Spectroscopic Evidence for Aggregation of Stilbene Derivatives in Solution

M. Aguiar, L. Akcelrud, M. R. Pinto[1], T. D. Z. Atvars[1], F. E. Karasz[2] and Jack Saltiel[3]*

Departamento de Química, Universidade Federal do Paraná, Curitiba 81531-900 Brazil

[1]Instituto de Química, Caixa Postal 6154, UNICAMP, Campinas 13083-970 Brazil

[2]Polymer Science & Engineering, University of Massachusetts, Amherst MA 01002 USA

[3]Department of Chemistry and Biochemistry, Florida State University, Tallahassee FL 32306-4390 USA

The absorption, fluorescence and fluorescence-excitation spectra of concentrated toluene solutions of selected para substituted *trans*-stilbene derivatives provide strong evidence for aggregation. A red-shifted fluorescence spectrum peaking at 420 nm gains in intensity as the stilbene concentration is increased. The excitation spectrum of this new emission is well to the red of the normal stilbene absorption spectrum, consistent with the appearance of a red shifted shoulder in the UV spectrum. Formation of a fluorescent ground state dimer (or higher aggregate) is proposed to account for these observations. The presence of polar substituents is crucial to the formation of this ground state complex.

key words: Absorption, fluorescence and fluorescence-excitation spectra, *trans*-stilbene derivatives, aggregation

INTRODUCTION

The photochemical interconversion of the stilbenes continues to be of great interest because of their prototypical role in the elucidation of the mechanism of olefin cis-trans photo-isomerization. Photochemical studies have been complemented by photophysical and theoretical investigations [1]. At low concentrations in solution at ambient temperature the lifetime of the lowest excited singlet state of *trans*-stilbene, $^1t^*$, is short (~100 ps) due to fast torsional relaxation over a small energy barrier (~3 kcal/mol) [2]. Formation of a twisted intermediate is postulated whose partitioning between cis and trans isomers accounts for photoisomerization [3]. Fluorescence is observed from $^1t^*$ as a complementary process which gains in importance as the temperature is lowered. As the *trans*-stilbene concentration is increased, the diffusion controlled encounter of $^1t^*$ with ground state *trans*-stilbene, ^1t, gives cyclobutane photodimers [4,5] with a very large limiting quantum yield (0.77) [5]. An excimer intermediate was proposed for the dimerization [5]. A transient species, whose absorption was studied by ps pulsed laser spectroscopy at high *trans*-stilbene concentration (0.2-0.5 M) in benzene, forms at the diffusion controlled rate by $^1t^*/^1t$ interaction and decays with a lifetime of 420 ps [6]. Since it is likely that this transient is a precursor to photodimer(s), its assignment to an excimer or to a biradicaloid species at the pericyclic minimum [7] was considered, but an unequivocal choice between the two was not made.[6] No excimer fluorescence accompanies

the $^1t^*/^1t$ interaction as one might expect from an excimer intermediate with a 420 ps lifetime, but the position of the transient absorption is close to that expected from a superposition of the spectra for the stilbene radical anion/radical cation pair [6].

Structured and structureless red-shifted fluorescence spectra are observed from two or more interacting stilbene moieties, provided conditions favor preassociation in the ground state. A structureless red-shifted emission observed as an afterglow on warming γ-irradiated *trans*-stilbene solutions in squalane at 77 K has been assigned to excimer fluorescence [8], as has a similar emission from *trans*-stilbene hosted in a γ-cyclodextrin cavity along with one molecule of cyclohexane [9]. Emissions reflecting the response of two or more interacting *trans*-stilbene moieties have been observed in molecules designed to bring stilbene units into close contact either directly or through association in supramolecular assemblies [10-15]. Spectroscopic observations for such systems fall roughly into two categories: (a) the first is characterized by relatively small changes in the stilbene absorption spectra and the appearance of broad excimer-like structureless fluorescence spectra [8-10,13], and (b) the second exhibits excitonic bands in absorption [16] and structured red-shifted fluorescence [11,12,14,15]. The difference in the spectral responses of the complexes is attributed to differences in their molecular structure. Face-to-face association allows closer approach between stilbene partners and leads to excimer-like fluorescence and the possibility of photodimerization. In contrast, edge-to-face (herringbone, pinwheel) association holds the partners further apart, leads to excitonic spectral manifestations, including structured fluorescence, and is not prone to photodimerization [11-14].

These relationships were evident in early photophysical and photochemical studies of crystals of *trans*-stilbenes. The four *trans*-stilbene molecules in the unit cell of the crystal adopt an edge-to-face relationship [17]. This arrangement is associated with very strong structured red-shifted fluorescence and leads to no photodimerization. Solid state photodimerization of stilbenes, as of other alkenes, is subject to topochemical control, the two reactive double bonds must be parallel and separated by no more than about 4.2 Å [18,19]. *trans*-2,4-Dichlorostilbene [19a] and its 3' methyl derivative [19b] have been shown to adopt face-to-face intermolecular relationships in the crystal. They exhibit excimer-like fluorescence and undergo photodimerization. The methyl derivative is especially interesting because it is dimorphic. In one crystal modification the molecules are arranged head-to-head in stacks and in the other they are arranged as head-to-tail pairs (lower energy excimer fluorescence) [19b]. Dimerization and excimer fluorescence appear to be complementary processes in such face-to-face crystals, the former being favored by higher temperatures. In the case of *trans*-2,4-dichlorostilbene photodimerization efficiency decreases with cooling but is still measurable at -180 °C [19a].

One of us has described a procedure for cooling dilute *trans*-stilbene solutions in isopentane below the mp of the medium such that the kinetics of solute aggregation, probably reflecting the onset of the *trans*-stilbene crystallization process, could be followed by monitoring the development of excitonic bands in absorption and structured red-shifted fluorescence in emission [20]. Red-shifted fluorescence also occurs through the interaction of pendant stilbene groups attached to polymer backbones such as polyglutamic acid [21] or copolymers containing poly(methacrylate) units [22]. Some of us have encountered related spectroscopic observations in our studies of the photo and electroluminescence properties of polymers bearing stilbene-based pendant groups [15]. It was the latter work that motivated this study of the aggregation of *trans*-stilbenes substituted so as to model the pendant stilbenes, but free of a polymeric backbone.

In this report we describe absorption and fluorescence observations on three model *trans*-stilbene derivatives that lead us to propose the formation of new fluorescent species in solution, under normal conditions of concentration and at ambient temperatures. These fluorescent species are identified as ground state dimeric complexes or molecular aggregates.

EXPERIMENTAL

Materials

trans-Stilbene (Aldrich, 99%), *trans*-p-methylstilbene (Aldrich, 96%), *trans*-p-chloromethylstilbene (ClMS) (Aldrich, 95%), and *trans*-p-hydroxymethylstilbene (HOMS) (Aldrich 99%) were recrystallized from chloroform. The synthesis of *trans*-p-(p-ethylphenoxy)methylstilbene (POMS) has been described [15b].

Briefly, a 1 g (0.0082 mol) solution of *p*-ethylphenol (Aldrich, 99%) in 40 mL dimethylformamide (DMF) (Fisher A. C. S.) was heated to reflux. To the refluxing solution was added potassium carbonate (Fisher, A. C. S.) (1 g, 0.0072 mol) and a second solution composed of 1 g (0.004 mol) of *trans*-p-(chloromethyl) stilbene in 10 mL DMF. The solution was stirred and refluxed overnight and the resulting mixture poured into distilled water. The precipitate was collected after standing 4 h, dried in air at ambient temperature, washed with acetone, dried under vacuum overnight, and recrystallized from chloroform (Fisher A. C. S.). Characterization of PMS by NMR, FTIR and elemental analysis was described in ref 15b. Other materials were the best available commercially and, unless noted otherwise, were used as received.

Spectroscopic Measurements

Absorption spectra, obtained for chloroform and toluene solutions, were measured either with an IBM 9420 or with a Perkin-Elmer lambda 5 UV-visible spectrophotometer. Short pathlength UV cells were employed in order to extend the measurements to concentrations as high as 10^{-2} M. A Neslab-RTE 4DD constant temperature circulation bath that maintains selected temperatures to within ±0.1 °C was employed for measurements at different temperatures. Temperatures were monitored continuously during each scan with an Omega Engineering Model 199 RTD digital thermometer in a reference cell placed in the same constant temperature cell holder. Fluorescence and excitation spectra of the model stilbenes in chloroform or toluene solution were measured with the use of either a Perkin-Elmer MPF 44 or the previously described [23] modified Hitachi/Perkin-Elmer MPF-2A fluorescence spectrophotometer.

RESULTS AND DISCUSSION

The structures of the three *trans*-stilbene derivatives studied in this work and the acronyms that will be used in referring to them are shown below. Each has a relatively polar substituent in the para position (chloromethyl, hydroxymethyl, aryloxy-methyl) whose polar component is not in direct conjugation with the stilbene moiety, being insulated from the phenyl

ClMS

HOMS

POMS
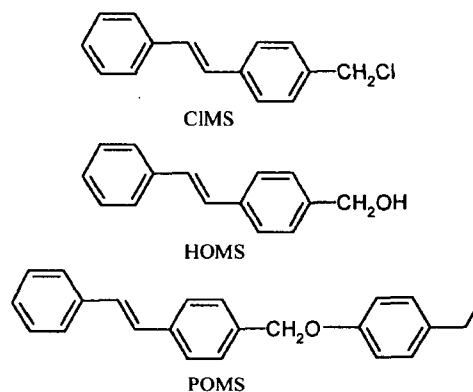
group by a methylene unit. Since the parent trans-stilbene does not exhibit the phenomena described herein, in each case it is the substituent that enhances the tendency to aggregate. Aggregation is revealed by changes in the absorption spectra as the concentration is increased and accompanying excitation wavelength dependent changes in the fluorescence spectra.

Absorption measurements

In dilute solution the UV spectra bear a close resemblance to the spectrum of trans-stilbene. Spectra for 10^{-5} M toluene solutions of CIMS, HOMS and POMS, plotted in arbitrary absorbance units, are shown in Figure 1. They have been scaled differentially to facilitate comparison. As expected, their λ_{max} is close to 320 nm. A subtle difference is that the vibronic structure is somewhat less pronounced in POMS.
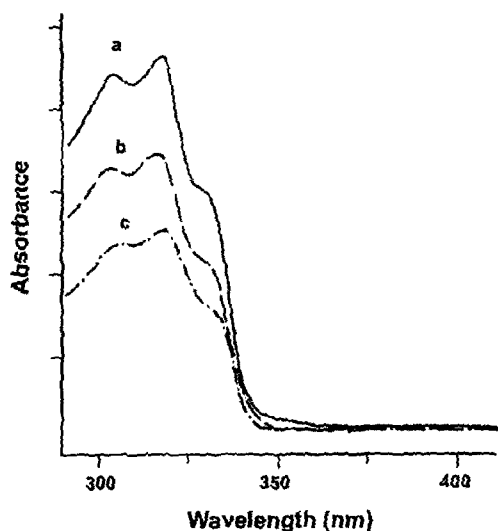
Figure 1. Absorption profiles of CIMS (a), HOMS (b) and POMS (c), 1×10^{-5} M in toluene.
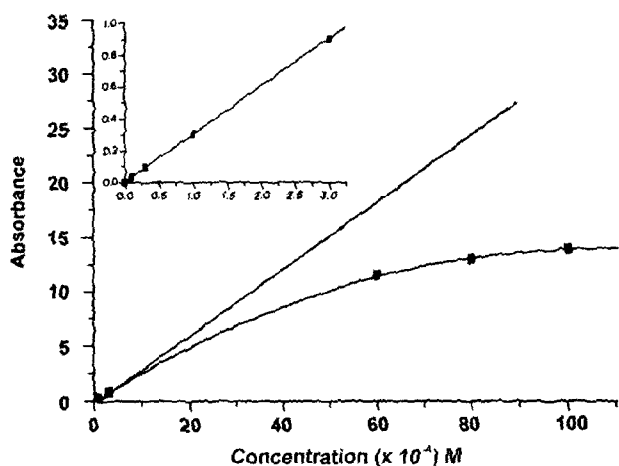
Figure 2. Absorbance at 320 nm for CIMS in toluene as a function of initial CIMS concentration. The inset is a detail of the low concentration part of the curve.
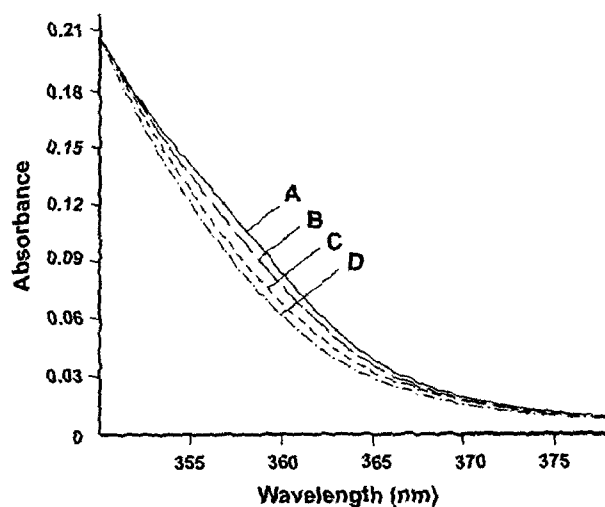
Figure 3. The onset region of the absorption spectrum of a 5×10^{-3} M solution of CIMS in toluene as a function of temperature: Curves A, B, C, and D are for 26.6, 40.9, 61.5, and 80.4°C, respectively.

With increasing concentration the spectra undergo pronounced distortion, which is reflected in significant deviation from ideal Beer-Lambert Law behavior. This is illustrated for CIMS in Figure 2 for absorbance at 320 nm. The inset in Figure 2 shows that the Beer-Lambert Law is obeyed at low concentrations up to about 3×10^{-4} M. Above that concentration the plot curves downward, reflecting the formation of new species with lower molar absorptivity at the monitored wavelength. This decrease in relative absorbance in the region of monomer trans-stilbene absorption, Figure 1, is accompanied by the development of a shoulder at the red edge of the spectrum whose intensity diminishes with increasing temperature, Figure 3. The spectra in Figure 3, for a 5×10^{-3} M CIMS in toluene, are corrected for the temperature dependence of the density of the solvent. They reveal an isosbestic point at about 350 nm indicating reversible formation of a single ground state aggregate species that tends to revert to the monomer as the temperature is raised. The opposite temperature dependence was observed when the stilbene moieties are bound to a polymer chain as pendant groups [15]. Increasing the temperature enhances aggregate fluorescence in the polymer. The difference is probably related to the intermolecular nature of the process described in this work vs the intramolecular nature of the earlier observations.

Emission measurements

The effect of concentration on the fluorescence spectra is shown in Figure 4. Standard 1.00-cm^2 quartz cells were employed and excitation was at 320 nm, close to the absorption maximum of monomer absorption. The resulting spectra were arbitrarily scaled to facilitate shape comparison. No attempt was made to maintain the relationship between relative spectral area and fluorescence quantum yield. In all three model stilbenes the major change as the concentration is increased

from 10^{-5} to 10^{-4} M in toluene is loss of the highest energy vibronic band to self-absorption [24]. The spectra in this concentration range have λ_{max} close to 360 nm and exhibit mirror relationships with the absorption spectra in Figure 1, consistent with fluorescence from the monomers. Further increases of the concentration to 10^{-3} and 10^{-2} M values lead to suppression of monomer fluorescence and appearance of new red-shifted spectra (labeled complex in Figure 4). The new spectra have λ_{max} in the 390-420 nm range and diffuse but clearly defined vibronic structure. Observation of the red-shifted spectra coincides with the deviation from Beer-Lambert Law in Figure 2 and the appearance of the shoulder at the onset of the absorption spectra. The spectroscopic observations are consistent with excitation and emission of edge-to-face ground state complexes. Formation of the ground state complexes can be detected by exciting at 360 nm where the monomers are transparent and monitoring the fluorescence at 420 nm where the monomer fluorescence contribution is small. This is illustrated in Figure 5 for ClMS in toluene. Figure 5 shows
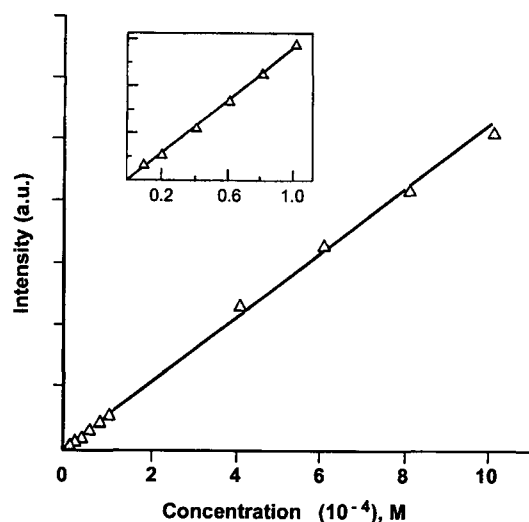

Figure 5. The dependence of complex fluorescence intensity (λ_{em}= 420 nm) on initial ClMS concentration in toluene (λ_{exc}=360 nm). The inset shows the low concentration range.
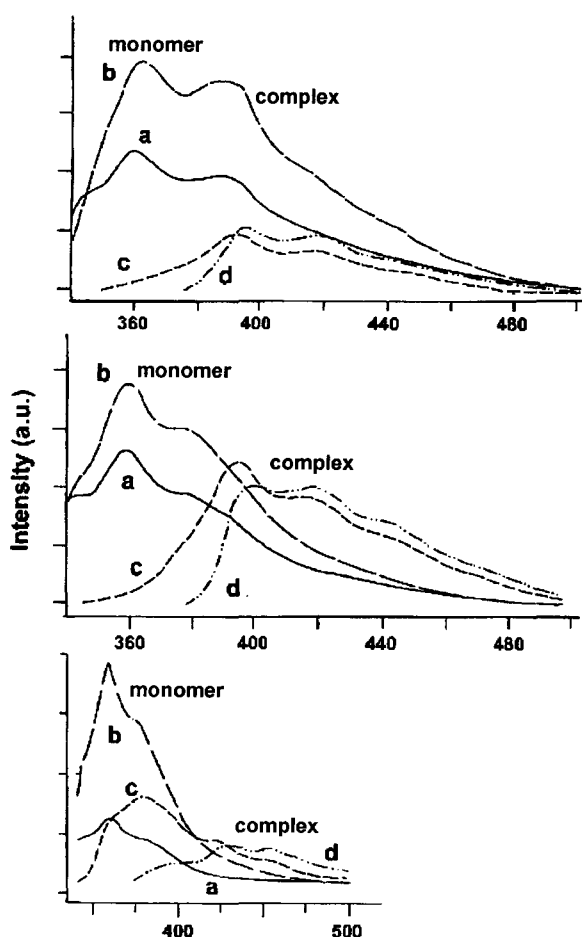

Figure 4. Fluorescence spectra of the model stilbenes in toluene for λ_{exc}=320 nm as a function of concentration. Panels A, B and C are for ClMS, HOMS and POMS, respectively by multiples of ten in the order a, b, c to d with a designating the lowest, 1×10^{-5} M, and d the highest, 1×10^{-2} M. concentrations.
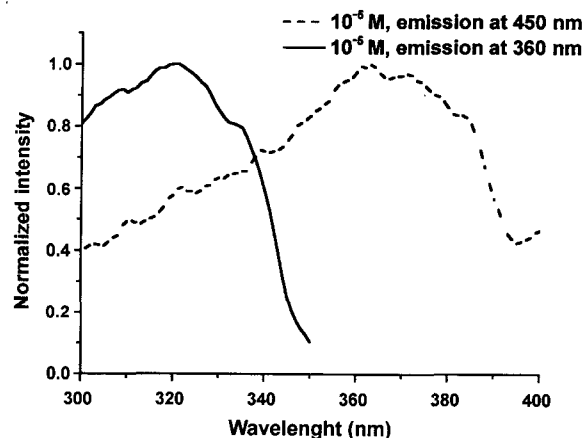

Figure 6. Normalized excitation spectra of ClMS in toluene (1×10^{-5} M) obtained by monitoring monomer emission at 380 nm and aggregate fluorescence at 450 nm (see text).

that complex absorbance at 360 nm depends linearly on the concentration of the model stilbene and that the formation of the complex is already evident at concentrations as low as 10^{-5} M. The latter conclusion is confirmed by the fluorescence excitation spectra in Figure 6 recorded for a 10^{-5} M ClMS solution in toluene. Monitoring monomer fluorescence at 380 nm gives a fluorescence excitation spectrum that is consistent with the monomer absorption spectrum in Figure 1, whereas monitoring fluorescence at 450 nm, where little, if any, contribution from the monomer is expected, gives a strongly red-shifted excitation spectrum with an onset at about 400 nm. In Figure 6 fluorescence intensity was normalized to facilitate comparison of the excitation spectra. The low fluorescence intensity at 450 nm leads to some distortion of the corresponding excitation spectrum by scattered light, but there is no doubt as to the difference in the origins of the two spectra.

The intensity of the fluorescence excitation spectrum at λ_{em} =450 nm increases as the concentration of ClMS is increased. However, the shape of the spectrum (not shown) is progressively distorted at the shorter wavelengths due to self-absorption. The shape of the red onset of the fluorescence excitation spectrum is independent of concentration up to at least 10^{-3} M suggesting that the phenomenon involves formation of a discrete aggregate, instead of a series of aggregates in which the number of associated monomer units increases as the concentration is increased.

The linear dependence of the fluorescence intensity of the complex on the initial (i.e., total) stilbene concentration, Figure 5, is surprising. Assuming formation of a single ground state complex species, C, its formation from the para substituted *trans*-stilbenes (pS), excitation and fluorescence can be represented by eq 1-3, respectively.

$$n pS \xrightleftharpoons{K_C} (pS)_n \tag{1}$$

$$(pS)_n \xrightarrow{h\nu} {}^{1}(pS)_n^* \tag{2}$$

$${}^{1}(pS)_n^* \rightarrow (pS)_n + h\nu \tag{3}$$

$${}^{1}(pS)_n^* \rightarrow (pS) \tag{4}$$

It follows from eq (1) that $[(pS)_n]=K_C[pS]^n$ so that, at negligibly small concentrations of $(pS)_n$, the fluorescence intensity of the complex, I_C, should be proportional to $[pS_0]^n$ where $[pS_0]$ designates the initial concentration of the model stilbene and $n \geq 2$ is the number of aggregated stilbenes in the complex. Upward curvature in the plots in Figure 5 is expected under such conditions and close scrutiny of the plot in the inset of Figure 5 reveals systematic deviation from the straight line consistent with such curvature. At the higher stilbene concentrations, the concentration of the complex is not negligible and the initial concentration of the stilbene is significantly larger than its effective concentration (see Figure 2). Coincidentally, the use of the initial, instead of the smaller but unknown, stilbene concentration in Figure 5 compensates for the curvature nearly exactly. Nonetheless, the small curvature in the inset in a concentration range for which the extent of aggregation must be small, Figure 2, suggests that n must be small. We tentatively assume that the complex, at least in the lower concentration range, is dimeric and take n=2.

The monomer solid state can be taken as the high concentration limit. Fluorescence behavior at this limit was explored recording fluorescence and fluorescence excitation spectra of solid ClMS using front-face excitation and detection. Normalized fluorescence spectra excitation spectra for λ_{em}=432 and 470 nm and fluorescence spectra for λ_{exc}=380 and 400 nm are shown in Figure 7. The shapes of the spectra are clearly
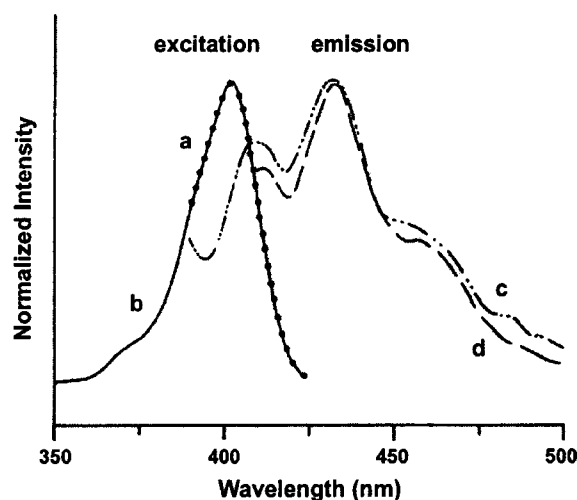

Figure 7. Normalized excitation and fluorescence spectra of ClMS in the solid state. Monitored emission wavelengths 432 and 470 nm, curves a and b, respectively, and excitation wavelengths 380 and 400 nm, curves c and d, respectively.

insensitive to the changes in monitoring and excitation wavelengths. In contrast to the broad fluorescence excitation spectrum of the aggregate in solution, Figure 6, the excitation spectrum of the solid sample consists of a relatively narrow band centered at about 400 nm and starting at about 425 nm. The emission spectrum of the solid sample is also strongly red-shifted with much better defined vibronic structure; compare the emission spectra in Figure 7 with spectra c and d in panel A of Figure 4. If the spectra in Figure 7 can be taken as representative of those of a microcrystal, we can safely conclude that the aggregates that we characterized in solution have much too low stoichiometry to be assigned to microcrystals. The solid state emission spectra bear a closer similarity to the spectra of homopolymers with pendant stilbene moieties [15].

The crucial role of the polar substituents in promoting ground state complex formation was demonstrated by control experiments using toluene solutions of the parent *trans*-stilbene and *trans-p*-methylstilbene. Emission spectra of solutions in the 10^{-5}-10^{-4} M range showed expected distortions in monomer emission due to self-absorption (contributions from reemission are expected to be negligible due to the low fluorescence quantum yields of stilbene solutions at ambient temperatures [25]). There was no evidence for aggregate formation in the emission spectra. Probably related to the observation with our model stilbenes is the aggregation of *trans-p*-ketostilbenes at low temperatures [26]. The importance of polar substituents in promoting aggregation has been demonstrated in other aromatic molecules [27,28].

Aggregation of a stilbene derivative in the absence of polar substituents at room temperature has been reported for the rigid stilbene analogue *trans*-1,1'-biindanylidene in methyl-cyclohexane or ethanol solutions at concentrations as low as 10^{-4} M [29]. However, in contrast to our observations, the

fluorescence of the *trans*-1,1'-biindanylidene ground state complex is structureless suggesting face-to-face interaction of the stilbene chromophores in that case.

SUMMARY

Spectroscopic evidence supports the formation of fluorescent ground state complexes from substituted stilbenes having a relatively polar substituent in the para position. The concentration dependencies of absorption and fluorescence studied in greater detail for the chloromethyl substituent suggest that the complex is dimeric. The structured fluorescence spectra are consistent with edge-to-face associations of the stilbene moieties. Complex formation is detected by fluorescence at concentrations as low as 10^{-5} M in toluene at ambient temperature. At higher concentrations, up to 10^{-2} M, the red-shifted complex fluorescence completely replaces monomer fluorescence. Parallel studies with the parent *trans*-stilbene reveal no spectroscopic evidence for aggregation.

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