

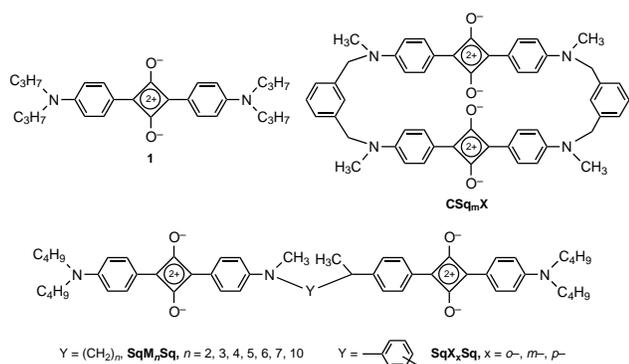
## Exciton Interactions in Nonconjugated Squaraine Dimers. Mechanisms for Coupling and Consequences for Photophysics and Photochemistry

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Exciton coupling between formally nonconjugated chromophores is frequently encountered in solids,<sup>1,2</sup> aggregates in solution<sup>3,4</sup> and microheterogeneous media,<sup>5,6</sup> and in polymers.<sup>7</sup> The theory of exciton coupling<sup>8–12</sup> has been fairly well developed and tested for a number of moderate-to-large aggregates; however, there have been relatively few elucidations of specific excitonic interactions between chromophores as a function of geometry and distance. In the point dipole approximation, the exciton theory indicates that the interaction between chromophores should be inversely proportional to the cube of the interchromophoric distance and proportional to the square of the transition moment of the interacting chromophores.<sup>9</sup> Thus, long-range excitonic couplings should only be observed for chromophores having very high oscillator strengths. Although a few systematic studies of intramolecular exciton coupling have been carried out for nonconjugated bichromophoric systems, they have mostly involved chromophores, such as porphyrins,<sup>13–15</sup> phthalocyanines,<sup>16,17</sup> or cyanines,<sup>18</sup> characterized by either close-lying transitions or transition dipoles with exchangeable directions. Squaraine chromophores offer the attraction of high extinction coefficients ( $\epsilon \approx 3 \times 10^5$ ) with only a single isolated transition dipole lying along the long axis.<sup>19</sup> In this paper, we report a study of exciton coupling in a series of bis-squaraines linked by simple polymethylene spacers (SqM<sub>n</sub>Sq,  $n = 2–10$ ) and more restricted xylyl-separated squaraines (SqX<sub>x</sub>Sq,  $x = o-, m-, p-$ ) and in a relatively rigid doubly bridged squaraine, CSq<sub>m</sub>X. Our study shows that



at least two types of exciton-coupled states are detectable, the relative prominence of each depending on the specific bis-squaraine structure and on solvent. Moreover, our study indicates that in flexible systems the ready accessibility of different dimer (aggregate) structures can have significant effects on the squaraine photophysics which can in turn affect photochemical reactivity.

The bis-squaraines were synthesized by straightforward techniques (Supporting Information). Exciton interaction is readily

**Table 1.** Physical Properties of Bis-squaraines in Organic Solvents at Room Temperature

	$\lambda_{\text{abs}}$ (nm) <sup>a</sup>	$\epsilon$ ( $10^5$ $\text{M}^{-1} \text{cm}^{-1}$ ) <sup>a</sup>	$\lambda_{\text{f}}$ (nm) <sup>a</sup>	$\Phi_{\text{f}}$ <sup>a</sup>	$\tau$ (ps, $\text{CH}_2\text{Cl}_2$ ) <sup>b,c</sup>	$\tau$ (ps, SOA) <sup>b,d</sup>
<b>1</b>	638	3.39	655	0.92 <sup>e</sup>	2900	
SqM <sub>2</sub> Sq	662, 594	5.41	678	0.044	5.3	1300
SqM <sub>3</sub> Sq	656, 610	5.45	666	0.087	25	1800
SqM <sub>4</sub> Sq	650, 616	5.44	658	0.18		
SqM <sub>5</sub> Sq	646, 628	5.43	658	0.39		
SqM <sub>6</sub> Sq	646, 630	5.32	658	0.46	330	2200
SqM <sub>7</sub> Sq	646, 631	5.37	657	0.50		
SqM <sub>10</sub> Sq	638	5.43	656	0.59	1100	
SqX <sub>o</sub> Sq	650, 616	5.39	658	0.15	80	
SqX <sub>m</sub> Sq	650, 618	5.40	663	0.26		
SqX <sub>p</sub> Sq	648, 624	5.42	660	0.39	420	
CX <sub>m</sub> Sq	576			~0	320	

<sup>a</sup> CHCl<sub>3</sub> solution. <sup>b</sup> Single-exponential lifetimes (>95% of signal intensity) determined from ground state bleaching recovery after pulsed excitation ( $\lambda_{\text{ex}} = 570–610$  nm) (Chen, H.; Farahat, M. S.; Law, K.-Y.; Whitten, D. G. *J. Am. Chem. Soc.* **1996**, *118*, 2584. Liang, Y. Y.; Baba, A. I.; Kim, W. I.; Atherton, S. J.; Schmehl, R. H. Submitted). <sup>c</sup> Corresponding fluorescence lifetimes obtained by time-correlated single-photon counting exhibited bi- or triexponential behavior. <sup>d</sup> Sucrose octaacetate glass at room temperature. <sup>e</sup> Quantum yield for a closely related squaraine (Law, K. Y. *J. Photochem. Photobiol. A* **1994**, *84*, 123).

detectable by the pronounced differences from a representative monomer (**1**) in absorption, emission, and transient spectra in organic solvents, partially aqueous organic solutions, room temperature (sucrose octaacetate), or low temperature (methyltetrahydrofuran) glasses. All squaraines in the SqM<sub>n</sub>Sq series show split absorption spectra compared with the monomeric squaraine **1** in organic solvents such as CHCl<sub>3</sub>, ethanol, or acetonitrile. The absorption spectra are concentration-independent,<sup>20</sup> and the splitting decreases as the number of methylene groups increases until  $n = 10$  where the absorption is virtually a single peak, only slightly broadened compared with that of **1**. The long-wavelength transition is the more intense with an extinction coefficient close to twice that of monomer **1** (Table 1). The SqM<sub>n</sub>Sq show fluorescence in these solvents with maxima to the red of **1** and with quantum yields and decay times decreasing as the number of methylenes decreases (Table

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- (20) The absorption spectra of both organic and aqueous organic solutions were found to be concentration-independent over the range of  $10^{-5}$ – $10^{-7}$  M.

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**Table 2.** Comparison of Experimental and Calculated Lowest Energy Absorption Band Splittings

compd	conformation	structure energy <sup>a</sup> (kcal/mol)	$\Delta\bar{\nu}$ (cm <sup>-1</sup> ) <sup>b</sup>	
			expt <sup>c</sup>	calcd <sup>d</sup>
SqM <sub>2</sub> Sq	extended	0	1740	1720
	folded	2.2	1920	1900
SqM <sub>3</sub> Sq	extended	3.7	1130	1340
	folded	0	1860	2170
SqM <sub>6</sub> Sq	extended	4.7	423	382
	folded	6.3		575

<sup>a</sup> The energy difference relative to that of the global minimum structure calculated by Monte Carlo simulation. <sup>b</sup> The energy difference between the two lowest energy excitonic levels for a given structure. <sup>c</sup> Determined as the difference in energy for the two lowest energy absorption bands in pure organic (for extended structure) or mixed aqueous (for folded structure) solvents. <sup>d</sup> Calculated using the extended dipole model<sup>11</sup> for the simulated geometries. Transition moment = 11.4 D computed from the oscillator strength of the monomer in chloroform. Dipole length = 13.8 Å estimated from the monomer N-to-N distance. Dielectric constant = 1.0.

1). The xylyl-separated bisquaraines show similar behavior; in contrast, the cyclic bisquaraine CSq<sub>m</sub>X shows a spectrum dominated by a sharp band blue-shifted (576 nm) from **1** with no detectable fluorescence. The spectrum resembles those of dimers detected in previous investigations.<sup>21</sup>

Very similar split spectra are observed for the bisquaraines (except CSq<sub>m</sub>X) in rigid glasses of organic "solvents" such as methyltetrahydrofuran (77 K) or sucrose octaacetate (SOA, room temperature). In contrast to organic solvents, in aqueous acetonitrile or aqueous alcohol most SqM<sub>n</sub>Sq give spectra similar to those of CSq<sub>m</sub>X.<sup>20</sup> In each case, this species is nonfluorescent. The absorption maxima in aqueous acetonitrile are generally near 580 nm, very similar to that reported earlier for the intermolecular squaraine dimer, likely a face-to-face or "H" dimer.<sup>21</sup> Consequently, we infer that in aqueous acetonitrile these bisquaraines are in a "folded" configuration with an "H" dimer relationship between the two chromophores. The lack of fluorescence from the folded forms is in accord with previous observations for dimers and "H" aggregates of structurally related squaraines<sup>21</sup> and can be attributed to the very low oscillator strength for the low-energy component of the split exciton band (and perhaps also to the low energy of this state for which rapid nonradiative decay should be expected).

Monte Carlo simulations<sup>21</sup> have been carried out for several bisquaraines to determine the lowest energy configurations (in the absence of solvent). The specific minimum energy configuration of individual bisquaraines depends upon the spacer, but in several cases there are energetically close-lying structures having folded and relatively extended geometries. Table 2 compares the lowest energy arrangements predicted for SqM<sub>2</sub>Sq, SqM<sub>3</sub>Sq, and SqM<sub>6</sub>Sq together with excitonic shifts calculated for these structures by the extended dipole approach.<sup>11,12</sup>

From these data it is inferred that for organic solvents in fluid and glassy states the bisquaraines are predominantly in a generally extended configuration such that the chromophores form "J" dimers. Here, excitonic coupling gives a low-energy transition (allowed) and a higher energy transition (less allowed); that the high-energy transition does not vanish ( $\epsilon \neq 0$ ) is attributed to the chromophores not being strictly parallel. Excitonic interactions for covalent dimers of simple aromatics have been studied using the point dipole approximation,<sup>9</sup> and through space and through bond contributions have been considered.<sup>22,23</sup> However, the use of the point dipole approximation is not warranted when the transition moment length

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is greater than interchromophore separation.<sup>11,24</sup> The agreement between the experimentally determined band splittings and those calculated using the extended dipole model (Table 2) suggests that the interaction in the present dimeric squaraine systems is strictly through space.

The striking decrease in fluorescence efficiency and decay times for the "J" dimers in organic solutions as the splitting increases for the SqM<sub>n</sub>Sq series is initially hard to understand, since the low-energy exciton transition has a high oscillator strength and thus a high  $k_f$ . The low fluorescent quantum efficiencies reflect shortened excited state decay times (Table 1); the lack of transients having longer decay time than a few picoseconds for SqM<sub>2</sub>Sq indicates that formation of triplets cannot account for the rapid decay of the lower lying (than monomer) exciton singlet. Indications of sources of the rapid nonradiative decay are found by comparing their fluorescence and transient spectroscopy in fluid solution and in SOA glass at room temperature. Thus, while absorption spectra are nearly identical in the two media (which should be of comparable polarity), the corresponding fluorescence is slightly red-shifted in the latter and much more intense. Increased quantum yields of 0.80, 0.54, and 0.30 are observed for SqM<sub>6</sub>Sq, SqM<sub>3</sub>Sq, and SqM<sub>2</sub>Sq in SOA, respectively, values quite close to that for **1** in fluid solution. These increases correlate closely with increased decay times (more than 2 orders of magnitude for SqM<sub>2</sub>Sq, Table 1) determined from recovery of transient bleaching upon picosecond laser photolysis. Since the most evident difference between fluid CHCl<sub>3</sub> (CH<sub>2</sub>Cl<sub>2</sub>) and glassy SOA is the rigidity of the latter, it seems most reasonable to attribute the short singlet decay times and reduced fluorescence for the bisquaraines in solution to a process which involves change in geometry. Since folded "H" dimers are nonfluorescent and relatively short-lived, a possible source may be conversion of the strongly fluorescent "J" dimer into something close to the folded "H" dimer.<sup>25</sup> Since the excited state of the J dimer is expected to be highly polar, collapse to the lower energy "H" dimer may occur on the order of picoseconds, especially when the spacer is short.<sup>26,27</sup>

The results obtained from this study may be instructive for understanding the photophysics, photochemistry, and decay processes occurring for flexible polychromophoric systems where the presence of even small amounts of low-energy traps like the folded "H" dimers or aggregates may sharply reduce excited state lifetimes and emission yields.

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**Supporting Information Available:** Experimental details and characterization data (7 pages). See any current masthead page for ordering and Internet access instructions.

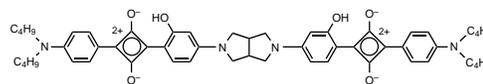
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(25) Additional evidence suggesting a folding mechanism comes from a study of the rigid bisquaraine which shows a splitting in absorption and fluorescence similar to SqM<sub>3</sub>Sq but a fluorescence efficiency of 0.3 and decay times in both media in the range 500–700 ps compared to the 25 ps decay time for SqM<sub>3</sub>Sq in CHCl<sub>3</sub>.



(26) Compare with the conversion of the *cis*-stilbene singlet to the twisted minimum, a similar "large amplitude" motion occurring in ~1 ps.<sup>27</sup>

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