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Medium-Controlled Aggregation of *trans*-Stilbene

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The photochemistry and photophysics of the stilbenes have been investigated thoroughly.[1] At low concentrations in hydrocarbon solvents the lowest excited singlet state of *trans*-stilbene, $^1t^*$, undergoes efficient trans → cis isomerization by overcoming a 2.9 kcal/mol torsional barrier which is augmented by 0.4 of the activation energy for viscous flow of the solvent.[2] Fluorescence competes with photoisomerization.[3] Interaction of $^1t^*$ with ground-state *trans*-stilbene, ^1t, gives cyclobutane photodimers as a diffusion-controlled reaction.[4] No excimer fluorescence accompanies the $^1t/^1t^*$ interaction, and there is no evidence for an intermediate in photodimerization.

Spectroscopic observations reflecting collective response from two or more *trans*-stilbene moieties have in common preassociation in the ground state. The afterglow observed on warming γ-irradiated *trans*-stilbene solutions at 77 K in squalane includes a structureless red-shifted emission that was attributed to excimer fluorescence.[5] Excimer fluorescence has also been assigned to a complex of *trans*-stilbene, cyclohexane, and γ-cyclodextrin.[6] Related observations rely on synthesis of materials that require close contact between covalently incorporated *trans*-stilbene structures or allow formation of multimolecular assemblies in which association between stilbene units occurs.[7−16] Spectroscopic consequences of the association of stilbene units fall roughly into two groups. In one group are systems exhibiting broad structureless red-shifted emission spectra reminiscent of excimer fluorescence,[5,7,14] and subtle changes in the absorption spectra.[14] Systems in the second group exhibit red-shifted structured fluorescence,[8−13,15,16] and absorption spectra usually attributed to excitonic delocalization of the excitation.[9−13,17] The structural distinction between the two groups appears to be face-to-face (card-pack) vs face-to-edge (herringbone, pinwheel) arrangements, respectively.

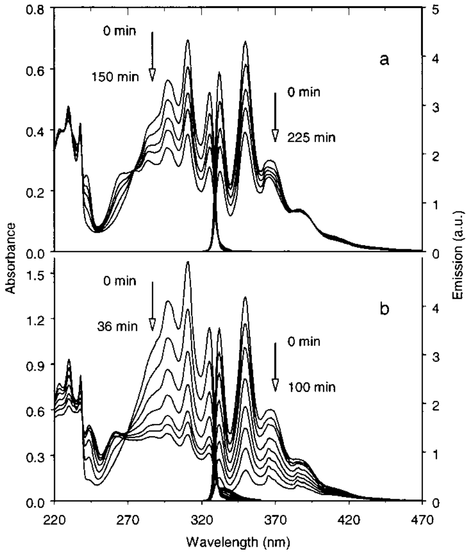

Figure 1. Absorption and fluorescence emission spectra of *trans*-stilbene in isopentane. (a) $T = 98$ K, $[^1t] = 4.6 \times 10^{-5}$ M, path length 0.4 cm. (b) $T = 110$ K, $[^1t] = 4.2 \times 10^{-5}$ M, path length 1 cm.

Ultraviolet and fluorescence spectra of *trans*-stilbene solutions in isopentane at low temperatures (98−110 K) undergo changes indicative of association, Figure 1. Typically, the sample at room temperature is placed in a cryostat whose temperature is controlled to ±0.1 K. The temperature is lowered slowly to 120 K and maintained for 2−3 h. No change in the UV absorption spectrum occurs during the latter period. The temperature is then decreased slowly to 114 K (above the mp of 113.3 K)[18] and then rapidly to the desired temperature. Aggregation begins after a 20−40 min induction period (longer at lower *T*). No spectral changes are observed until a concentration threshold ($\sim 7 \times 10^{-5}$ M) is exceeded. Isosbestic points are maintained at 98 K (Figure 1a), but not at higher *T*s (Figure 1b). Fluorescence spectra ($\lambda_{exc} = 274$ nm) reveal corresponding changes.

Singular value decomposition was employed to resolve the spectral matrices.[19] Absorption spectral sets at 98 K behave cleanly as two components. A third component emerges at higher temperatures which is minor at 104 K but dominant at 110 K. Fluorescence spectral sets behave as two components for all temperatures, indicating that the higher aggregate is non- fluorescent. Resolved absorption and fluorescence spectra are shown in Figure 2 for 98 and 110 K. Initial aggregate spectra are in agreement with fluorescence and fluorescence excitation spectra obtained by selectively exciting this aggregate ($\lambda_{exc} = 340$ nm) and selectively monitoring its emission ($\lambda_{em} = 409$ nm). No fluorescence is observed when a sample, aggregated at 110 K, is

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Table 1. Results of the Model Fit to the Kinetics in Figure 3[a]

	T (K)	k_1 (M^{-1} s^{-1})	$k_{-1} \times 10^4$ (s^{-1})	k_2 (M^{-1} s^{-1})	$k_{-2} \times 10^7$ (s^{-1})	$a_1 \times 10^4$ (s^{-1})	$a_2 \times 10^4$ (s^{-1})	$a_3 \times 10^4$ (s^{-1})
absorption	98	2.07	1.0			0.93	0.99	
emission	98	2.94	3.9			1.15	1.25	
absorption	110	23.8	10.4	10.2	5.0	10.0	9.5	10.8
emission	110	7.09	5.0	9.0	2.0	11.2	9.6	13.1

[a] The parameters a_1, a_2, and a_3 take into account the time-dependent available volume for stilbene monomer, dimer, and trimer, respectively, in the form $V = V_0 \exp(-a_i t)$.

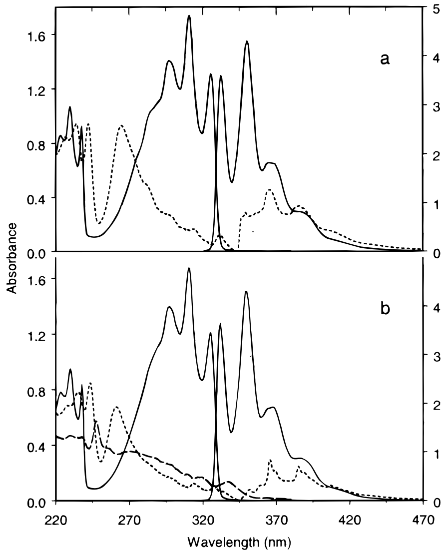

Figure 2. Absorption and emission spectra of the pure monomer, dimer and trimer forms of *trans*-stilbene in isopentane at $T = 98$ K (a) and at $T = 110$ K (b). Solid lines: monomer, dotted lines: dimer, dashed line: trimer. The trimer has no emission and does not accumulate at 98 K.

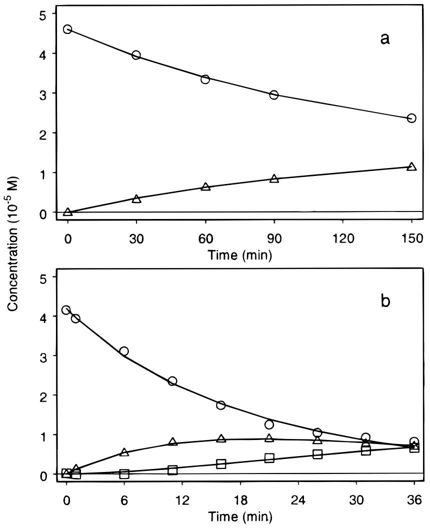

Figure 3. Time evolution of the various forms of *trans*-stilbene at $T = 98$ K (a) and at $T = 110$ K (b). Circles: monomer, triangles: dimer, squares: trimer. Solid lines show the fit to eqs 1 and 2, see text.

excited at 350 nm where only the higher aggregate absorbs. The aggregate absorption spectrum at 98 K is broader but has the same features as the initial aggregate at higher T spectra. The resemblance of these spectra to those observed by Whitten and co-workers for stilbene moiety aggregates in monolayer assemblies and vesicles suggests face to edge monomer interaction.[9-13] The simplest mechanism that accounts for our observations is

$$^1t + {}^1t \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} {}^1t_2 \tag{1}$$

$$^1t_2 + {}^1t \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} {}^1t_3 \tag{2}$$

Substitution of $^1t_2$ dimerization for eq 2 leads to less satisfactory agreement with the results. Precedent for the proposed $^1t_2$ dimer is formation of anthracene dimers upon slow, warming of dilute monomeric anthracene dispersed in a rigid 3:1 isopentane/methylcyclohexane glass, initially at 77 K.[20] Kinetics fits are improved if the effective volume, in which *trans*-stilbene and its reactions are confined, decreases exponentially with time. Exclusion of *trans*-stilbene from more ordered isopentane regions could also explain the induction period that precedes the onset of aggregation. The fits in Figure 3 take this exclusion into account. Association of stilbene molecules eventually slows down, possibly as a result of solidification of the medium in competition with acceleration of association due to volume exclusion. A sample heated to 110 K after a 240 min period at 104 K shows little further aggregation, contrary to expectations based on eqs 1 and 2 and the rate constants in Table 1. Exclusion and solidification should be sensitive to experimental conditions and solvent purity, accounting for deviations of rate constants determined independently from absorption and fluorescence experiments. The aggregation process slows abruptly below 100 K, indicating a sudden medium change at $T < 100$ K. The initial concentration dependence indicates that ^{1}t exclusion and, thereby, increased local [^{1}t] are prerequisites for aggregation. Since the initial effective volume, V_0, at the onset of aggregation is unknown, actual rate constants may be smaller than those in Table 1.

It is possible that rate-determining dimer formation is followed by much faster dimer association to give tetramer as the initially observed aggregate.[21] Minimum rate constants for dimer association in the 10^3-10^5 M^{-1} s^{-1} range required by this mechanism are probably consistent with expected viscosities for isopentane in the temperature range employed.[22-25] If such were the case, the nonfluorescent aggregate would be a pentamer or higher aggregate. Experiments designed to distinguish between aggregation mechanisms are in progress.

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Note Added in Proof. A paper by Gegiou, D.; Muszkat, K. A.; Fischer, E. *J. Am. Chem. Soc.* **1968**, *90*, 3907−3918 briefly describes aggregation of *trans*-4-ketostilbenes.

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