The Formation and Behavior of Fluorescent Lewis Acid−Base Exciplexes and Triplexes

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The formation of fluorescent exciplexes has been observed for numerous combinations of excited-state electron acceptors with ground-state electron donors and vice versa.[1] Some exciplexes have been observed to react with a second molecule of donor or acceptor to form triplexes; however, in most cases the triplexes are either nonfluorescent or only weakly fluorescent at room temperature in solution.[2] Nonfluorescent triplexes have also been implicated as intermediates in exciplex quenching processes[3,4] and photochemical addition reactions.[5] In addition to the well-known charge-transfer stabilized excited-state complexes, a second class of excited-state complexes in which a polar excited molecule or exciplex serves as an electron pair acceptor and a small polar molecule as a lone pair donor was described by Chandross[6,7] 30 years ago. These complexes, which we shall refer to as Lewis acid−base (LAB) exciplexes and triplexes, have received far less attention than their charge-transfer-stabilized counterparts. We report here an investigation of the formation and behavior of the strongly fluorescent LAB exciplexes and triplexes formed between singlet *trans*-3-aminostilbene and three alkylamines. The overlapping fluorescence spectra of the monomer, exciplex, and triplex have been deconvoluted and the kinetics of their formation and decay have been resolved using a combination of Singular Value Decomposition (SVD) and kinetic modeling.[8,9]

The lowest excited singlet state of *trans*-3-aminostilbene ($^1S^*$) has a large fluorescence quantum yield ($\Phi_f = 0.78$) and long singlet lifetime ($\tau_s = 7.5$ ns) in cyclohexane solution as a consequence of a high barrier for singlet state isomerization.[10] Its fluorescence maximum, but not its absorption maximum, is strongly red-shifted in polar solvents as a consequence of a larger

dipole moment in its $^1S^*$ vs S_0 state (11.9 vs 1.5 D). ZINDO calculations indicate that its $^1S^*$ state has significant CT (aniline → styrene) character. As shown in Figure 1a, addition of incremental amounts of di-*n*-propylamine (Pr_2NH) to a cyclohexane solution of 3-aminostilbene results in broadening of the fluorescence band, a continuous red-shift in the emission maximum, and a decrease in the integrated band intensity. No shift is observed in the absorption maximum at the highest amine concentrations and no fluorescence is observed when Pr_2NH is the solvent. Similar results were obtained with *n*-propylamine ($PrNH_2$) and triethylamine (Et_3N). The fluorescence decay of $^1S^*$ is single exponential; however, in the presence of added amine the decays are either bi- or triexponential, depending upon the amine concentration and emission wavelength.

The observation of continuous red-shifts and multiple exponential decay suggests the presence of more than one excited-state complex. Analysis of the spectral matrices for the fluorescence by means of SVD using the self-modeling algorithm of Volkov[8] indicates the presence of three components. The resultant pure component spectra obtained with Pr_2NH are shown in Figure 1b and are assigned to the monomer, exciplex, and triplex. Similar results were obtained for $PrNH_2$ and Et_3N. Emission maxima for the exciplexes and triplexes (Table 1) are red shifted by ca. 20 and 40 nm, respectively, from that of the monomer (387 nm). The concentration vectors obtained from the SVD analysis of the Pr_2NH spectra are shown in Figure 2. The concentration dependence of the vectors clearly indicates that the second and third components are formed sequentially. Qualitatively similar results are obtained for $PrNH_2$ and Et_3N. The growth of the second (exciplex) component shows similar concentration dependence for all three amines; however, the growth of the third (triplex) component is noticeably retarded for EtN_3 when compared to the other two amines.

A kinetic model for reversible sequential formation of the exciplex and triplex and quenching of the triplex by amine is shown in Scheme 1, where k_d, k_{de}, and k_{dt} are the sum of the radiative and nonradiative rates for the monomer, exciplex, and triplex, respectively. Kinetic modeling of the concentration vectors for $PrNH_2$ in Figure 2 and for the other two amines using a multistep numerical integration technique[11] provides the rate constants reported in Table 1. Rate constants were optimized using an iterative BFGS quasi-Newton[12] or Nedler-Mead Simplex[13] optimization procedure and represent best fits. Rate constants for exciplex formation (k_e) for $PrNH_2$ and Pr_2NH are diffusion-limited in cyclohexane solution and the value for Et_3N is slightly slower.[14] Triplex formation (k_t) is somewhat slower than exciplex formation and these rates decrease with amine *N*-alkylation. Rate constants for dissociation of the exciplex and triplex (k_{-e} and k_{-t}) are much slower than those for their formation; however, assumption of irreversible exciplex formation leads to inferior results for the kinetic modeling. Unimolecular decay rate constants for the exciplexes (k_{de}) are smaller than those for the monomer (k_d) whereas those for the triplexes (k_{dt}) are larger. On the basis of the concentration dependence of the total fluorescence intensity (Figure 1a) it is likely that the exciplex, like the monomer, decays predominantly via fluorescence, whereas nonradiative decay pathways are more important for the triplex.

Several lines of evidence indicate that the 3-aminostilbene−

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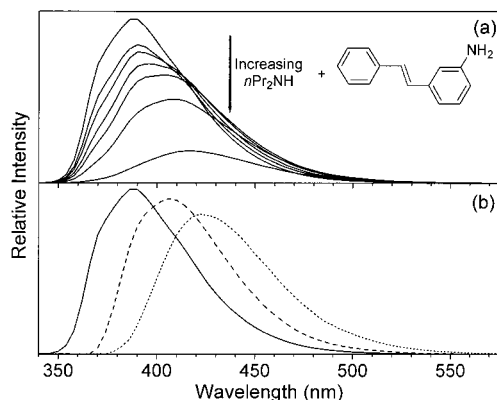
Figure 1. (a) Fluorescence spectra of *trans*-3-aminostilbene in cyclohexane solution in the presence of 0, 7.3, 15, 29, 41, 73, and 219 mM di-*n*-propylamine and (b) Deconvoluted fluorescence spectra of the monomer (—), exciplex (- - -), and triplex (···).

Table 1. Exciplex and Triplex Emission Maxima and Kinetic Data for Exciplex and Triplex Formation and Decay[a]

	n-propylamine	di-*n*-propylamine	triethylamine
emission max[b]			
λ_e	404	406	407
λ_t	424	422	418
rate $\times 10^{-9}$ [c]			
k_d	0.13	0.13	0.13
k_{de}	0.04	0.09	0.09
k_{dt}	0.18	0.24	0.67
k_e	10.1	11.0	8.11
k_{-e}	0.13	0.25	0.10
k_t	7.82	4.00	0.70
k_{-t}	0.38	0.19	0.05
k_{qt}	0.58	2.00	

[a] All data for cyclohexane solutions deoxygenated by purging with nitrogen to the point of constant fluorescence intensity. [b] Maxima of the exciplex and triplex fluorescence (± 3 nm) obtained from SVD analysis. [c] First-order rate constants (s^{-1}) except in the case of k_e, k_t, and k_{qt}, which are second-order rate constants ($M^{-1} s^{-1}$). Estimated accuracy $\pm 15\%$.

amine exciplex and triplex are not normal charge-transfer-stabilized excited-state complexes.[1] First, the rate constants k_e and k_t are larger for the primary or secondary vs tertiary amine. Thus the stability of the exciplex and triplex is not enhanced by lowering the amine oxidation potential upon *N*-alkylation.[15] Second, in the more polar solvents dibutyl ether and acetonitrile quenching is less efficient than in cyclohexane. Furthermore, only a small fluorescence shift is observed for 3-aminostilbene in the presence of 0.2 M $PrNH_2$ in dibutyl ether (from 420 to 423 nm). No exciplex or triplex fluorescence is observed in acetonitrile. These observations are analogous to those reported by Chandross[7] for quenching of the CT singlet state of 9-(4-(dimethylamino)-phenyl)anthracene by low concentrations of small polar molecules such as dimethyl formamide in methylcyclohexane solution. The observation of continuously shifting emission with increasing DMF concentration was attributed to the formation of 1:1 and 1:2 complexes with Lewis acid−base (LAB) character; however, methods were not readily available at that time for the deconvolution of the spectra and kinetic analysis.

(15) The approximate oxidation potentials of the primary, secondary, and tertiary amine are 2.2, 1.3, and 1.0 V vs SCE. Burget, D.; Jacques, P.; Vauthey, E.; Suppan, P.; Hasselbach, E. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 2481−2487.
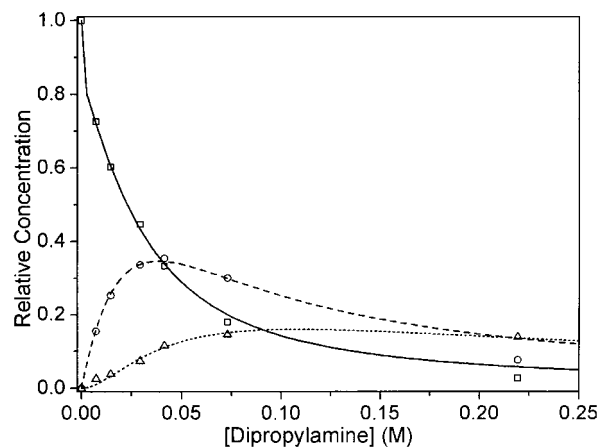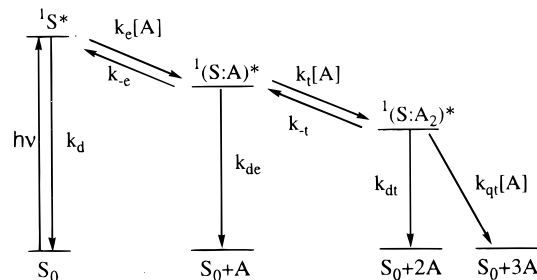

Figure 2. Concentrations of the *trans*-3-aminostilbene monomer (□), exciplex (○), and triplex (△) obtained from singular value decomposition of the data in Figure 1a. The lines are fits of the concentrations to Scheme 1.

Scheme 1. Proposed Kinetic Scheme for *trans*-3-Aminostilbene (S) Exciplex and Triplex Formation with Ground State Amine (A)

The most probable structure for a LAB-stabilized 3-aminostilbene−amine exciplex would involve interaction of the electron-deficient amino group of the aminostilbene singlet state with the lone pair of the ground-state amine to form a two-center three-electron bond.[16] Amines are known to form stable ground-state LAB complexes with strong Lewis acids such as BF_3 in which the association constants decrease in the order $RNH_2 > R_2NH \gg R_3N$,[17] similar to the trend we observe for the rate constants for triplex formation. Interaction of an electron-deficient nitrogen with a ground state amine has previously been proposed to account for the quenching of arene−amine exciplexes and the TICT state of 4-(dimethylamino)benzonitrile by amines;[3, 4] however, the putative exciplex and triplex intermediates in these reactions are nonfluorescent. Further studies of the formation and structure of LAB exciplexes and triplexes are in progress.

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