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The Luminescence Spectra of the 8-Methoxypsoralen Excited-State Complexes and Photochemical Product in Argon, Methanol/Argon, and Water/Argon Matrices at 10 K[†]

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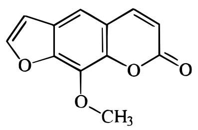
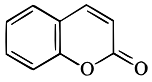
The luminescence spectra of the 8-methoxypsoralen, 8-MOP, excited-state complex have been observed in argon matrices at 10 K. The excited-state complex is most probably an excimer, formed for cases in which high concentrations of 8-MOP are deposited in a pure-argon matrix. For cases in which 8-MOP is in the presence of alcohol or water, another excited-state complex, an exciplex, is formed. Finally, when the 8-MOP/methanol/argon or 8-MOP/water/argon mixtures are photolyzed, a unique photochemical product is observed. This product is most probably the ground-state dimer, similar to the coumarin dimer formed in alcohol solutions upon UV irradiation. The luminescence emission spectra of all three of the complexes are different and overlapping, resulting in spectra that seem anomalous. These results are similar to the reported anomalous emission spectrum of coumarin by Song, et al., which is chemically and spectroscopically similar to 8-MOP.[1,2,3]

1. Introduction

8-MOP, a compound naturally occurring in the *Psoralea* plant, has been used over the centuries to prevent more than 23 different skin diseases, including psoriasis and vitiligo.[4] Descriptions from the early Vedic literature from India and from Egyptian writings indicate that the roots, leaves, and seeds of the plant were ingested by the patient. Then he or she sat in the intense sunlight to induce the photochemical reaction.[4] It has been determined that 8-MOP is the active ingredient and that it intercalates between the strands of the double helix in DNA.[5]



8-Methoxypsoralen



Coumarin

8-MOP undergoes a two-photon cross-linking reaction with thymines on the DNA strands.[5] 8-MOP is a coumarin derivative, and the two compounds have similar spectra and reactivities. Previous room-temperature solution studies of coumarin have shown that it has the tendency to form dimers when its concentrated solutions are photolyzed with UV light.[6] Direct irradiation of coumarin in ethanol or water solutions yields the cis head-to-head dimer. Triplet phosensitization of coumarin by benzophenone in alcohol solutions yields the trans head-to-head dimer. Irradiation of coumarin solutions in benzene solutions does not yield any product.[6] The formation of the coumarin dimers is due to the 2 + 2 cycloaddition reaction to form the cyclobutane moiety. This is the same chemistry as that which occurs when the 8-MOP photoreacts with the thymines in the DNA. The formation of the cis coumarin dimer is thought to proceed via the excited singlet state. The formation of the trans coumarin dimer is thought to proceed via the excited triplet state obtained by photosensitization. The formation of the 8-MOP cross-linked complex with DNA is thought to proceed via the excited triplet state of 8-MOP.[5]

There have been earlier reports of the anomalous phosphorescence to fluorescence intensity ratio (P/F ratio).[1,2,3] The literature reports that the ratio is high (approximately 10) for cases in which 8-MOP is in alcohol or water solutions at room temperature or in 77 K glassy solutions. The ratio is much lower (approximately one) when 8-MOP is in hydrocarbon solutions. The present 10 K matrix-isolation study involves varying the concentration of 8-MOP in argon matrices, varying the concentration of 8-MOP and methanol or water in argon, and photolyzing the 8-MOP/methanol/argon or 8-MOP/water/argon mixtures. In all three cases, the P/F ratio differs from that of the isolated 8-MOP in argon.

2. Experimental Section

Argon (Air Products, 99.999%) matrices of 8-MOP (Aldrich, 99.99%) were prepared by depositing 1−2 mmol of the 8-MOP/argon mixture at approximately 1 mmol/hr onto quartz substrate windows held at 10 K in a closed-cycle helium refrigerator (Air Products CS202). Solid 8-MOP was placed in an oil diffusion vacuum-pumped stainless-steel tube (oven) at room temperature. Heating tape was wrapped around the stainless steel tube positioned as closely as possible to the substrate window. Argon was passed through the heated tube containing 8-MOP. Separate deposition experiments were carried out with the oven heated to 50, 85, and 145 °C. The temperature was read with a thermometer that was placed in the heating tape. The resulting mixture was sprayed onto the substrate window held at 10 K. It should be emphasized that the different oven temperature depositions at 50, 85, and 145 °C were prepared in order to prepare low, medium, and high concentrations, respectively, of 8-MOP in the rare-gas matrix. The exact concentrations were not known. However, the low concentration matrix spectra were consistent with the literature spectra of the 8-MOP monomer. Methanol (Aldrich, 99.9%) or water (deionized) was vaporized on the vacuum line and combined with argon in the mole percent concentrations of 10, 5, 2, 1, and 0.5. The methanol/argon or water /argon mixture was passed over the heated 8-MOP sample and then deposited. The refrigerator containing the prepared matrix sample was placed in the sample chamber of the

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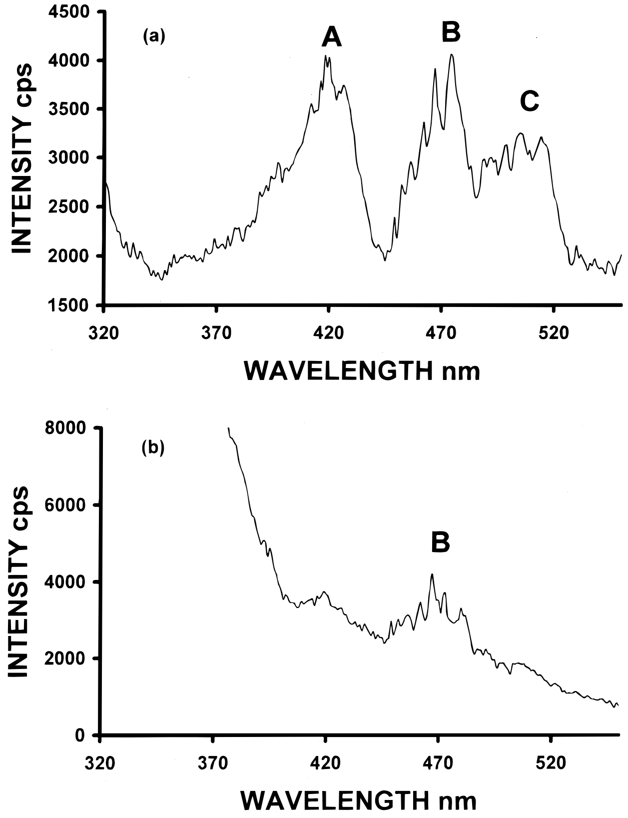

Figure 1. Luminescence emission spectra of 8-MOP in argon deposited at 50 °C. (a) The excitation wavelength was 300 nm. (b) The excitation wavelength was 350 nm.

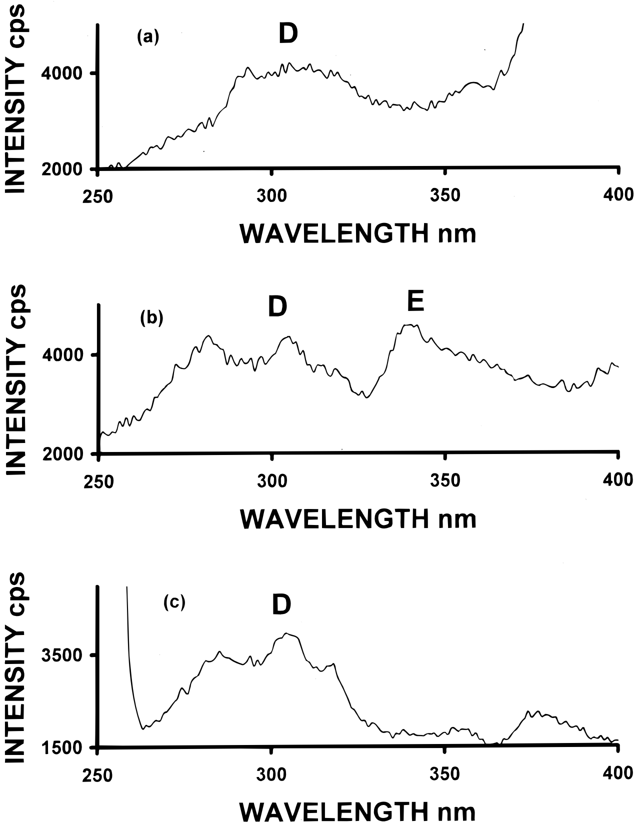

Figure 2. Luminescence excitation spectra of 8-MOP in argon deposited at 50 °C. (a) The emission wavelength was 420 nm. (b) The emission wavelength was 467 nm. (c) The emission wavelength was 495 nm.

spectrometer. Luminescence spectra were obtained with a Spex Fluorolog 1681 spectrometer. The photolysis of the matrix samples was achieved using the unfiltered light of the Oriel 200 W xenon arc lamp.

3. Results

3.1 Luminescence Spectra of 8-MOP in Argon. Figure 1a,b shows the 10 K emission spectra of 8-MOP in argon for cases in which the matrix, prepared by a 50 °C oven deposit, was excited at 300 and 350 nm, respectively. In Figure 1a, three separate bands, labeled A, B, and C, with emission maxima at 420, 467, and 495 nm, respectively, and with fairly equal intensity, were observed when the matrix was excited at 300 nm. Figure 1b shows that when it was excited at 350 nm, the band labeled B with the emission maximum at 467 nm (spacing 1924 cm^{-1}) was observed with the highest intensity. Band A also appears to be present, but with much lower intensity. Figure 2a−c shows the luminescence excitation spectra when the emission was monitored at 420, 467, and 495 nm, respectively. In parts a and c of Figure 2, only one excitation band, labeled D, was observed at approximately 300 nm. In Figure 2b, two excitation bands, labeled D and E, were observed with the band maxima at approximately 300 and 350 nm. Thus, it appeared that two species were present in the matrix, which were available for excitation. The first had an excitation band D, at 300 nm, and two emission bands A and C, at 420 and 495 nm, respectively. The second had an excitation band E, at 350 nm, and an emission band B, at 467 nm. On the basis of the polarization studies already presented in the literature, it is assumed that bands A and C associated with the first 8-MOP species are the fluorescence and phosphorescence spectra, respectively.[1,2,3] It is also assumed that band B at 467 nm associated with the second 8-MOP species is a phosphorescence band because the Stokes shift relative to the excitation band at 350 nm is large.

Figure 3 shows the emission spectra for the matrices prepared using three different 8-MOP oven temperatures of 50, 85, and 145 °C. A dramatic increase in the phosphorescence intensity of band B was seen as the deposition temperature increased. Spectral band C appeared to increase in intensity as well, but this can be interpreted as being on the shoulder of the dramatically increasing band B. Figure 4 shows that there was a concomitant increase in the excitation band E, at 350 nm, with increasing temperature, whereas excitation band D exhibited only small changes. Taken together, it appeared that the second 8-MOP species, associated with excitation band E, at 350 nm, and phosphorescence band B, at 467 nm, increased in intensity as the concentration of 8-MOP increased with increasing oven-deposition temperature. Photolysis of the matrix samples did not yield any changes in the spectra.

3.2 Luminescence Spectra of 8-MOP/Water/Argon and 8-MOP/Methanol/Argon Matrices. Fifteen experiments were performed to investigate the role of varying the concentration ratio of 8-MOP to water. Another fifteen experiments were performed using methanol instead of water. Essentially, identical results were obtained. The fifteen experiments involved 8-MOP deposition temperatures of 50, 85, and 145 °C, representing increasing 8-MOP concentration. For a given temperature deposit, the water concentration was varied between 10, 5, 2, 1, and 0.5 mole percent. The results of four of these experiments, representing the extreme values of 8-MOP and water concentrations are presented in Figures 5 and 6. Figure 5 represents the

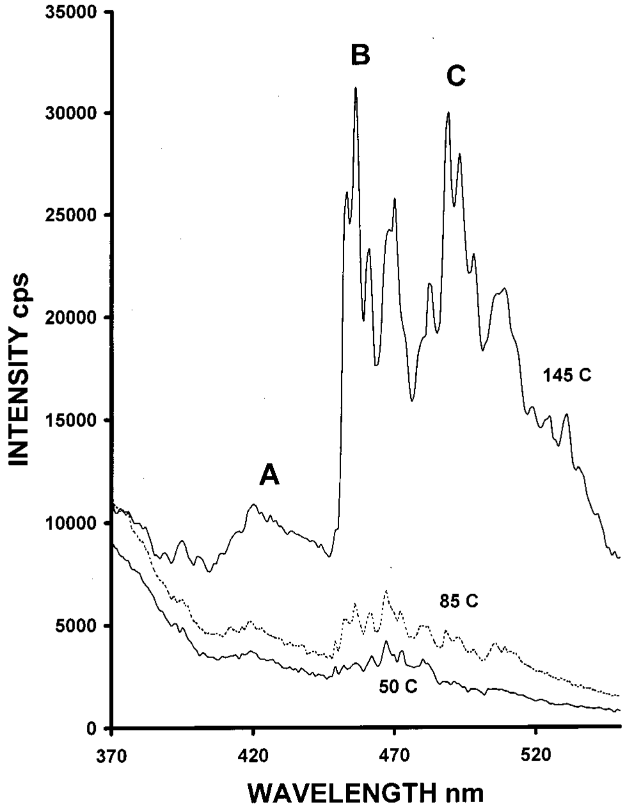

Figure 3. Luminescence emission spectra of 8-MOP in argon deposited at 50, 85, and 145 °C. The excitation wavelength was 350 nm.

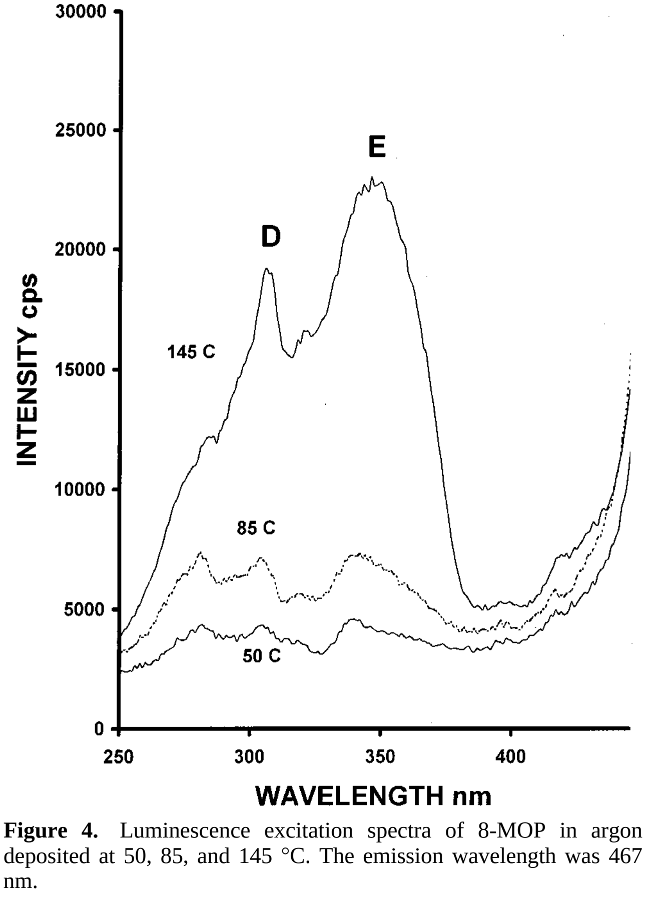

Figure 4. Luminescence excitation spectra of 8-MOP in argon deposited at 50, 85, and 145 °C. The emission wavelength was 467 nm.

excitation spectra and Figure 6 represents the emission spectra of the following argon matrices: (a) 145 °C 8-MOP deposit, 10% water, (b) 50 °C 8-MOP deposit, 10% water, (c) 145 °C 8-MOP deposit, 0.5% water, and (d) 50 °C 8-MOP deposit, 0.5% water.

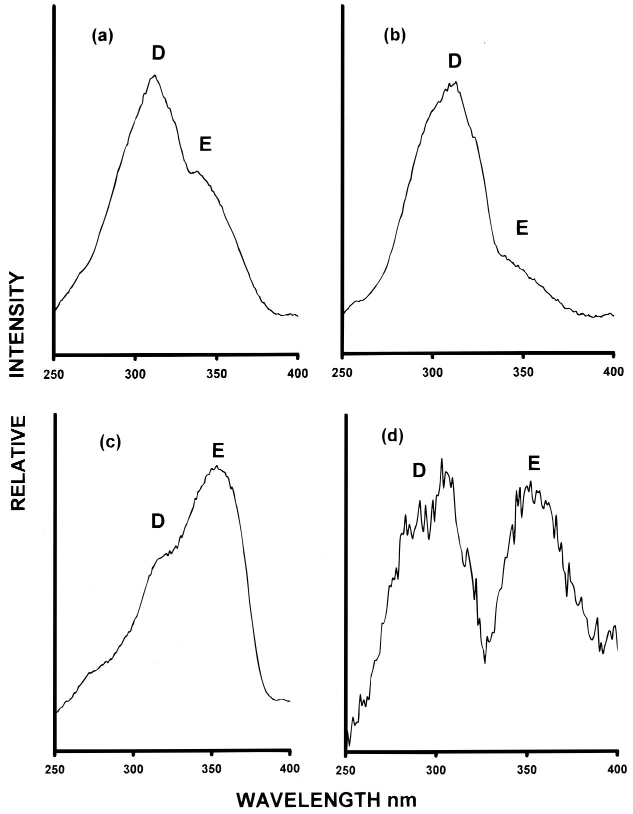

Figure 5. Excitation spectra of 8-MOP in argon monitored at 467 nm: (a) 145 °C 8-MOP deposit, 10% water; (b) 50 °C 8-MOP deposit, 10% water; (c) 145 °C 8-MOP deposit, 0.5% water; and (d) 50 °C 8-MOP deposit, 0.5% water.

3.3 Luminescence Spectra of 8-MOP/Water/Argon Matrices after 1 h of Photolysis. Figures 7 and 8 are the luminescence excitation and emission spectra, respectively, of a 145 °C, 10% water matrix of 8-MOP before and after photolysis. The excitation spectra in Figure 7 show that when monitored at 420 nm, there is a dramatic increase in the excitation band intensity at 350 nm, after photolysis. The excitation spectra monitored at 467 and 495 nm are not shown. These spectra show a decrease in the excitation band intensity at 300 nm after photolysis. The emission spectra in Figure 8 show that there is a dramatic increase in the emission band intensity at 420 nm and decrease in the emission band intensities at 467 and 495 nm, respectively. Taken together, the results show that after photolysis, a new species is produced that absorbs at 350 nm and emits at 420 nm.

Discussion

Table 1 summarizes the results described in the Experimental Section. Four distinct species can be identified from the data. The first species is 8-MOP in the “normal” monomer form. It is the isolated or nearly isolated 8-MOP in a pure argon environment. It is found when a 50 °C deposit of 8-MOP in argon matrix is prepared. It is characterized by an excitation band at 300 nm, a fluorescence band at 420 nm, and a phosphorescence band at 495 nm.

The second species is present in small amounts in the 50 °C argon matrix. As the concentration of 8-MOP increases, the excitation band at 350 nm and the phosphorescence band at 467 nm increase in intensity in the 85 °C deposit spectra and

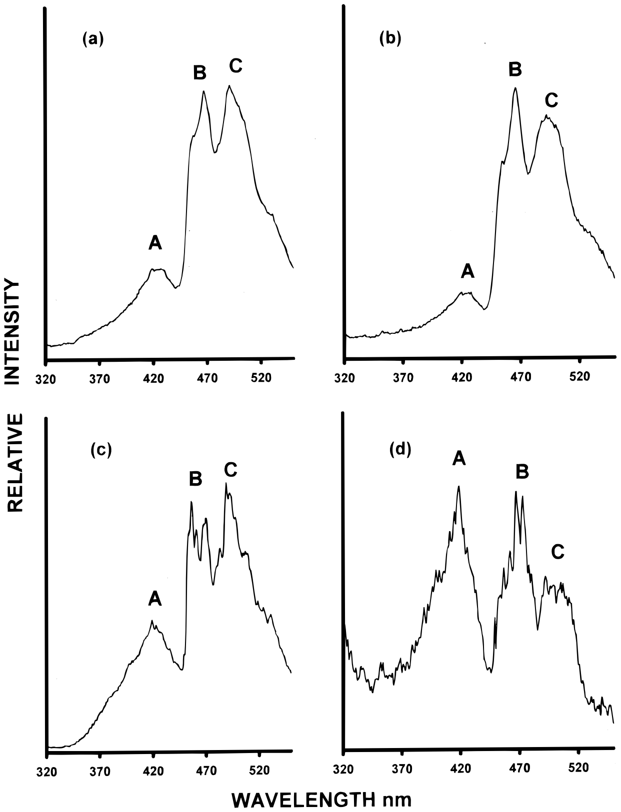

Figure 6. Emission spectra of 8-MOP in argon excited at 350 nm: (a) 145 °C 8-MOP deposit, 10% water; b) 50 °C 8-MOP deposit, 10% water; c) 145 °C 8-MOP deposit, 0.5% water; and d) 50 °C 8-MOP deposit, 0.5% water.

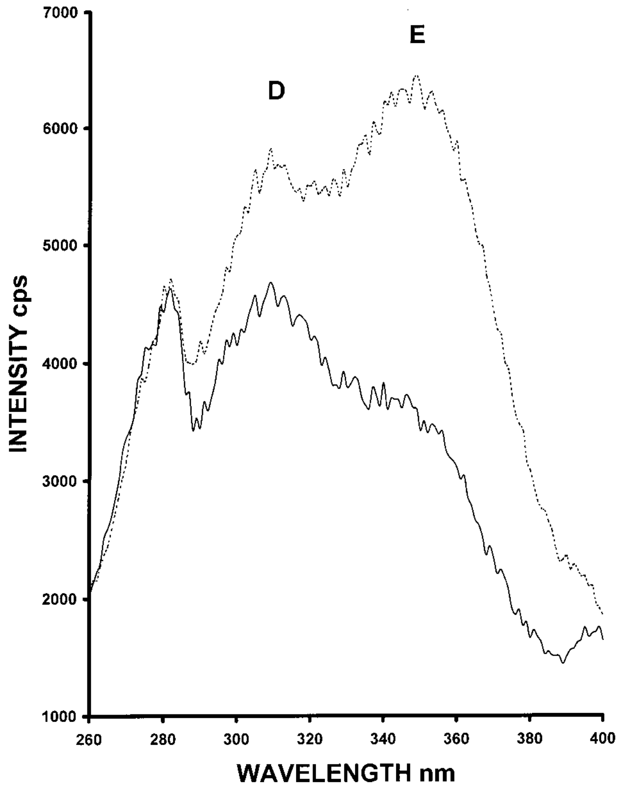

Figure 7. Excitation spectrum of a 145 °C deposit of 8-MOP in argon and 10% water, monitored at 420 nm, (a) before photolysis and (b) after photolysis.

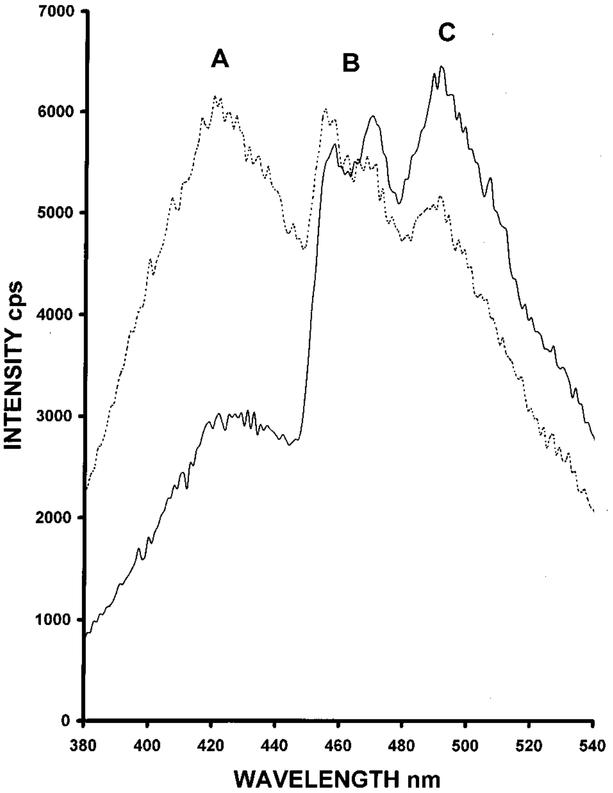

Figure 8. Emission spectrum of a 145 °C deposit of 8-MOP in argon and 10% water, excited at 350 nm, (a) before photolysis and (b) after photolysis.

then dramatically dominate the spectra of the 145 °C deposit. Photolysis of the 8-MOP/argon matrixes for 1 h did not produce any changes in the spectra. Therefore, the second species is associated with an excited-state complex. Because the 8-MOP molecules are large and planar, one would expect a stacking alignment during the preparation of the matrix. The interaction could be a $\pi-\pi^*$ type between stacked molecules or an end-on interaction related to the known photochemically induced 2 + 2 cycloaddition found in the 8-MOP/thymine reactions in DNA or the coumarin end-on cis and trans photodimers. It is known that in order to form the cross-linked complex in DNA, two photons are required to cause the stepwise reaction between distinct π electrons in 8-MOP and two thymines. In the 8-MOP/thymine cross-linked complex in DNA, the stereochemistry is cis at both ends, resulting in a folded S-shaped structure.[5] Given the restrictions of the rigid matrix and the two-photon requirement, a structure involving three 8-MOP molecules in an excited-state complex is improbable. Therefore, an excited-state dimer, or excimer, which absorbs at 350 nm and phosphoresces at 467 nm, is proposed. The 8-MOP excimer emission spectrum is similar to the spectrum of coumarin in methylcyclohexane at 77 K.

The coumarin spectrum is broad and is centered at 435 nm. Possibly the literature spectrum of coumarin is, in fact, of an excimer.[7]

The third species is found for cases in which 8-MOP is excited in the presence of water or methanol in the argon matrix. In the 8-MOP/argon matrix results discussed above, the presence of the excimer is noted for cases in which the P/F ratio of approximately one in the ‘normal’ monomer spectrum (Figure 6d) changes to approximately 10 (Figure 6c), due to an increase in the 467 nm band intensity. Coincidentally, this intensity change also occurs when the third species is present. Figure 6a,b shows that the band at 467 nm increases in intensity concomitantly with increasing water or alcohol concentration,

TABLE 1. Summary of Experimental Conditions, Results, and Interpretation

			emission bands (nm)			
	excitation bands (nm)		fluorescence	phosphorescence		
experimental conditions	D	E	A	B	C	interpretation
dilute 8-MOP in argon	300		420		495	normal 8-MOP monomer
8-MOP/H$_2$O/Ar or 8MOP/MeOH/Ar	300			467		water or MeOH exciplex with 8-MOP
concentrated 8-MOP in argon		350		467		8-MOP excimer
8-MOP/H$_2$O/Ar or 8MOP/MeOH/Ar photolyzed 1 h		350	420			ground-state 8-MOP dimer

resulting in a P/F ratio of approximately 10. This is attributed to an excited-state complex because the spectrum differs from that obtained after the matrix is photolyzed for 1 h. Thus, the third species is an exciplex formed between an 8-MOP and water or methanol, presumably as a 1:1 complex. The excitation spectra in Figure 5a,b confirm that the exciplex absorbs at 300 nm and phosphoresces at 467 nm. Although this is consistent with the 77 K spectrum of 8-MOP in ethanol,[1,2,3] it differs from the 77 K spectrum of coumarin in ethanol.[8] The coumarin spectrum exhibits monomer phosphorescence centered at 520 nm only. Thus, it appears that the exciplex formation is unique to 8-MOP.

The fact that the water exciplex and the methanol exciplex have identical emission spectra could indicate that the exciplex is similar in nature to the indole-water and indole-methanol exciplexes.[9] In these examples, solvated electrons have been detected in a solid matrix surrounding the exciplex. This is explained by a model in which the nonbonding electron on the water or methanol interacts with the empty π orbital of indole, generated by the indole electron excitation to the π^* state. The excited electron cannot get back to the ground state because of the presence of the nonbonding water or methanol electron interaction, and so the electron is ejected. A few other similar exciplex systems are given in reference 10.[10] At this point, the orbital nature of the 8-MOP exciplex can only be speculated upon because no direct evidence is provided in this work.

The fourth species was discovered when the 8-MOP/water/argon or 8-MOP/methanol/argon matrices were irradiated for 1 h with UV light. As mentioned in the Introduction, irradiation of coumarin in a nonpolar solvent like benzene does not yield a photoproduct. In alcohol solution, however, the cis head-to-head dimer is formed. These results are exactly analogous to the matrix results. Upon irradiation, the 8-MOP in argon matrix spectrum is unchanged, and the 8-MOP in water/argon or methanol/argon spectra exhibit a photoproduct. Although the structure of the new photoproduct cannot be determined using these experiments, the results are consistent with a ground-state dimer, possibly in the cis head-to-head configuration, generated by singlet excited-state photochemistry, as in the case of coumarin.

Although the spectra and photochemistry of 8-MOP and coumarin have already been published, this paper involving matrix isolation represents a significant contribution to the understanding of the role that the molecular environment plays on the P/F ratio. Furthermore, the excited-state dimer and exciplex have been identified and distinguished from the photochemically produced dimer.

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