

Exciton and Charge-Transfer Interactions in Nonconjugated Merocyanine Dye Dimers: Novel Solvatochromic Behavior for Tethered Bichromophores and Excimers

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Abstract: A series of merocyanine dye dimers tethered at different sites with spacers ranging from 0 to 5 methylene groups and the corresponding monomer have been synthesized. The formation, structure, and excited-state properties of the consequent merocyanine dye “aggregates” in solutions and in rigid glass have been studied by UV-visible absorption spectra, steady-state fluorescence, and fluorescence lifetime measurements. The dimers with 0 and 1 methylene spacers must exist in more-or-less extended conformations; consequently, they show a very weak and distance-dependent “J”-type exciton coupling, evident in both absorption and fluorescence spectra. For the dimers with 2, 3, and 5 methylene spacers, absorption spectra in nonpolar solvents are consistent with a largely extended configuration and little or no evident exciton coupling. However, for more polar solvents, a blue-shifted absorption spectrum is observed, suggesting a folded configuration resulting in an “H” dimer. For the latter dimers, fluorescence spectra in a variety of solvents show a pronounced red-shift, which is attributed to a folded “excimer”. As anticipated from its structure, the merocyanine monomer shows a weak positive solvatochromic effect that may be correlated using the Taft–Kamlet π^* parameter. Remarkably, both the “J” coupled dimer ($n = 0$) and the dimers having 2–5 methylene groups show a much stronger solvatochromic behavior than the monomer. The strong solvatochromic effects in these tethered dimers may be attributed to interchromophoric charge-transfer interactions in both ground and excited states.

Introduction

Due to the wide applications of cyanine, squaraines, and related dyes in color photography, photovoltaics, and other imaging processes and their use in solid-state or interfacial systems, their aggregation and their photophysical and photochemical behavior have been the subject of considerable research interest. Most of the previous work on these dyes involved investigation of moderate-to-large intermolecular aggregates, including both red-shifted “J” aggregates and blue-shifted “H” aggregates, and the relationship between aggregate structure, size, and associated spectral features.^{4–6} Relatively few experimental studies have dealt with tethered dimers and their photophysics;^{7,8} however, recently some interesting results have been obtained for tethered squaraine dimers.⁹ In these systems, strong excitonic interactions are observed which are ascribed to different configurations. In nonpolar solvents, a prominent red-shifted spectral transition is observed (“J”-type coupling),

which has been attributed to an extended configuration. This coupling falls off with an increase in tether length but is perceptible up to six methylene groups. In contrast, in polar solvents, a predominantly blue-shifted spectrum is observed for the “dimers”, which is attributed to an “H”-type or folded configuration. Comparison of the fluorescence of the “J” dimers in fluid nonpolar solvents with that in rigid sucrose octaacetate (SOA) glass shows that the extended form rapidly converts to a folded form upon excitation to the excited singlet of the “J” dimer. As an extension of these studies, we have synthesized a series of tethered merocyanine dye dimers to examine excitonic interactions and photophysical behavior and their solvent sensitivity in a system in which the corresponding monomer would be expected to exhibit moderate to strong solvatochromic behavior. The results obtained with this series of dimers show both some similarities and interesting differences from the previously investigated squaraines and other tethered dimers. As might be anticipated from their lower oscillator strengths, the merocyanines in extended configurations show a less pronounced “J”-type exciton coupling, which quickly falls off as the tether length is increased. However, quite analogously to the flexible squaraine dimers, we find strong evidence indicating that an extended configuration is preferred for nonpolar organic solvents, while in polar solvents a folded form may be favored. Also, in accord with the behavior of the squaraines, we find evidence that the extended form may rapidly undergo a change in geometry following photoexcitation, even in nonpolar solvents, resulting in very short fluorescence

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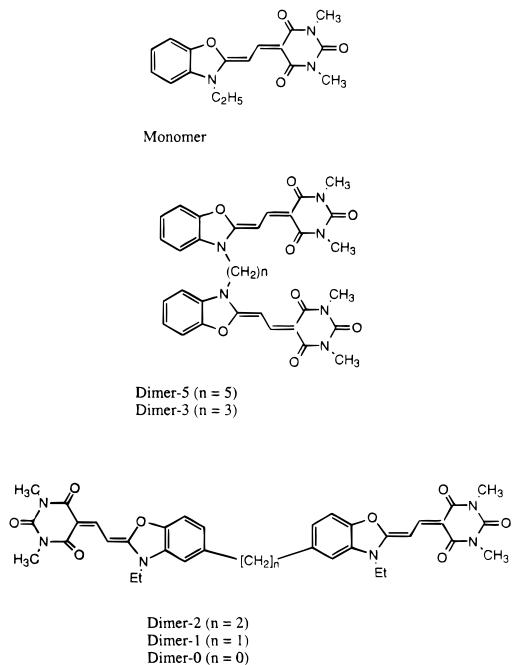
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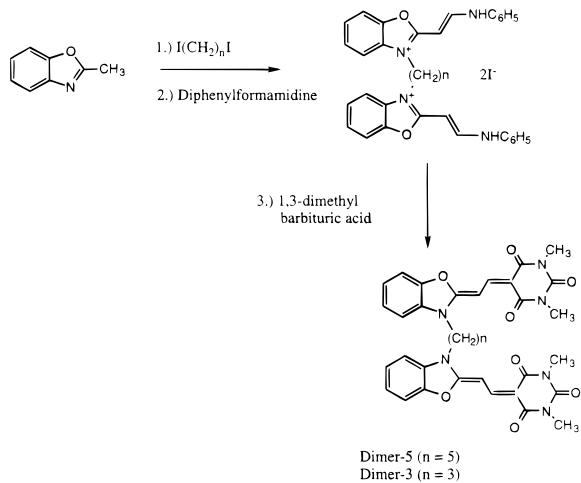
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Chart 1. Merocanine Dyes Used in This Study



Scheme 1. Syntheses of Dimer-5 and Dimer-3



lifetimes. In contrast to the squaraines, we observe prominent fluorescence from the folded forms of the merocyanine dimers that closely resembles the excimer fluorescence observed from tethered dipyrenyl alkanes and related compounds.^{10,11} Perhaps the most striking results of the present study are the findings of strong solvatochromic effects on both absorption and fluorescence spectra of the folded and extended exciton coupled states.

Results

The structures of the monomer merocyanine dye and the tethered dimers synthesized in this study are shown in Chart 1. The syntheses of the different dyes are outlined in Schemes 1 and 2. Although it is usually difficult to grow single crystals of merocyanine dyes suitable for structure analysis, we were able to grow crystals of the monomer and obtain structural data, summarized in Table 1 (a more detailed table is included as Supporting Information). The structure of the monomer is shown

Scheme 2. Syntheses of Dimer-0, Dimer-1, and Dimer-0

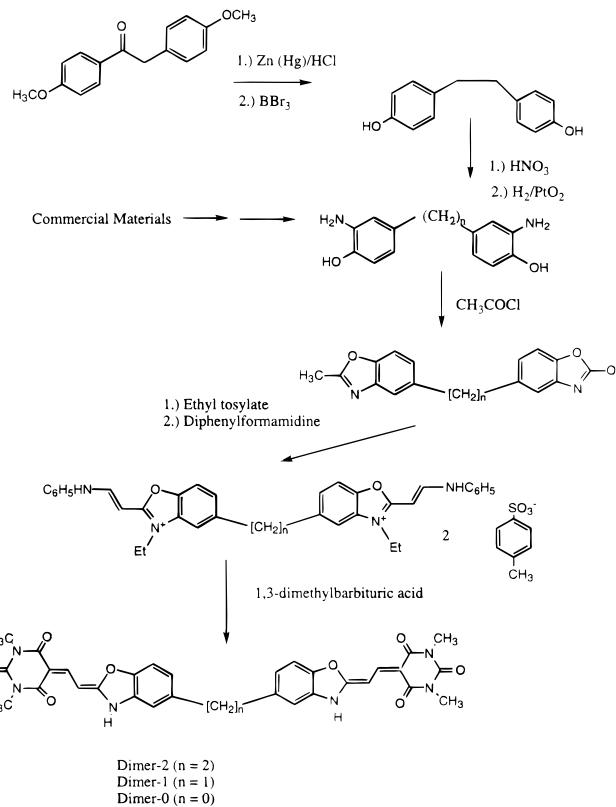


Table 1. Crystallographic Data and Structure Refinement for the Monomer Dye

empirical formula/weight	C ₁₇ H ₁₇ N ₃ O ₄ /327.34
crystal system/space group	monoclinic/P2(1)
cell constant	$a = 7.0506(4)$ Å
	$b = 28.390(2)$ Å, $\beta = 109.2780(10)^\circ$
	$c = 8.0611(5)$ Å
volume/Z	1523.1(2) Å ³ /4
crystal size	0.06 × 0.08 × 0.32 mm ³
θ range	1.43–23.26°
index ranges	-6 ≤ h ≤ 7, -31 ≤ k ≤ 30, -8 ≤ l ≤ 6
reflections collected	6184
independent reflections	2129 [$R(\text{int}) = 0.0379$]
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	5876/1/371
goodness-of-fit (F^2)	1.105
final R indices	$R_1 = 0.0539$ [$I > 2\sigma(I)$] $wR_2 = 0.1224$ [all data]

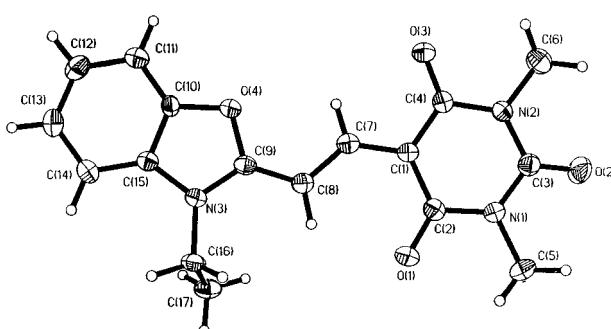
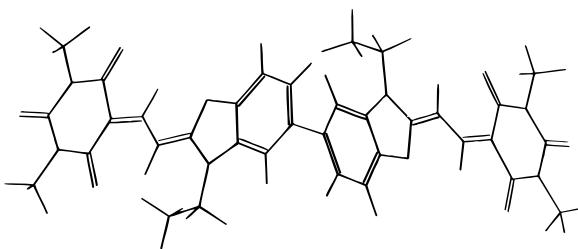
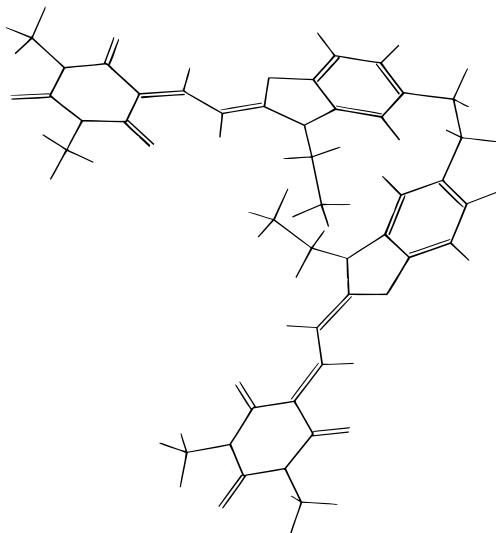


Figure 1. X-ray structure of the merocyanine monomer.

in Figure 1. The monomer has one molecule in an asymmetric unit, and the whole molecule is planar, with the benzoxazole and barbiturate subunits trans to one another. The ethyl attached at the nitrogen atom of the benzoxazole and the directly attached alkenic proton point in the same direction. Bond lengths are

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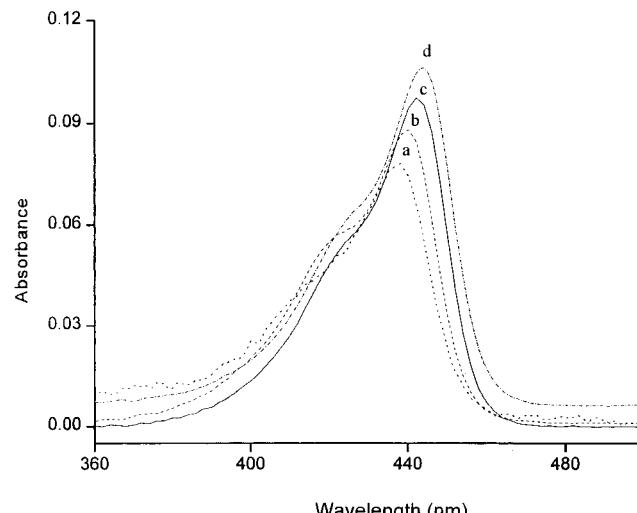
**Figure 2.** Extended configuration of dimer-0 from molecular modeling.**Figure 3.** Folded configuration of dimer-2 from molecular modeling.

included as Supporting Information. Remarkably, the diene unit connecting the benzoxazole and barbiturate rings shows nearly identical bond lengths for all three C–C bonds (ca. 1.38 Å), and these are only slightly longer than those for an isolated carbon–carbon double bond. If we assume that the merocyanine should exist in the ground state as a largely uncharged species, we would expect that the central C–C bond might be considerably longer due to its largely single bond character. Using the X-ray structural information for the monomer, a Monte Carlo (MC)-simulated annealing using a modified MM2 force field has been carried out for dimer-0, dimer-1, dimer-2, and dimer-3 (in the absence of solvent). The configurations corresponding to the global energy minimum from these calculations are extended (Figure 2), V-shaped, folded (Figure 3), and edge-to-face, respectively.

UV/Visible Absorption and Solvatochromic Effect. Table 2 compares the absorption maxima of the monomer and dimer-0. The monomer shows a maximum at ca. 440 nm and a shoulder at ca. 417 nm (Figure 4), which are independent of concentration over the range 10^{-5} – 10^{-7} M. When the solvent is changed from nonpolar cyclohexane, to tetrahydrofuran (THF), to ethanol (protic), to methylene chloride, and to very polar dimethyl sulfoxide (DMSO), the absorption maximum undergoes a modest red shift (437–444 nm). The merocyanine dyes are generally expected to have a π,π^* transition with weak charge-transfer character in the ground state but considerably stronger charge separation in the excited state; consequently, a positive solvatochromic effect is anticipated,^{12–15} as is observed.

Table 2. Absorption Maxima of Monomer and Dimer-0 in Different Solvents

solvent	Taft ^a π^*	monomer λ_{\max}		dimer-0 λ_{\max}	
		nm	kcal	nm	kcal
cyclohexane	0	437	65.4		
triethylamine	0.14	439	65.1		
diethyl ether	0.273	438	65.2		
toluene	0.535	441	64.8		
ethanol	0.54	440	65.0		
tetrahydrofuran	0.576	440	65.0	470	60.9
methanol	0.586			467	61.2
CHCl_3	0.76	443	64.6	472	60.4
CH_2Cl_2	0.802	442	64.7	471	60.7
dimethylformamide	0.875	442	64.7	473	60.4
dimethyl sulfoxide	1.000	444	64.4	475	60.2

^a From ref 9.**Figure 4.** Absorption spectra of the monomer in (a) cyclohexane, (b) ethanol, (c) CH_2Cl_2 , and (d) DMSO.

The transition energies of several merocyanine dyes show reasonable quantitative correlations with a number of empirical solvent polarity parameters, such as $E_T(30)$ and the Kamlet–Taft π^* parameter.^{12–15} In the case of the latter, a plot of the transition energy vs the empirical solvent polarity parameter π^* gives a linear plot with a negative slope ($-s$) in the case where there is more charge separation in the excited state than in the ground state.¹⁵ The Kamlet–Taft treatment is attractive since it allows the separation of “polarity” from other solvent–solute interactions, such as hydrogen bonding. When the absorption maxima of the monomer dye used in this study are plotted versus the Kamlet–Taft π^* solvent polarity parameter,¹² a reasonable linear plot with a relatively small slope (for a merocyanine) is obtained by fitting eq 1 using a least-squares regression method:

$$E_{\max}(\text{monomer}) = 65.4 \text{ kcal} - 0.87\pi^* \quad R = 0.92, \quad N = 10 \quad (1)$$

The absorption energies from Table 2 have also been plotted against the Brooker χ_R values,¹⁴ and this plot gives only a fair ($R = 0.86$) fit, even though the χ_R parameter is based on a merocyanine dye.

(a) “J”-Type Exciton Coupling.^{16,17} Dimer-0 is anticipated to be an extended structure, with the two monomer units connected by a single bond. The predicted dihedral angle

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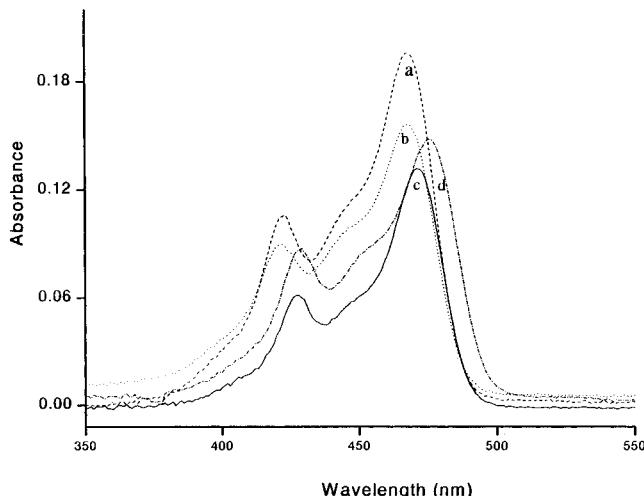


Figure 5. Absorption spectra of dimer-0 in different solvents: (a) CH_3OH , (b) 50 vol % $\text{CH}_3\text{CN}/\text{H}_2\text{O}$, (c) CH_2Cl_2 , and (d) DMSO.

between the two planes of the monomer units of dimer-0 in its lowest energy configuration is 28.2° based on the Monte Carlo calculations. On the basis of the anticipated extended configuration of dimer-0, the anticipated exciton coupling is expected to be a “J”-type splitting, characterized by a more intense long-wavelength transition and a less intense short-wavelength band. Compared to the monomer, dimer-0 shows a splitting with two bands in its absorption spectrum (Figure 5) in a series of organic solvents having an intensity ratio of ca. 2 (A_{470}/A_{420}).¹⁸ These bands both show a red shift as the solvent polarity increases in the series THF, methanol, methylene chloride, dimethyl sulfoxide (Figure 5). As in the case of the monomer, the solvatochromic effect of the dimer-0 may be correlated quantitatively with the Kamlet-Taft π^* parameter, and the relationship shown in eq 2 is obtained.

$$E_{\max}(\text{dimer-0}) = 62.2 \text{ kcal} - 2.02\pi^* \\ R = 0.90, \quad N = 6 \quad (2)$$

Due to the low solubility of dimer-0, we were only able to obtain a correlation with solvents having π^* values larger than 0.5. Remarkably, dimer-0 shows a greater sensitivity to solvent polarity than the monomer.

For dimer-1 and dimer-2 (Figure 6), the two monomers are connected at C_{13} by one and two methylene groups, respectively, and their absorption spectra in chloroform or rigid sucrose octaacetate (SOA) glass are very similar to that of the monomer, except for small red shifts for the dimers of ca. 10 and 8 nm, respectively. These may be attributed to a progressively weaker “J”-type exciton-coupling through longer distances; the direction of the observed shifts is consistent with the predominant configuration in these solvents being an extended one. The behavior observed here is similar to that observed for squaraine dimers with flexible tethers;⁹ however, the fall-off in splitting with distance (length of tether) is much more rapid for the merocyanines.

(b) “H”-Type Exciton Coupling. Dimers-3 and -5 have the merocyanines connected at the nitrogens in the benzoxazole ring by three and five CH_2 groups, respectively. The absorption

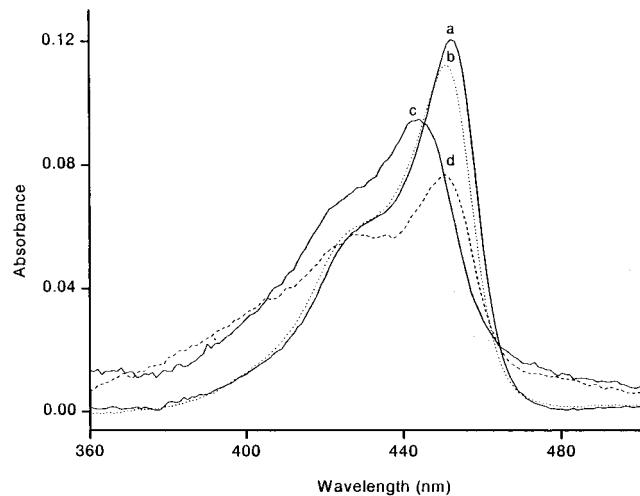


Figure 6. Absorption spectra of dimer-2 in different solvents: (a) CHCl_3 , (b) CH_2Cl_2 , (c) $\text{C}_2\text{H}_5\text{OH}$, and (d) DMSO.

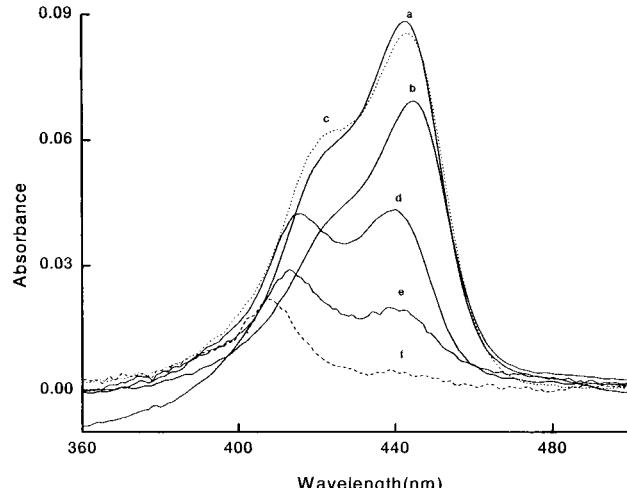


Figure 7. Absorption spectra of dimer-3 in different solvents: (a) SOA glass, (b) CHCl_3 , (c) CH_2Cl_2 , (d) CH_3CN , (e) CH_3OH , and (f) 80 vol % $\text{H}_2\text{O}/\text{CH}_3\text{CN}$.

spectrum of dimer-3 shows a pronounced variation with solvent which is independent of concentration at low concentrations (ca. 10^{-6} M) (Figure 7). In rigid SOA glass, chloroform, and methylene chloride, the spectral shape and position for dimer-3 are similar to those of the monomer, except that a slightly wider and more pronounced shoulder is observed. This implies that any intramolecular exciton interaction is very weak in these nonpolar solvents and that the chromophores are probably quite far apart. As the solvent polarity increases, a blue-shifted band appears (ca. 415 nm) in addition to the band at 440 nm associated with “monomer” or extended dimer, and in acetonitrile its intensity is almost the same as the monomer in intensity. In methanol and ethanol, the blue-shifted band becomes stronger than the monomeric peak (ca. 440 nm). Based on similar spectral shifts for the tethered squaraines,⁹ the short-wavelength band may be attributed to a folded “H”-type dimer.¹⁹ These shifts are also similar to those observed for “H” aggregates for other merocyanine dyes.¹⁷

In water-acetonitrile mixtures, the relative intensity (blue-shifted “exciton” band vs monomeric band) increases as the percentage of water increases. In the extreme case, when the

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(18) There is also a shoulder on the short-wavelength side of the more intense “red” band which resembles the shoulder observed for dilute solutions of the monomer. None of the spectra shown in Figures 5–7 are concentration-dependent.

(19) We expect, in a “well folded” cofacial structure, that the excitonic splitting (allowed-forbidden character) may be more pronounced than in the somewhat bent structures.

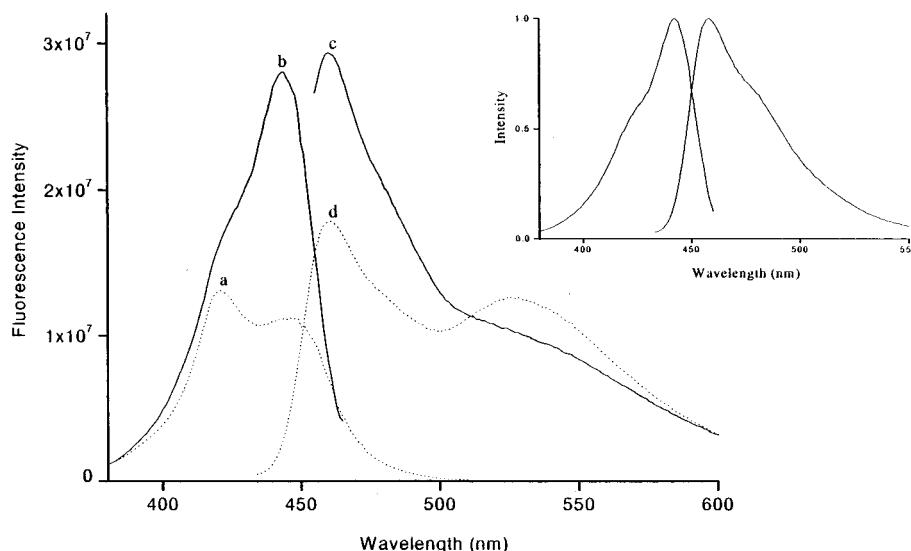


Figure 8. Excitation spectra: a ($\lambda_{\text{em}} = 530 \text{ nm}$) and b ($\lambda_{\text{em}} = 475 \text{ nm}$) of dimer-3 in CHCl_3 ; and its emission spectra c ($\lambda_{\text{ex}} = 445 \text{ nm}$) and d ($\lambda_{\text{ex}} = 420 \text{ nm}$). Inset: The fluorescence spectra of the monomer in CHCl_3 ($\lambda_{\text{em}} = 475 \text{ nm}$ and $\lambda_{\text{ex}} = 420 \text{ nm}$).

Table 3. Absorption Data of Dimer-3 and Dimer-5 (10^{-6} M)

dye molecule	solvent	$\lambda_{\text{max1}}, \lambda_{\text{max2}}$ (nm)	absorbance ratio ($A_{\text{max1}}/A_{\text{max2}}$)
dimer-3	CH_2Cl_2	442, 422	1.41
	CH_3CN	440, 416	0.99
	CH_3OH H ₂ O/ CH_3CN (1/1 vol)	440, 414	0.74
		441, 411	0.57
	CH_2Cl_2	442, 424	1.37
dimer-5	CH_3CN	438, 418	1.11
	CH_3OH	440, 416	0.93
	H ₂ O/ CH_3CN (1/1 vol)	439, 415	0.87

percentage of H₂O is $\geq 80\%$, the dominant band is the exciton band, with a low absorbance due to the low solubility of dimer-3 in the mixture (when the solution was heated, the absorbance increases to close to that of other aqueous mixtures).

Dimer-5, with five CH₂ groups as the spacer, shows spectra similar to those of dimer-3 in the same solvents at ca. 10^{-6} M and shows a spectral change pattern similar to that of dimer-3 as solvent properties change (Table 3). The "H"-type exciton splitting shows a very small decrease as the chain length increases from three to five carbon units, and there is no evidence for "J"-type exciton coupling for either dimer-3 or dimer-5 in any solvent.

Fluorescence. The emission spectra and excitation spectra of the monomer in chloroform are shown in Figure 8 (ca. 10^{-6} M). The emission spectra are independent of excitation wavelengths, and the excitation spectra do not change with emission wavelengths. The emission maxima show small red shifts with increasing solvent polarity, corresponding to the shifts in the absorption spectra. Similar fluorescence spectra are obtained in the same solvents for dimer-0 and dimer-1; here again, there is no wavelength dependence of either fluorescence or excitation. Although the same general trend of red shifts in emission maximum is observed for monomer, dimer-0, and dimer-1, due to the breadth of the fluorescence maxima for all three compounds, no sensible quantitative correlation of solvatochromic effects could be made.

Excimer Formation. The emission and excitation spectra of dimer-3 in chloroform (ca. 10^{-6} M) are compared in Figure 8. The fluorescence spectrum consists of a sharp band at 460 nm and a broader band at 530 nm; the relative intensity of the two bands is dependent on the excitation wavelength. The excitation

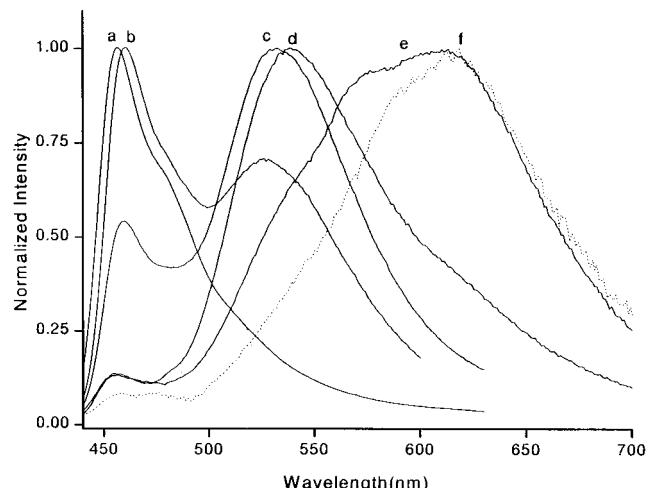


Figure 9. Emission spectra of dimer-3 ($\lambda_{\text{ex}} = 420 \text{ nm}$) in (a) SOA glass, (b) CHCl_3 , (c) CH_2Cl_2 , (d) CH_3CN , (e) CH_3OH , and (f) 80 vol % $\text{H}_2\text{O}/\text{CH}_3\text{CN}$.

spectrum obtained by monitoring the fluorescence at 460 nm resembles that for the monomer (inset, Figure 8) and also tracks quite closely the absorption spectrum (Figure 7). The intensity of the broad band at 530 nm is much higher when the sample is excited at 420 nm, which corresponds quite closely to the maximum of the blue-shifted "H" exciton band observed for dimer-3 in more polar solvents. The excitation spectrum monitoring the fluorescence at 530 nm resembles the absorption spectrum of dimer-3 in more polar solvents (Figure 7), such as methanol. The broad, structureless nature of the long-wavelength emission and the excitation corresponding to the folded "H"-type configuration suggest that this emission may be attributed to a folded excimer-like state, similar to that associated with diphenyl propane.²⁰

Figure 9 compares the fluorescence spectra of dimer-3 in a series of different solvents. In SOA, which may be regarded as a rigid, nonpolar solvent, the only emission that is observed is the sharp band at ca. 455 nm which corresponds quite closely to monomer. As mentioned above, dimer-3 in chloroform shows absorption very similar to that for monomer but also both the sharp emission, similar to that of monomer and dimer-3 in SOA,

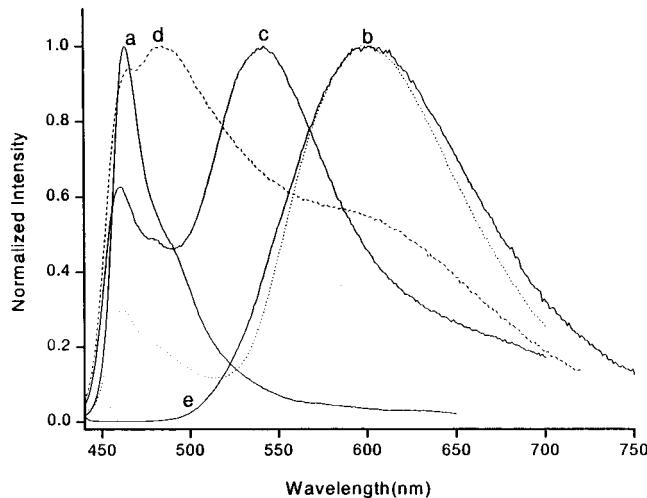


Figure 10. Emission spectra ($\lambda_{\text{ex}} = 420 \text{ nm}$) of the dimers in DMSO: (a) dimer-1, (b) dimer-2, (c) dimer-3, (d) dimer-5, and (e) emission spectra of dimer-2 in a solid state.

Table 4. Stabilization Energy of Dimer-2, Dimer-3, and Dimer-5

dimer	stabilization energy (cm^{-1})	
	in DMSO	in methanol
dimer-2	5000	
dimer-3	3200	5300
dimer-5	900	5000
	5000 (minor)	

and the broad, red-shifted band at 530 nm. In methylene chloride, which shows only a slight broadening of the absorption spectrum and a small blue shift compared to monomer or dimer-3 in SOA and chloroform, the major emission upon excitation in the “monomer” transition is the broad “excimer” band. The “excimer” emission becomes predominant when dimer-3 is excited in acetonitrile and shows a red-shift compared to methylene chloride and chloroform. In protic solvents such as methanol or 80% $\text{H}_2\text{O}/\text{CH}_3\text{CN}$, the excimer band becomes even broader and is further red-shifted to 600–620 nm. The red shift in the “excimer” emission maxima of dimer-3 with increase in solvent polarity (excluding chloroform and methylene chloride, as discussed below) may be correlated with the Kamlet–Taft π^* solvent polarity parameter;^{12,15} a linear plot is obtained by fitting eq 3 with a least-squares regression method.

$$E_{\text{max}}(\text{dimer}) = 55.0 \text{ kcal} - 2.28\pi^*, \quad R = 0.93, \quad N = 5 \quad (3)$$

The excimer emission for the different dimers shows an interesting structure dependence. The emission spectra of dimers with different spacers in DMSO are shown in Figure 10. Not surprisingly, dimer-1, which cannot fold, shows only monomer-like emission. Dimer-2 shows a predominant excimer band at 600 nm in addition to a weak emission corresponding to monomer, while only excimer emission is observed for dimer-2 in the solid state. For dimer-3, the excimer band is less red-shifted, and both monomer and excimer emission are observed. In the case of dimer-5, the emission is more complex, with maxima at 483 nm, partially overlapped with the monomer-like emission, and a less prominent red-shifted emission spread over the range 530–700 nm. The stabilization energy of the excimers in DMSO and in methanol (Table 4), which is the spectroscopic energy difference between the monomer emission and excimer emission maxima,²¹ varies from 5000 to 900 cm^{-1} for dimer-2 and dimer-5, respectively.

Table 5. Quantum Yields of the Monomer and Dimer Dyes in Different Degassed Solvents

dye	solvent	excitation wavelength (nm)	excitation wavelength (nm)		
			ϕ_t^a	ϕ_{mon}	ϕ_{ex}
monomer	CHCl_3	420 or 430	0.0064	0.0064	
	CH_3CN	420 or 430	0.0024	0.0024	
	SOA ^b	420 or 430	0.23	0.23	
	CHCl_3	420	0.019		
dimer-5		430	0.016		
	DMSO	420 or 430	0.028		
	CHCl_3	420	0.012	0.0041	0.0079
		430	0.010	0.0043	0.0059
dimer-3	DMSO	420	0.026	0.0029	0.023
	CHCl_3	430	0.024	0.0039	0.020
	CHCl_3	420	0.012		
		430	0.010		
dimer-2	DMSO	420	0.083	0.010	0.073
		430	0.071	0.011	0.060
	CHCl_3	420 or 430	0.011	0.011	
		430	0.013		
dimer-1	DMSO	420 or 430	0.014		
	CHCl_3	420	0.14		
		460	0.12		
	DMSO	420	0.050		
dimer-0		460	0.039		
	CHCl_3	420	0.65		
		460	0.39		
	SOA	420			

^a ϕ_t is the quantum yield with 5% error, which could consist of two parts: quantum yield of the monomer-like species (ϕ_{mon}) and that of the excimer (ϕ_{ex}). ^b The dimer-5, dimer-3, dimer-2, and dimer-1 show similar quantum yields (0.15–0.20) similar to that of the monomer in SOA glass.

Fluorescence Quantum Yields and Lifetime Measurements. The fluorescence quantum yields and lifetimes of the monomer and the various dimers in different solvents are listed in Tables 5 and 6, respectively. The fluorescence lifetimes of the monomer in fluid solvents are in the range of 5–20 ps, and the quantum yield (less than 1%) is very low, probably due to isomerization⁴ and/or torsional motions which provide rapid nonradiative decay.²² The emission quantum yield and lifetime of the monomer are independent of excitation wavelength and emission wavelength in all solvents. Both the fluorescence lifetime and the quantum efficiency are enhanced dramatically when the monomer is “solubilized” in rigid SOA glass, reinforcing the idea that conformational changes are responsible for the short lifetimes in fluid media.²² Compared with the monomer, dimer-0 shows a higher fluorescence efficiency in fluid solvents and a longer fluorescence lifetime (at least in the one common solvent studied) as well as an increased fluorescence quantum efficiency. Similar to the monomer, there is a big increase in both fluorescence lifetime (see below) and efficiency when dimer-0 is studied in SOA. In fact, all of the dimers synthesized (except dimer-0) show similar quantum efficiencies (0.15–0.20), only slightly lower than that of the monomer in SOA. In heterogeneous environments such as bilayer vesicles or SOA glasses, where a number of different solute states with differing emission properties may be populated, the use of the usual multiexponential decay model for the decay data may not be justified.²³ An appropriate model describing such a system is one that attributes a range of lifetimes to a single emitting species corresponding to a nonequilibrium population of chromophores. Such a method was

(22) As suggested by a reviewer, a “TICT” state could be involved in such isomerization processes. Previous papers have reported evidence for twisted excited states as intermediates in merocyanine isomerization (e.g.: Harriman, A. *J. Photochem. Photobiol. A: Chem.* 1992, 65, 79).

(23) Whitten, D. G.; Farahat, M. S.; Gaillard, E. R. *J. Photochem. Photobiol.* 1997, 65 (1), 23.

Table 6. Lifetimes of the Monomer, Dimer-5, Dimer-3, Dimer-2, Dimer-1, and Dimer-0 in Degassed Solvent and in Solid SOA Glass (Excitation Wavelength = 420 nm)

dye	solvent	emission wavelength (nm)	τ_1 (ns) ^a	τ_2 (ns) ^b	B1/B2 (%)	χ^2
monomer	CHCl ₃	460 or 530	0.02			
	CH ₃ CN	460 or 530	0.005			
	SOA ^c	460 or 530	0.16	0.90	35/65	1.4
dimer-3	CHCl ₃	460	0.03			4.6
		530	0.03	6.5	19/81	1.1
	DMSO	460	0.02			
		530	0.02	5.8	13/87	2.8
		SOA ^c	460	0.10	40/60	1.0
	dimer-5	530	0.11	1.2	48/52	0.99
		460	0.03	2.1	85/15	1.9
		530	0.03	1.7	22/78	0.97
dimer-2	CHCl ₃	460	0.02			
		530	0.02	2.3	88/12	
	DMSO	460	0.02	2.1	22/78	1.6
		530	0.02	1.7	35/65	0.98
		SOA ^c	460 or 530	0.15		
	dimer-1	CHCl ₃	460 or 530	0.03		
		DMSO	460	0.01		
		530	0.02	4.4	36/64	3.0
dimer-0	SOA ^c	460 or 530	0.11	0.96	40/60	1.1
		CHCl ₃	460 or 530	0.19	45/55	1.1
	DMSO	460				
		530	0.02	1.2	38/62	2.1
	SOA ^c	460	0.11	1.2	19/81	1.2
		530	0.27	1.5		

^a The short lifetime (5–30 ps), close to the instrument response (60 ps), fitting by $A + B1 \exp(-t/\tau_1) + B2 \exp(-t/\tau_2)$, is not precise, the measurement is subject to considerable error, and only the order of magnitude can be approximated. ^b The long lifetime (0.10–7.5 ns) has an error of ± 1 on the second significant number. ^c The lifetime is mean lifetime from a distribution of lifetimes by simulation analysis of the fluorescence decay.

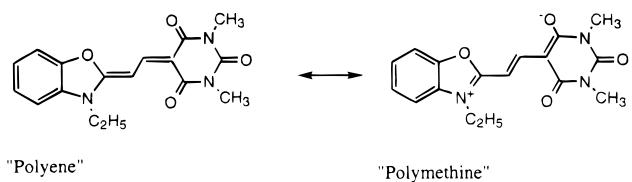
used to fit the fluorescence decay of the monomer and various dimers in SOA glass, and it was found that the decay curves of the monomer and dimers in SOA glass can be fitted nicely with two lifetime distributions: the shorter one is 0.1–0.3 ns, and the longer one is 1–2 ns.

As mentioned above, the emission spectra of dimers-2, -3, and -5 in fluid environments exhibit both monomer-like (460 nm) and excimer emission; therefore, two lifetimes and quantum yields are expected. Due to the overlap of the monomer and excimer bands of dimer-5, no attempt was made to evaluate the individual quantum efficiencies, and only the overall quantum yield is listed. The overall quantum yield is higher when the sample is excited at 420 nm than that at 430 nm, because the blue-shifted exciton band is situated around 420 nm. For dimer-3 in fluid media, a species of a short lifetime (10–30 ps) close to that of monomer was found when the sample was monitored at an emission wavelength of 460 nm, while a much longer-lived species (ca. 6 ns) is found at an emission wavelength of 530 nm; therefore, the short-lived species may be assigned to a monomer-like or extended dimer state, while the long-lived species is the excimer. The quantum yield is higher in polar solvents such as acetonitrile due to the predominance of excimer emission; the quantum yield is much lower in solvents such as chloroform, where monomer-like emission is dominant.

Oxygen was found to have no effect on the fluorescence intensity and lifetimes of both monomer and dimers. This is in accord with their short fluorescence lifetimes of no longer than a few nanoseconds.⁸

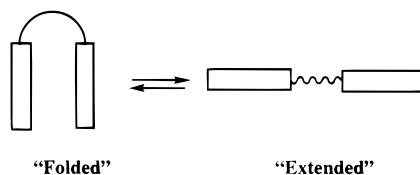
Discussion

The merocyanine monomer and corresponding suite of tethered dimers were selected for the anticipated contrast to the squaraines previously studied that these might offer, and it is relevant to compare the behaviors observed for the two series of linked dye dimers. For the merocyanine series, some of the important anticipated differences from the squaraines may be seen by comparing differences between the two monomers. Thus, the merocyanine has a lower extinction coefficient and a consequent lower transition moment, which would be expected to lead to a lower excitonic coupling for dimers having the same spacing. However, since the merocyanine was anticipated to have a substantial dipole moment in the ground state and an even greater charge separation in its lowest excited singlet state, additional possibilities for interactions in both ground and excited states of the tethered dimers might be expected. The merocyanine dyes consist of an electron-donating group (D) linked to an electron-accepting group (A) through conjugation. The ground-state electronic structure of the dyes lies somewhere between that of the polyene form and that of the polymethine form, depending on solvent polarity.¹²



As pointed out in the Results section, there is a general red shift with increase in solvent polarity in the absorption spectra of monomer and dimer-0, which is anticipated for positive solvatochromic dyes in which electronic excitation is accompanied by a pronounced increase in charge separation. The finding of very little bond alternation in the diene unit linking the two halves of the merocyanine supports the idea of some charge-transfer interactions already present in the ground state; the small negative slope for the plot of λ_{\max} vs π^* ($-s = 0.87$) indicates that there is increased charge transfer in the excited state.

Turning to the dimeric merocyanines, it is useful to first consider what might be anticipated in terms of possible excitonic interactions. All of the “tethers” linking the merocyanine chromophores provide some flexibility in terms of the arrangement between chromophores; in terms of potential excitonic interactions, according to the point dipole approximation, two limiting arrangements are most interesting: a folded and an extended configuration.²⁴ Both of these configurations may not



be possible for each dimer in the series, and they may or may not be able to interconvert, depending upon the individual dimer

(24) For the merocyanine dimers, several folded configurations are possible. MC simulations indicate an edge-to-face configuration is one minimum. Two limiting face-to-face configurations (one with the chromophores aligned parallel and one with them antiparallel) are possible and reasonable on energetic grounds. It is not possible to determine which configuration or configurations may exist for either the ground or the excited (excimer) state. For purposes of illustration, we assume a “parallel” folded arrangement.

structure. For those dimers that can assume an extended configuration, this configuration may be anticipated to be more stable in the ground state for solutions with nonpolar solvents due to the lack of gauche or eclipsed conformations in the tether, provided there are no or weak dipoles. The extended or nearly extended configuration (open "V" shape, for example) should give rise to a "J"-type excitonic coupling, characterized by a split in the monomer long-wavelength transition (if polarized along the long axis), leading to lower energy (more allowed) and higher energy (less allowed) transitions compared to those of the monomer. Since our calculations indicate that dimers such as dimer-2 or dimer-3 are not likely fully extended and the coupling may fall off, it is reasonable that both long- and short-wavelength transitions may be of comparable intensity. The folded configuration may be favored in cases where there is attraction between the two chromophores (for example dipole-dipole attraction) or in solvents where strong solvent-solvent interactions favor a minimization of the solute area to be solvated (solvophobic effects).²⁴ A completely folded configuration should result in an "H"-type excitonic coupling, also characterized by a split in the monomer transition, resulting in a lower energy (forbidden) and a higher energy (more allowed) transition.²⁵ Although the cartoon above shows limiting extended and folded configurations, a variety of additional configurations may be possible when the tether is long and flexible and depending upon the site of the tether and other properties of the solute and solvent.

If we compare the properties of dimers-0, -1, and -2 with those of the monomer and the roughly corresponding series of methylene-linked squaraines,⁹ we observe some similarities as well as pronounced differences. In fluid nonpolar solvents and in SOA, the most prominent effect for the series of merocyanines is the splitting and red shift in the absorption spectrum of dimer-0 compared to the monomer. Dimer-0 shows a "J"-type splitting (ca. 30 nm, depending slightly on solvent) in the long-wavelength transition and a corresponding red shift in its fluorescence. Dimers-1 and -2 show almost no changes from the monomer in absorption. This may be compared to the squaraine series, where (while we have no $n = 0$ dimer) we observe a shift of 24 nm for $n = 2$, and a perceptible splitting persists to $n = 7$. Since the extinction coefficient of the merocyanine ($\sim 1 \times 10^5$ in chloroform) is lower than that of the squaraine monomer ($\sim 3 \times 10^5$ in chloroform) and exciton theory predicts that the coupling should be in proportion to the cube of the interaction distance and the square of the transition moment of the interacting chromophores,²⁶ it is not surprising that the "J" exciton splitting is much smaller for the merocyanine dimers than for the squaraines. In fact, if we examine the splitting observed for dimer-0 compared to that for the monomer, it is not clear that it is really correct to ascribe it solely to excitonic interactions. First, while the two "halves" of dimer-0 are surely in a somewhat extended configuration in all solvents, it is reasonable to question how much conjugation there is between the two halves. For the MC simulated global minimum of dimer-0, we obtain a dihedral angle between the two halves

(25) If the configuration results in strong face-face or edge-edge interactions, we may anticipate that the difference between the "allowed" (short wavelength) and "forbidden" components of the split bands may be very great. Thus, for example, with the intermolecular "H" aggregates of squaraines, we are able only to detect the short-wavelength band in absorption, while for corresponding aggregates of stilbenes, only the short-wavelength transition is readily observable in absorption but emission clearly originates from a "hidden" lower energy "forbidden" state.

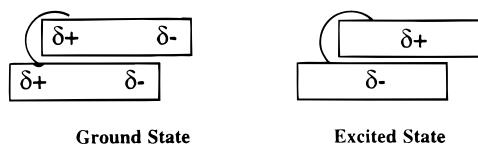
(26) McRae, E. G.; Kasha, M. *Physical Process in Radiation Biology*; Academic Press: New York, 1964; p 17.

of 28° (Figure 2); while there should be little charge transfer between the two merocyanine units in the ground state, it seems quite likely that extensive charge delocalization may occur in the excited state. This could lower the energy of the excited state and partially account for the observed red shift. That this may be important is also suggested by the relatively large (compared to the monomer) positive solvatochromic sensitivity of the absorption spectrum of dimer-0. The value of the slope ($-s$) of 2 is more than twice that of the monomer.

The similarity of the absorption and fluorescence spectra of dimer-1 and dimer-2 to those of the monomer in nonpolar solvents and SOA is consistent with these dimers existing in a more-or-less extended configuration in the ground state, in which there is little or no excitonic coupling between the two merocyanine units. The finding that dimer-2 exhibits dual fluorescence in solvents of moderate to high polarity is consistent with a folded form of the dimer playing an important role in these situations, quite analogous to the behavior of the tethered squaraines with two or more methylene units in the tether. The absorption spectra of dimer-2 in different solvents suggest that there may be relatively little ground-state population of folded forms in chloroform or less polar solvents. In solvents such as DMSO, where there is dual emission, the fluorescence lifetime and the quantum efficiency corresponding to the monomer are very similar to those measured in chloroform, where only "monomer" fluorescence is observed. Given the extremely short fluorescence lifetime, it seems unreasonable to assume that interconversion from an extended to a folded form occurs in competition with fluorescence and most reasonable that the observed "excimer" emission may be attributed to a small amount of folded dimer-2 present in the solution. The much higher quantum efficiency for fluorescence observed for dimer-2 is most reasonably attributed to the much longer lifetime of the excimer.

The behavior of dimers-3 and -5 is also consistent with interconversion between extended and folded forms, with a steady increase in the population of the folded form as solvent polarity and/or solvent-solvent hydrogen bonding increase. Here again, "excimer" fluorescence, which presumably arises primarily from folded ground-state configurations, is the most prominent emission in polar solvents, and the lifetime of the excimer is much longer than that for the monomer. As indicated in the Results section, the excimer emission from dimer-5 is complex, and it is not possible, at this time, to offer a simple analysis for its complexity. On the other hand, the excimer emission from dimer-3 seems somewhat simpler and perhaps easier to understand. Since the blue-shifted absorption of dimer-3 that is attributed to the folded "H" configuration shows relatively little solvent sensitivity, it may be assumed that the folded ground-state structure does not change appreciably as the solvent is changed. On the other hand, the corresponding "excimer" fluorescence shows a strong solvatochromic effect with a slope ($-s$) of 2.3, the highest value observed in this study. The observation that the excimer emission is nearly structureless in all solvents (Figure 9) suggests that it is truly excimer-like and involves emission to an unbound ground state. A reasonable interpretation for the solvatochromic behavior of the excimer fluorescence as well as the strong "Stokes" shift observed is that the excimer may have a much smaller interchromophore separation than does the folded ground state. Here again, as was suggested for the extended configuration of dimer-0, there exists the attractive possibility that charge transfer (or charge

delocalization) across the two chromophores occurs as shown below:²⁴



In this case, especially with the relatively small spacer present in dimer-3, the ground state may have a relatively larger separation due to dipole–dipole repulsions (and other steric considerations), while interchromophore charge resonance can result in increased attraction and hence reduced separation (within 3–4 Å)¹¹ in the excimer. It is interesting to note that the strong solvatochromic behavior observed for the dimero-cyanine propane (dimer-3) is in strong contrast with the behavior observed for analogous propyl-tethered aromatic dimers and may be attributed specifically to the fact that the merocyanine chromophore has strong donor and acceptor sites, whose reactivity is enhanced following photoexcitation. Thus, the classical attribution of excimer stabilization^{20,27} to a combination of dominant excitation resonance with very minor charge resonance contributions may be reversed in this case, with the latter playing a very important and perhaps dominant role.

Experimental Section

Instrumentation and Methods. ¹H NMR spectra were recorded on a General Electric QE 300-MHz spectrometer. FAB mass spectra were obtained at the Center for Mass Spectrometry at the University of Nebraska in Lincoln, NE. HPLC was performed on a Hewlett-Packard liquid chromatograph series 1050 with a variable-wavelength absorbance detector and a Rannin 150-mm × 4.6-mm silica gel column. UV-vis absorption spectra were measured on a Perkin-Elmer Lambda 19 spectrophotometer. Fluorescence emission and excitation spectra were recorded on a Spex Fluorolog-2 spectrofluorimeter and were corrected. Solid-state spectra were obtained as a fine dispersion in a KBr pellet. Fluorescence quantum yields were determined by comparison with a standard, coumarin 6, in ethanol (0.78).²⁸

Fluorescence Lifetime Measurements. Time-correlated single-photon-counting experiments were carried out on an instrument consisting of a mode-locked Nd:YLF laser (Quantronix) operating at 76 MHz as the primary laser source. The second harmonic (KTP crystal) of the Nd:YLF laser was used to synchronously pump a dye laser (Coherent 700), circulating Rhodamine 6G in ethylene glycol as the gain medium. The pulse width of the dye laser was typically 8 ps, as determined by autocorrelation, and was cavity-dumped at a rate of 1.9 MHz. The dye laser was tuned to the desired excitation wavelength (420 nm). Emission from the sample was collected by two convex lenses, focused at the entrance slit of a Spex 1681 monochromator (0.22 m), and detected by a multichannel plate detector. The single-photon pulses from the detector were amplified and used as the start signal for a time-to-amplitude converter (TAC), while the signal from a photodiode, detecting a small fraction of the dye output, was used as the stop signal for the TAC. The start and stop signals for the TAC were conditioned before entering the TAC by passing through two separate channels of a constant fraction discriminator (CFD). The output of the TAC was connected to a multichannel analyzer (MCA) interface board inside a PC. The MCA was controlled by software from Edinburgh Instruments. The same software was used to deconvolute the data and do exponential fitting by the nonlinear least-squares method. Measurements were made on air-saturated or Ar-degassed samples.

Molecular Modeling. Possible geometries of the tethered dimers were determined by carrying out a Monte Carlo-simulated cooling

experiment to search for the apparent global minimum and nearby local minima. The method is similar to that used earlier in predicting the geometries of tethered squaraine dyes⁹ and for determining packing patterns for Langmuir monolayers.²⁹ Starting geometries for the simulation consisted of an energy-minimized “stretched out dimer”. Bond lengths and bond angles for each half of the dimer were taken from the X-ray structure. The simulations consisted of cooling the starting geometry from 4000 to 300 K in 10% increments, with rotation about all single bonds as variables. At each temperature, each single bond was randomly rotated an angle <10°. The nonbonded and electrostatic energy of the dimer was then computed using a modified MM2 force field.³⁰ Structures were saved or rejected on the basis of the Boltzmann criteria until the final temperature was reached. The lowest energy structure at the final temperature was then saved as a local minimum. The cooling cycle was then repeated, starting with the saved structure, until 700 structures were collected.

Crystal Growing, Data Collection, Structure Solution, and Refinement. A bright yellow plate of the monomer dye, grown from concentrated solution of CH₂Cl₂ by slow evaporation, of approximately 0.06 × 0.08 × 0.32 mm³ was mounted on a glass fiber. All aspects of data collection were performed on a standard Siemens SMART CCD area detector using Mo K α radiation ($\lambda = 0.710\text{73}\text{\AA}$) at 193 K. The unit cell parameters were determined by a least-squares analysis of 2751 reflections. The intensity measurements were then performed using ω -scans (maximum 2 θ of 56.6). Instrument and crystal stability was verified by monitoring three check reflections every 100 data points. No measurable decay was detected. The space group was assigned P_{2_1}/n on the basis of intensity statistics. The structure was solved using direct methods and refined against F^2 using the SHELXTL/PC v5.04 software suite.³¹ All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were included in calculated positions, using a standard riding model and thermal parameters proportional to the non-hydrogen atom to which they were attached. The final refinement converged with the residuals $wR_2 = 0.1181$ (based on F^2) for all data and $R_1 = 0.0539$ (based on F) for data with $I > 2\sigma(I)$. Additional details of data collection and refinement parameters can be found in Table 1. Full details including atomic positions and anisotropic displacement parameters are included in the Supporting Information.

Synthesis. All starting materials and liquids were reagent grade or better and were used as received except where indicated otherwise.

(a) **Synthesis of Dimer-5 According to Scheme 1.** (i) **2,2'-Dimethyl-3,3'-pentamethylenedibenzoxazolium Iodides.** To a round-bottom flask were added 8 mL (68 mmol) of 2-methylbenzoxazole and 1.5 mL (12 mmol) of 1,5-diiodopentane, stabilized by copper particles. The mixture was heated at 108–110 °C for 20 h to give a yellowish precipitate. Acetonitrile (20 mL) was added to the solid precipitate, which was filtered and washed with CH₃CN (3 × 10 mL). A yellowish solid (4.0 g, 56%) was obtained. ¹H NMR (300 MHz/CD₃OD): δ 8.20–7.77 (m, 8H, aromatic), 4.67–4.62 (t, $J = 7.2$ Hz, 4H, N-CH₂), 3.16 (s, 6H, CH₃), 2.13–2.05 (q, $J = 7.2$ Hz, 4H, N-C-CH₂), 1.78 (m, 2H, N-C-CH₂).

(ii) **2,2'-(2-Anilidovinyl)-3,3-pentamethylenedibenzoxazolium Iodide.** In a mortar, 1.0 g (1.7 mmol) of 2,2'-dimethyl-3,3'-pentamethylenedibenzoxazolium iodides and 1.0 g (5.1 mmol) of *N,N'*-diphenylformamidine were mixed well by pounding, and the mixed solid was heated with stirring at 150–157 °C for 5 min under a dry atmosphere. The solution was cooled to give a reddish solid. The solid was dissolved in ethanol (50 mL), and diethyl ether (500 mL) was added to precipitate the product, which was filtered. The crude product was dissolved in hot ethanol (30 mL), and diethyl ether (3 mL) was added to the cold ethanol solution to induce a precipitate. A yellow solid (0.8 g, 60%) was obtained. ¹H NMR (300 MHz/CD₃OD): δ 8.88–8.70 (d, $J = 12$ Hz, 2H, CH=), 7.70–7.23 (m, 8H, aromatic), 5.99–5.95 (d, $J = 12.3$ Hz, 2H, CH=), 4.36–4.31 (t, $J = 6.9$ Hz, 4H, N-CH₂), 2.05–1.95 (m, 2H, N-C-CH₂), 1.66–1.60 (m, 2H, N-C-C-CH₂).

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(iii) Dimer-5. Under nitrogen, 0.2 g (0.25 mmol) of 2,2'-(2-anilidovinyl)-3,3-pentamethylenedibenzoxazolium iodide and 0.16 g (0.82 mmol) of 1,3-dimethylbarbituric acid were dissolved in dried methylene chloride (100 mL). Triethylamine (0.5 mL) was added to the above solution.³² The reaction mixture was stirred for 3 days to yield an orange precipitate, which was filtered and then washed with methanol (3×5 mL) to give the crude product. The crude product was chromatographed first with a mix of 5:40:55 methanol/chloroform/ethyl acetate(0.5 L) and then with a mix of 10:75:15 methanol/chloroform/ethyl acetate to yield 70 mg of yellow solid (42%, one peak by HPLC with 1:19 methanol/chloroform). ^1H NMR (300 MHz/CD₃CO₂D): δ 8.61–8.57 (d, $J = 10.5$ Hz, 2H, CH=), 7.68–7.40 (m, 10H), 4.35–4.20 (t, 4H, N-CH₂), 3.40–3.20 (s, 12H, NCH₃), 2.10–1.90 (m, 4H, N-C-CH₂), 1.65–1.55 (m, 2H, N-C-C-CH₂). MS (FAB): m/e 667.2 (M⁺ + 1).

(b) Dimer-3 and the Monomer Were Synthesized by a Method Similar to That for Dimer-5. **(i) Dimer-3.** A yellow solid, in 65% (one peak by HPLC with 1/19 methanol/chloroform). ^1H NMR (300 MHz/CF₃CO₂D): δ 8.90–8.75 (d, $J = 14.4$ Hz, 2H, CH=), 8.4–7.5–(m, 10H), 5.2–4.8 (t, $J = 7.2$ Hz, 4H, N-CH₂), 3.8–3.5 (s, 12H, NCH₃), 2.90–2.75 (m, 2H, C-CH₂-C); MS (FAB) m/e 639.2 (M⁺ + 1).

(ii) Monomer Dye. A yellow solid, in 89% (one peak by HPLC with 1/19 methanol/chloroform). ^1H NMR (300 MHz/CDCl₃): δ 8.83–8.70 (d, $J = 14.4$ Hz, 1H, CH=), 7.60–7.20 (m, 5H), 4.20–4.10 (m, 2H, CH₂-N), 3.41 (s, 3H, NCH₃), 3.31 (s, 3H, NCH₃), 1.56–1.50 (t, $J = 7.2$ Hz, 3H, N-C-CH₃). Elemental analysis: calculated for C₁₇H₁₇N₃O₄, C 62.38, H 5.23, N 12.84; found, C 61.97, H 5.28, N 12.50.

(c) Synthesis of Dimer-2 According to Scheme 2. **(i) Bis(4-methoxyphenyl)ethane.** To a round-bottom flask were added 10 g (0.039 mmol) of 4'-methoxy-2-(4-methoxyphenyl)acetophenone, 100 mL of toluene, 30 g of amalgamated zinc,³³ and 40 mL of 20% HCl. The mixture was stirred at 40 °C for 4 h and then at 100 °C overnight. The organic layer was separated and condensed to a solid residue, which was dissolved in CHCl₃ (250 mL) and combined with the extract from the aqueous layer. The CHCl₃ solution was washed with H₂O (2 × 100 mL), dried with MgSO₄, and evaporated under vacuum to yield 9.0 g of yellowish solid. The crude product was taken up in diethyl ether (50 mL) and filtered to give 6.5 g of an off-white solid. Finally, 5.5 g (0.023 mol, 59%) of white solid was obtained after the crude was chromatographed on silica gel using a mix of 1:3:6 of ethyl acetate/hexane/benzene (1.3 L). ^1H NMR (300 MHz/CDCl₃): δ 7.10–7.07 (d, $J = 8.2$ Hz, 4H), 6.84–6.81 (d, $J = 8.2$ Hz, 4H), 3.70 (s, 6H), 2.83 (s, 4H).

(ii) Bis(4-hydroxyphenyl)ethane. In a 150-mL Erlenmyer flask, fitted with a septum, was dissolved 3.6 g (0.015 mol) of bis(4-methoxyphenyl)ethane in 20 mL of dried CH₂Cl₂. The solution was cooled to –70 °C in a dry ice/2-propanol bath, and boron tribromide (1.6 mL, 0.011 mol) was added through septum. The reaction mixture was stirred at room temperature for 2 h and then poured into icy water (40 mL) in an icebath to give a suspension after the solution was neutralized with sodium acetate. The suspension was filtered, washed with H₂O (2 × 20 mL), and air-dried overnight to give a white crude product. Finally, 3.0 g (0.014 mol, 93%) of white solid was obtained after the crude was taken up in methanol (100 mL), filtered, and condensed. ^1H NMR (300 MHz/CD₃OD): δ 6.90 (d, $J = 8.2$ Hz, 4H), 6.65 (d, $J = 8.2$ Hz, 4H), 2.70 (s, 4H).

(iii) Bis(3-nitro-4-hydroxyphenyl)ethane. To a diluted nitric acid solution at 5 °C was added 5.0 g (0.023 mol) of bis(4-hydroxyphenyl)ethane.³³ The mixture was stirred at 25 °C for 20 h and then for another 2 d after 10 mL of acetonitrile was added to the above mixture. Finally, 4.0 g (57%) of yellow solid was obtained after the mixture was filtered and washed with water (10 mL × 5) and methanol. ^1H NMR (300 MHz/CDCl₃): δ 10.48 (s, OH), 7.88 (d, $J = 2.1$ Hz, 2H), 7.37–7.33 (dd, $J_1 = 8.4$ Hz, $J_2 = 2.1$ Hz, 2H), 7.10–7.07 (d, $J = 2.1$ Hz, 2H), 2.92 (s, 4H).

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(iv) Bis(3-amino-4-hydroxyphenyl)ethane. A suspension of 4.0 g (13.8 mmol) of bis(3-nitro-4-hydroxyphenyl)ethane with 0.21 g (0.92 mmol) of PtO₂ in 200 mL of absolute ethanol was hydrogenated on a Parr hydrogenator at 50 psi for 26 h. A total 1.5 g (45%) of greenish solid was obtained after another 200 mL of methanol was added to the reaction mixture, which was then sonicated, filtered, and washed with 700 mL of ethanol. ^1H NMR (300 MHz/DMSO-d₆): δ 8.65 (s, OH), 6.48–46 (d, $J = 8.2$ Hz, 2H), 6.4 (d, $J = 1.5$ Hz, 2H), 6.20–6.17 (dd, $J_1 = 8.2$ Hz, $J_2 = 1.5$ Hz, 2H), 4.35 (s, NH₂), 3.26 (s, 4H).

(v) 2,2'-Dimethyl-6,6'-ethylenedibenzoxazole. In 5 mL of acetic anhydride, 1.7 g (7.0 mmol) of bis(3-amino-4-hydroxyphenyl)ethane was first heated at 80–90 °C for 20 h under a dry atmosphere. The mixture was filtered, and the filtrate was precipitated by addition of H₂O (100 mL). A total 1.2 g of white solid was obtained after the solid was filtered and dried. The intermediate product was heated further at 240–280 °C for 10 min. The reaction residue was taken up in 40 mL of CHCl₃ with silica gel. The loaded silica gel was filtered, extracted with 1:3:6 CH₃CN/ethyl acetate/hexane (1 L), and condensed to a yellowish crude product, which was purified by chromatography with 1:3:6 CH₃CN/ethyl acetate/hexane (2 L) to afford 0.38 g (18%) of off-white solid. ^1H NMR (300 MHz/CDCl₃): δ 7.39 (s, 2H), 7.35–7.32 (d, $J = 8.4$ Hz, 2H), 7.08–7.05 (d, $J = 8.4$ Hz, 2H), 3.05 (s, 2H), 2.62 (s, 6H).

(vi) 3,3'-Diethyl-2,2'-dimethyl-6,6'-ethylenedibenzoxazolium Tosylates. To a round-bottom flask were added 0.35 g (1.3 mmol) of 2,2'-dimethyl-6,6'-ethylenedibenzoxazole and 2.0 g (10 mmol) of ethyl tosylate. The solid mixture was heated at 100 °C under nitrogen for 20 h to give a yellowish precipitate. White solid (0.7 g, 78%) was obtained after the precipitate was taken up in CH₂Cl₂ (8 mL), filtered, and washed with CH₂Cl₂ (5 mL × 3) and diethyl ether (5 mL × 2). ^1H NMR (300 MHz/CD₃OD): δ 7.97 (s, 2H), 7.85–7.82 (d, $J = 8.7$ Hz, 2H), 7.66–7.63 (d, $J = 8.7$ Hz, 2H), 7.63–7.60 (d, $J = 7.5$ Hz, 4H), 7.20–7.18 (d, $J = 7.5$ Hz, 4H), 4.60 (q, $J = 7.2$ Hz, 4H), 3.25 (s, 4H, CH₂), 3.06 (s, 6H, CH₃), 2.33 (s, 6H, CH₃), 1.54 (t, $J = 7.2$ Hz, 6H, CH₃-C).

(vii) 2,2'-Di(2-anilidovinyl)-3,3'-diethyl-6,6'-ethylenedibenzoxazolium Tosylates. To a round-bottomed flask were added 350 mg (0.51 mmol) of 3,3'-diethyl-2,2'-dimethyl-6,6'-ethylenedibenzoxazolium tosylates, 350 mg (1.8 mmol) of *N,N'*-diphenylformamidine, and 5 mL of acetic anhydride. The reaction mixture was heated with stirring at 124–128 °C for 7 min under a dry atmosphere and then cooled to yield an orange precipitate. A total 110 mg (0.12, 24%) of yellow solid was obtained after the mixture was filtered and washed with acetone (5 mL × 3). ^1H NMR (300 MHz/CD₃OD): δ 8.80–8.76 (d, $J = 12.3$ Hz, 2H, CH=), 7.72–7.20 (m, 16H, aromatic), 5.9–5.86 (d, $J = 12.3$ Hz, 2H, CH=), 4.33–4.31 (q, $J = 7.5$ Hz, 4H, N-CH₂), 3.19 (s, 4H, CH₂), 2.36 (s, 6H, CH₃), 1.51–1.46 (t, $J = 7.5$ Hz, 6H, N-C-CH₃).

(viii) Dimer-2. Under nitrogen, 100 mg (0.079 mmol) of 2,2'-di(2-anilidovinyl)-3,3'-diethyl-6,6'-ethylenedibenzoxazolium tosylates and 100 mg (0.45 mmol) of 1,3-dimethylbarbituric acid were dissolved in dried methylene chloride (100 mL). Triethylamine (0.4 mL) was added to the above solution. The reaction mixture was condensed to a solid residue after it was stirred for 4 d. The solid residue was chromatographed with a mix of 5:45:50 methanol/chloroform/ethyl acetate (1.3 L), and with a mix of 5:95 methanol/chloroform, to give 48 mg of yellow solid in 60% yield (99% pure by HPLC with 1:19 methanol/chloroform). ^1H NMR (300 MHz/CF₃CO₂D): δ 8.75 (s, 2H, CH=), 7.75 (m, 2H, aromatic H), 7.54 (m, 6H, aromatic H), 4.58 (t, 4H, N-CH₂), 3.66 (s, 12H, NCH₃), 3.33 (s, 4H, CH₂), 1.68 (t, $J = 6.0$ Hz, 6H, C-CH₃). MS (FAB): m/e 681.3 (M⁺ + 1).

(ix) Dimer-1. Synthesis of dimer-1 is two steps shorter because the intermediate, bis(4-hydroxyphenyl)methane, is commercially available. A yellow solid is obtained in 42% yield (one peak by HPLC with 1:19 methanol/chloroform). ^1H NMR (300 MHz/CF₃CO₂D): δ 8.754 (s, 2H, CH=), 7.794–7.766 (d, $J = 8.4$ Hz, 2H, aromatic H), 7.565 (m, 6H, aromatic H), 4.558 (t, 4H, N-CH₂), 4.487 (s, 2H, CH₂), 3.643 (s, 12H, NCH₃), 1.666 (t, $J = 6.3$ Hz, 6H, C-CH₃). MS (FAB): m/e 667.2 (M⁺ + 1).

(x) Dimer-0. Synthesis of dimer-0 is four steps shorter because the intermediate, 3,3'-diamino-4,4'-dihydroxybiphenyl, is commercially available. An orange solid is obtained in 52% yield (one peak by HPLC with 1:19 methanol/chloroform). ^1H NMR (300 MHz/CF₃CO₂D): δ

8.838 (s, 2H, CH=), 8.088 (s, 2H, aromatic H), 8.000–7.972 (d, $J = 8.4$ Hz, 2H, aromatic H), 7.823–7.795 (d, $J = 8.4$ Hz, 2H, aromatic H), 4.635 (q, $J = 7.2$ Hz, 4H, N-CH₂), 3.643 (s, 12H, NCH₃), 1.752–1.711 (t, $J = 7.2$ Hz, 6H, N-C-CH₃). MS (FAB): m/e 653.2 ($M^+ + 1$).

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Supporting Information Available: Complete crystallographic information for the monomer dye, including atomic coordinates for all atoms, bond lengths and angles, anisotropic displacement parameter, and torsion angles (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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