:1 mixture of toluene and CH_2Cl_2) was further selectively excited at 420 nm, where the unfolded form does not absorb. An emission spectrum having a similar spectral shape as that of the unfolded form with an extremely low yield ($\phi_f < 10^{-4}$) was observed in the case of the folded forms of **1** and **2**. It has been reported that intermolecular aggregates of cyanine dyes possess lower fluorescence yields and longer singlet lifetimes than their corresponding monomers.[20a] On the basis of the exciton theory, the transition to the upper energy level is allowed for the H-aggregates, which rapidly deactivate to the lower energy level via internal conversion. The emission from the lower energy level is theoretically forbidden[16] and hence the singlet excited state of the bichromophoric aggregate gets trapped in a low emissive state. Schematic representation of the energy level of the unfolded and the folded forms of the bichromophores is proposed in Scheme 3. The effect of addition of toluene on the quantum yield of fluorescence of **3** in CH_2Cl_2 is shown in the inset of Figure 4 for comparison. A slight increase in ϕ_f was observed for **3** on increasing the proportions

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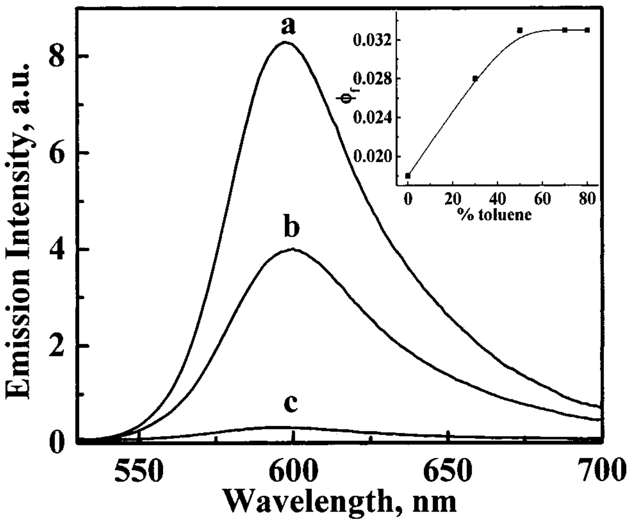
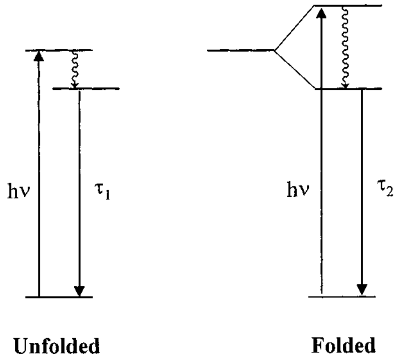


Figure 4. Emission spectra of **1** at 25 °C in mixtures of toluene and CH_2Cl_2 (toluene:CH_2Cl_2): (a) 3:7, (b) 1:1, and (c) 4:1. The solutions were excited at the isosbestic point (450 nm). The inset shows the effect of addition of toluene on the quantum yield of fluorescence of **3** in CH_2Cl_2. The solutions were isoabsorptive at the excitation wavelength (500 nm).

Scheme 3. Schematic Representation of the Energy Levels of the Unfolded and Folded Forms of the Bichromophores



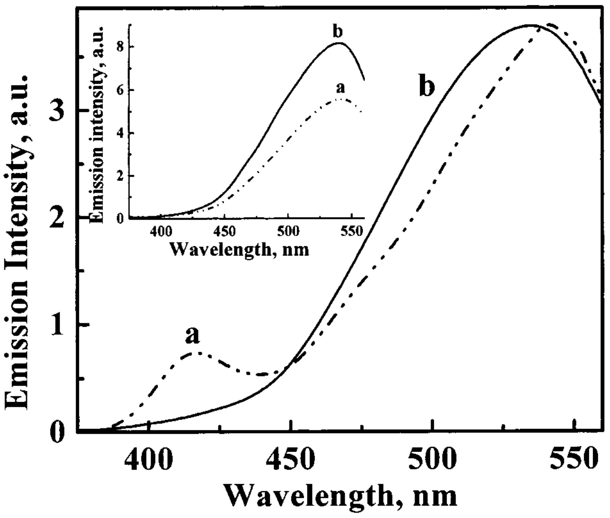


Figure 5. Excitation spectra of **1** (6 μM) in mixtures of toluene and CH_2Cl_2 (toluene:CH_2Cl_2): (a) 17:3 and (b) 1:1. The inset shows the excitation spectra of **3** (6 μM) in the same solvent mixtures (emission monitored at 580 nm for **1** and **3**).

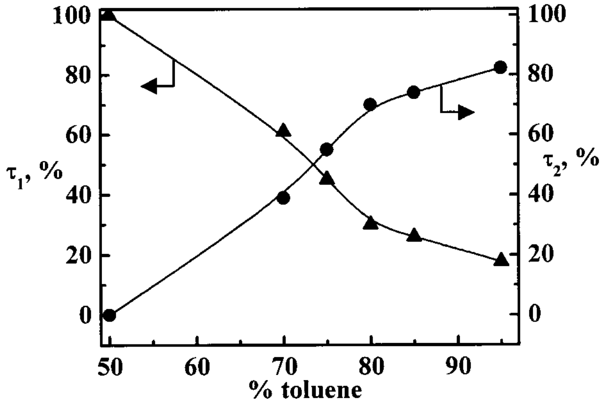


Figure 6. Relative distribution of the folded and unfolded forms of **1** at 20 °C, on addition of toluene to a solution of **1** in CH_2Cl_2.

Table 2. Fluorescence Lifetimes[a–c] and Fractional Contributions[d,e] of **2** in Mixed Toluene−CH_2Cl_2 Solvents at 20 °C

toluene:CH_2Cl_2	τ_1, ns (χ_1, %)	τ_2, ns (χ_2, %)
1:1	0.37 (100)	
3:1	0.33 (56)	3.08 (44)
17:3	0.33 (35)	3.76 (65)
19:1	0.76 (21)	4.20 (79)

[a] $\tau_1$and τ_2. [b] The quality of the fit is judged by means of the usual statistical parameters such as χ^2 (1.10−1.29); error limit ±5%. [c] Excited at 440 nm and emission followed at 600 nm. [d] χ_1 and χ_2. [e] Fractional contributions of **1** are presented in Figure 6.

of toluene and is attributed to the decrease in polarity of the medium. The lack of strong ϕ_f dependency of **3** in mixtures of toluene−CH_2Cl_2 further supports the formation of intramolecular H-aggregates of the bichromophores.

The origin of the emission of the folded and unfolded forms was confirmed by recording the excitation spectra of the bichromophores as a function of solvent composition (Figure 5). The excitation spectrum of **1**, recorded in a 1:1 mixture of toluene and CH_2Cl_2 (25 °C), possesses a broad band around 540 nm, which closely matches with the absorption characteristics of the unfolded bichromophore (Figure 2a). In a 17:3 mixture of toluene and CH_2Cl_2, the excitation spectrum of **1** (trace a) exhibits a band at 420 nm, apart from the long wavelength band, and matches with the corresponding absorption spectrum in spectral shape (Figure 2). The intensity of the long wavelength band is higher in the excitation spectrum due to the higher emission yield of the monomer, compared to the aggregated form. These results further confirm that the emission of the folded form originates from the 420 nm band and that of the unfolded form originates from the 540 nm band. The excitation spectrum of **3**, in both the solvent mixtures, is shown in the inset of Figure 5 for comparison and the 420 nm band is absent.

Fluorescence Lifetimes. Characterization of the singlet excited states of the folded form as well as the unfolded form of **1** and **2** was achieved by investigating the singlet lifetimes as a function of solvent composition and temperature. Both the bichromophores exhibited monoexponential decay with a short lifetime (~350 ps) in mixed toluene−CH_2Cl_2 solvents, with lower proportions of toluene (<50%) at 20 °C. Interestingly, both the bichromophores exhibited biexponential decay, with a short-lived (τ_1) and long-lived (τ_2) component (Figure 6 and Table 2) on increasing the proportions of toluene (>70%) at 20 °C. Gradual increase in singlet lifetimes was observed, for both forms, with a decrease in the temperature of the medium (Table 3). Biexponential behavior, observed for both bichromophores in CH_2Cl_2 containing a high composition of toluene, is due to the presence of folded and unfolded forms. The short-

Table 3. Fluorescence Lifetimes[a−c] and Fractional Contributions[d] of **1**[e] as a Function of Temperature

temp (°C)	τ_1, ns (χ_1, %)	τ_2, ns (χ_2, %)
17.5	0.51 (25)	4.23 (75)
21	0.41 (38)	3.69 (62)
25	0.42 (49)	3.72 (51)
27	0.33 (51)	3.15 (49)
33	0.27 (72)	3.06 (28)

[a] $\tau_1$and τ_2. [b] The quality of the fit is judged by means of the usual statistical parameters such as χ^2 (0.88−1.16); error limit ±5%. [c] Excited at 440 nm and emission followed at 600 nm. [d] χ_1 and χ_2. [e] 75% (v/v) toluene/CH_2Cl_2.

lived species is assigned as the unfolded form and the long-lived component as the folded form of the bichromophore. Intramolecular folding of **1** and **2** may result in the parallel stacking of the two chromophores, which can restrict the torsional dynamics of the hemicyanines, leading to longer lifetimes.[20a] Similar results were obtained for the model compound in viscous medium, in which the singlet excited state exhibits a longer lifetime, due to restricted motion (Supporting Information).

The interconversion between the folded and unfolded forms was further investigated by plotting their fractional contributions of lifetimes as a function of solvent polarity (Figure 6) and temperature. The population of the long-lived species increased substantially for both the bichromophores on (i) increasing the toluene content (Figure 6) and (ii) decreasing the temperature of the medium (Table 3). A complete reversal in the fractional contribution of lifetimes was observed on increasing the temperature of the medium.

Laser Flash Photolysis Studies. We have examined the photoprocesses in the folded and unfolded forms of bichromophores employing the laser flash photolysis technique. The folded form was excited using an excimer pumped dye laser (420 nm) and the unfolded form using a Nd:YAG laser (532 nm).

In polar solvents, such as methanol, both bichromophores exist in the unfolded form and no transient was observed in the nanosecond time scale. Interestingly, a transient absorption was observed around 420 nm for **1**, in a 1:1 mixture of toluene and CH_2Cl_2 (Figure 7a). The transient decay at 420 nm (inset of Figure 7a) consists of a major short-lived ($k_1 = 1.07 \times 10^4$ s^{-1}) and a minor long-lived component ($k_2 = 6.32 \times 10^3$ s^{-1}). The major component is quenched by O_2, ferrocene, and β-carotene.[25] On the basis of these results and the similarity of spectral behavior to those reported for other hemicyanines,[24d] the major transient species is assigned as a triplet. In less polar solvents, the bichromophores may be existing as a contact ion pair and the heavy atom induced intersystem crossing leads to the formation of a triplet. A transient species with similar properties, observed on addition of I^- to a methanolic solution of bichromophore, further confirmed the heavy atom induced triplet formation. The yield of the minor component (k_2) is less than 10% and hence no attempt was made to establish its identity.

Laser pulse excitation of the folded form of bichromophores results in their unfolding. The transient spectrum of the folded form of the bichromophore **1** in a 9:1 mixture of toluene and CH_2Cl_2, observed immediately after the laser pulse, is shown in Figure 7b. The unfolding process is prompt and we could not observe it in the nanosecond time scale. The transient formed was not quenched by O_2. The negative absorbance observed in the spectral region of 375−450 nm is due to the laser-induced depletion of the ground state of the folded form. The band observed at 450−600 nm corresponds to the ground-state absorption of the unfolded form and it does not decay up to 100 μs (100 μs is the highest detection limit of our equipment). The ground state absorption spectra recorded before and after the laser flash photolysis remained unchanged, indicating that the refolding process is completely reversible and occurs in the time scale longer than 100 μs. Intermolecular aggregates of cyanines were reported to disrupt under laser excitation through photoinduced thermal dissociation,[20b] whereas in the case of squaraines a photodissociation mechanism[20c] has been suggested. In the present case, laser excitation of the folded forms of **1** as well as **2** may cause a local temperature jump, leading to the unfolding of bichromophores.

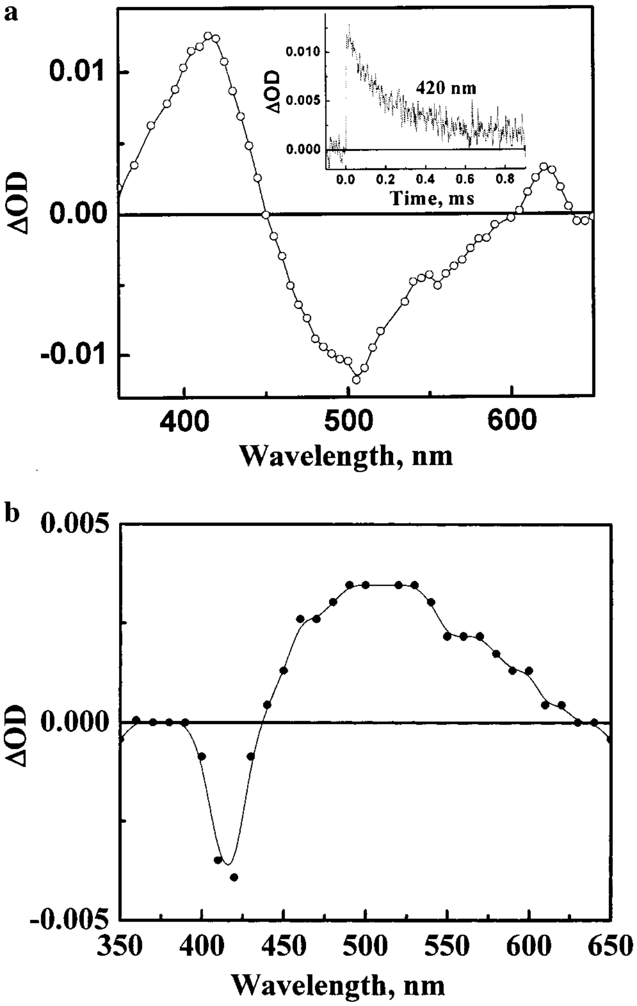


Figure 7. (a) Transient absorption spectrum measured following laser pulse excitation (532 nm, ∼120 mJ/pulse) of the unfolded form of **1** in a 1:1 mixture of toluene and CH_2Cl_2. The inset shows the transient decay at 420 nm. (b) Transient absorption spectrum measured following laser pulse excitation (420 nm, ∼10 mJ/pulse) of the folded form of **1** in a 9:1 mixture of toluene and CH_2Cl_2.

Conclusions

The newly designed hemicyanine-based bichromophores possess a unique property of folding−unfolding and their interconversion was achieved by varying the polarity of the medium or temperature. Both the bichromophores prefer a well-defined folded conformation in nonpolar medium and the solvent-dependent conformational changes of the poly(oxoethylene) linker group as well as the solvophobicity of the

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(25) Carmichael, I.; Hug, G. L. *J. Phys. Chem. Ref. Data* **1986**, *15*, 1.

chromophores in nonpolar solvents drive the folding process, overcoming the Coulombic repulsion. The laser flash excitation of the folded form results in fast conformational changes due to photoinduced thermal dissociation. The conformational switching in such bichromophores could lead to the design of a novel type of molecular switching devices. Also, similar strategies of chromophoric interactions can be employed for probing conformational changes in macromolecular systems.

Experimental Section

All melting points are uncorrected and were determined on an Aldrich melting point apparatus. IR spectra were recorded on a Perkin-Elmer Model 882 IR spectrometer and the UV−visible spectra on a Shimadzu UV-3101PC UV−vis−NIR scanning spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-300 MHz spectrometer. Emission spectra were recorded on a SPECTRACQ spectrofluorimeter and corrected using the program supplied by the manufacturer. The quantum yield of fluorescence was determined by a relative method using optically dilute solutions of the dyes (OD of 0.1 at the excitation wavelength) using Rhodamine 6G in ethanol ($\Phi_f = 0.9$) as standard. Fluorescence lifetimes were measured using a Tsunami Spectra Physics single photon counting system. A Ti Sapphire laser, having a fundamental wavelength of 880 nm, was used as an excitation source. The average output power is 680 mW with a pump power of 4.5 W. The pulse width of the laser is <2 ps. The flexible harmonic generator (FHG) gives the second harmonic (440 nm) output from the Tsunami laser system. The fluorescence was detected using a two-stage microchannel plate photomultiplier (MCP-PMT R38094). The fluorescence decay measurements were further analyzed using the IBH software library, which includes an iterative shift of the fitted function as part of χ^2 goodness of the fit criterion. Laser flash photolysis of the unfolded form was carried out in an Applied Photophysics model LKS-20 laser kinetic spectrometer using the second harmonic (532 nm) of a Quanta Ray GCR-12 series pulsed Nd:YAG laser with a pulse duration of 10 ns band energy of 120 mJ/pulse. Laser flash photolysis experiments of the folded form were carried out using a Lambda Physik Lextra 50 excimer laser pumped scanmate 2 dye laser. The excitation wavelength was 420 nm. All solutions for laser flash photolysis were deaerated by bubbling argon for 15 min unless otherwise indicated.

General Method for Synthesis of Bichromophores (1 and 2). A mixture of 2-methylbenzothiazoliummethiodide (1 mmol) and the appropriate *N*-methyl(*p*-formyl)aniline-tethered glycol (0.5 mmol) was refluxed in methanol (50 mL) in the presence of piperidine (2 drops) for 72 h under argon atmosphere. The solvent was removed under reduced pressure and the crude product was chromatographed over neutral alumina.

Bichromophore 1. Elution of the column using a mixture (2:5) of methanol and chloroform gave 0.2 g (43%) of **1** as a solid. Mp 217−218 °C dec; IR (KBr) ν_{max} 1776, 1739, 1668, 1534, 1457, 1392, 1273, 1183, 815, 758 cm^{-1}; ^{1}H NMR (CDCl$_3$ + DMSO-d_6) δ 8.23 (d, J = 7.75 Hz, 2H), 8.03 (d, J = 8.28 Hz, 2H), 7.94 (d, J = 15.2 Hz, 2H), 7.83 (d, J = 8.54 Hz, 4H), 7.71 (t, J = 7.67 Hz, 2H), 7.61 (t, J = 7.52 Hz, 2H), 7.49 (d, J = 15.33 Hz, 2H), 6.79 (d, J = 8.6 Hz, 4H), 4.17 (s, 6H), 3.2−3.9 (m, 12H), 3.04 (s, 6H); ^{13}C NMR (CDCl$_3$ + DMSO-d_6) δ 153.62, 151.23, 141.44, 133.99, 128.84, 127.15, 126.84, 123.98, 121.85, 114.87, 112.25, 107.55, 105.22, 98.27, 96.09, 71.07, 68.53, 52.13, 29.65; HRMS calcd for $C_{40}H_{44}N_4O_2S_2I_2$ [M − I]$^+$ 803.1950, found 803.1964 (FAB high-resolution mass spectroscopy).

Bichromophore 2. Elution of the column using a mixture (1:9) of methanol and chloroform gave 0.22 g (45%) of **2** as a solid. Mp 143−145 °C dec; IR (KBr) ν_{max} 1587, 1534, 1519, 1435, 1389, 1343, 1268, 1183, 1116, 1031, 985, 813, 758, 717, 638, 519 cm^{-1}; ^{1}H NMR (CDCl$_3$ + DMSO-d_6) δ 8.27(d, J = 7.83 Hz, 2H), 8.07(d, J = 8.37 Hz, 2H), 7.96 (d, J = 15.26 Hz, 2H), 7.85 (d, J = 8.54 Hz, 4H), 7.74 (t, J = 7.77 Hz, 2H),7.64 (t, J = 7.61 Hz, 2H), 7.54 (d, J = 15.32 Hz, 2H), 6.83 (d, J = 8.73 Hz, 4H), 4.20 (s, 6H), 3.2−3.9 (m, 16H), 3.07 (s, 6H); ^{13}C NMR (CDCl$_3$ + DMSO-d_6) δ 171.65, 153.29, 150.38, 142.33, 133.33, 129.29, 127.85, 127.22, 124.22, 121.93, 116.36, 112.45, 106.55, 104.79, 70.48, 70.39, 68.36, 51.68, 36.08; HRMS calcd for $C_{42}H_{48}N_4O_3S_2I_2$ 847.2213 [M − I]$^+$, found 847.2186 (FAB high-resolution mass spectroscopy).

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Supporting Information Available: Details of the synthesis of the intermediate compounds **5**−**8**, aggregation properties of **2**, and the absorption and emission properties of **3** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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