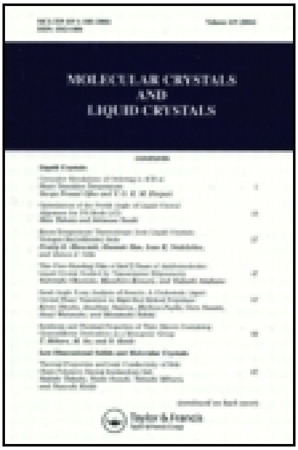

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Hole-Burning Structure and Mechanism of Acridine and Aminoacridines Doped in Polyvinyl Alcohol Films

Chien-Chih Chiang [a] [b] , Ji-Yen Cheng [a] [b] , Yah-Ru Cheng [a] [b] , Hsuan-Shen Chen [a] [b] , Chung-Yuan Mou [b] & Ta-Chau Chang [a]

[a] Institute of Atomic and Molecular Sciences, Academia Sinica. P. O. Box 23-166, Taipei, 10764, Taiwan, ROC

[b] Department of Chemistry, National Taiwan University, Taipei, Taiwan, ROC

Version of record first published: 04 Oct 2006.

To cite this article: Chien-Chih Chiang , Ji-Yen Cheng , Yah-Ru Cheng , Hsuan-Shen Chen , Chung-Yuan Mou & Ta-Chau Chang (1996): Hole-Burning Structure and Mechanism of Acridine and Aminoacridines Doped in Polyvinyl Alcohol Films, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 291:1, 175-181

To link to this article: http://dx.doi.org/10.1080/10587259608042745

Mol. Cryst. Liq. Cryst., 1996, Vol. 291, pp. 175–181
Reprints available directly from the publisher
Photocopying permitted by license only

HOLE-BURNING STRUCTURE AND MECHANISM OF ACRIDINE AND AMINOACRIDINES DOPED IN POLYVINYL ALCOHOL FILMS

CHIEN-CHIH CHIANG[ab], JI-YEN CHENG[ab], YAH-RU CHENG[ab],
HSUAN-SHEN CHEN[ab], CHUNG-YUAN MOU[b], TA-CHAU CHANG[a]*
[a]Institute of Atomic and Molecular Sciences, Academia Sinica. P. O. Box 23-166, Taipei, 10764, Taiwan, ROC; [b]Department of Chemistry, National Taiwan University, Taipei, Taiwan, ROC

Abstract Persistent hole-burning spectra of protonated acridine, 9-aminoacridine and proflavine doped in polyvinyl alcohol films have been studied to examine how the functional group affects chromophore-glass interactions. Proton transfer between the chromophore and the matrix upon electronic excitation is proposed to be the mechanism for the hole burned spectra of the three molecules studied. The high resolution of the spectrum of 9-aminoacridine is attributed to reduction of the electron-phonon coupling strength when substituting an amino group to the C(9) position of acridine. However, when substituting two amino groups to the C(3) and C(6) positions of acridine, significant increase of the electron-phonon coupling strength decreases the spectral resolution of proflavine.

INTRODUCTION

In amorphous glasses, the absorption bandwidth of a chromophore may be broadened inhomogeneously by a few hundred wavenumbers, even at low temperature. Spectral hole-burning (HB) methods eliminate the inhomogeneous broadening and yield high-resolution site-selective spectra[1-5]. Different HB mechanisms have been proposed for various systems[6-12]. Tautomerism induced intramolecular photochemical hole-burning (PHB) was observed in porphyrins[6]. The formation of hydrogen bonds to the matrix was suggested in the intermolecular PHB of quinizarin[7,8]. Solvent cage reorganization[9] and free volume motion[10] triggered by electronic excitation were proposed in the nonphotochemical hole-burning (NPHB) of several ionic dyes, such as resorufin and cresyl violet. Tunneling in the two-level system of the glass after excitation is a possible mechanism for the NPHB of tetracene[11] Recently, Chiang *et al.*[12] studied the HB mechanism of 9-aminoacridine (9AA) doped in glycerol/water glass at various pH values. They proposed that hole formation is driven by charge density migration along the short axis of 9AA and proton transfer between 9AA and the matrix during electronic excitation. In this work, three acridine derivatives, acridine, 9AA and 3,6-diaminoacridine (proflavine), doped in polyvinyl alcohol (PVOH) films are employed to study how the amino group affects the chromophore-glass interactions.

EXPERIMENTAL

Experimental setup of HB has been described elsewhere[13]. A home-made intracavity frequency-doubled optical parametric oscillator (OPO)[12] was used to serve as a burn source. The output of the OPO covers the wavelength from 380 to 480 nm with a bandwidth less than 2 cm^{-1} and average power ~ 10 mW. In addition, a CW argon ion laser was employed for the burn wavelength at 476 nm. The acridine derivatives were purchased from Acros and used without further purification. They were first dissolved in acidic water to form protonated cations, and then introduced into the polymer films.

RESULTS AND DISCUSSION

Acridine is a weak base and sparingly soluble in water. However, the formation of the acridinium ion in acidic solution increases its solubility. Figure 1a shows the absorption spectrum of the acridinium ion doped in PVOH at 6 K. Our absorption spectrum agrees with the previously reported ones[14]. Figure 1b is the red-side HB spectrum when the excitation is tuned to the red side (~ 440 nm) of absorption band. The arrow indicates the burning wavelength. The pulse energy is 3.5 μJ with a burn time of 90 min. A sharp zero-phonon hole (ZPH) and several vibronic satellite holes (SHs) in the blue side of the ZPH, associated with their phonon sideband holes (SBHs), are presented in figure 1b. The formation of blue-side SHs is attributed to Franck-Condon active vibronic modes. The blue-side SBH is due to real phonon sideband of the ZPH; while the red-side SBH results from burning at the phonon sideband and probing at the zero-phonon line. Since no antihole appears in the inhomogeneously broadened absorption band[5], we suggest that a photochemical reaction is responsible for the hole formation of the acridinium ion in PVOH films.

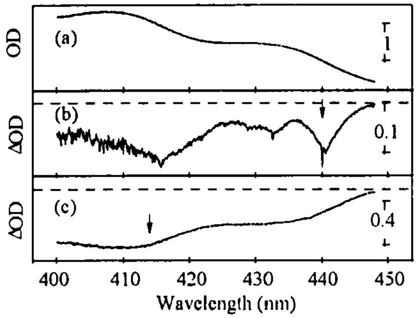

FIGURE 1 Absorption (a), red-side HB (b) and blue-side HB (c) spectra of acridinium ion in PVOH films. The dash line denotes the baseline of ΔOD.

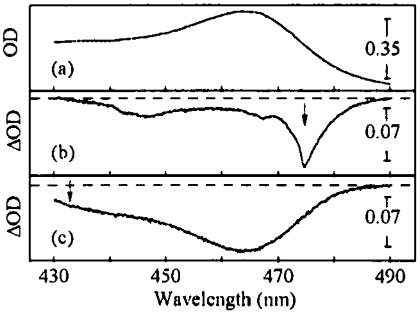

FIGURE 2 Absorption (a), red-side HB (b) and blue-side HB (c) spectra of proflavinium ion in PVOH films.

In nanosecond fluorometry, excited state proton-transfer of acridine has been identified[16] due to the pK_a value of the acridine molecule being higher in the excited state than in the ground state. In addition, an INDO CI calculation[17] showed that the electron density at the N(10) position increases for acridine and decreases for the acridinium ion in the excited state. As a result, the N(10) atom of acridine becomes more basic and may attract a proton in the excited state. In contrast, the N(10) atom of the acridinium ion becomes more acidic, and therefore binds fewer protons in the excited state. We propose that the charge redistribution upon excitation is the driving force for the proton transfer. Furthermore, the antihole which appeared in the wavelength region below 380 nm[15] corresponds to the absorption band of neutral acridine[14]. Therefore, we believe that the proton transfer in the excited state between the acridinium ion and the matrix is responsible for the photochemical HB spectra. A similar HB mechanism was described for 9AA doped in glycerol/water glasses[12].

An interesting spectral feature is observed when tuning the excitation in the vibronic band. Figure 1c is a blue-side HB spectrum taken at 414 nm with a pulse energy of 3 μJ and a burn time of 50 min. No sharp hole is observed, but two broader holes centered at 410 and 433 nm appear in figure 1c. It is important to note that these two broader holes are mirror images of the absorption spectrum, as shown in figure 1a.

Figures 2a-2c show the absorption, red-side HB, and blue-side HB spectra of the proflavinium ion doped in PVOH, respectively. The pulse energy is 10 μJ with a burn time of 20 min for each HB spectrum. The absence of a sharp ZPH in figure 2b implies that the ZPH is dominated by the SBH. A similar mirror image of a broader hole of the absorption band is also observed in the blue-side HB spectrum, as shown in figure 2c. Figure 3 shows the antihole structure of proflavinium ion in PVOH. The antihole in the region of 360 - 430 nm corresponds to the absorption band of neutral proflavine[15,18] Therefore we believe that the HB mechanism of proflavinium ion is also due to proton transfer in the excited state.

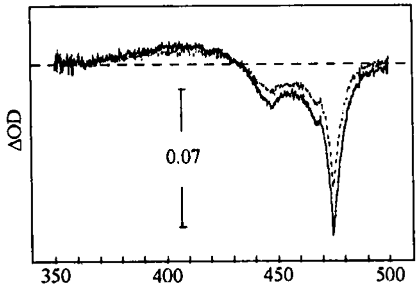

FIGURE 3 Antihole structure of proflavinium ion in PVOH. Burning times are 10 min (dotted line) and 40 min (solid line), respectively.

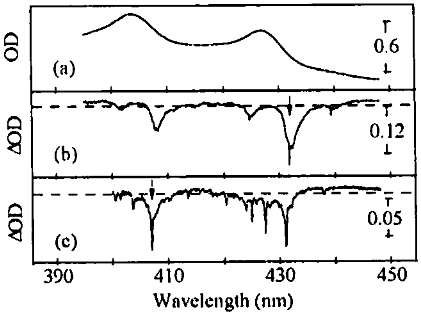

FIGURE 4 Absorption (a), red-side HB (b) and blue-side HB (c) spectra of protonated 9AA in PVOH films.

In our previous study of 9AA doped in glycerol/water glasses[12], several narrow SHs were observed on either side of the ZPH, especially in the blue-side HB spectrum.

Figures 4a-4c show the absorption, red-side HB, and blue-side HB spectra of protonated 9AA doped in PVOH, respectively. The pulse energies are 10 μJ and 3 μJ, with a burn time of 20 min for each HB spectrum. The ZPH and SHs shown in figure 4 are well distinguished from each other, implying that the electron-phonon coupling of 9AA is weaker than that of acridine and proflavine.

It is known that the SBH is a manifestation of linear electron-phonon coupling. The coupling strength, S_0, can be determined by the Debye-Waller factor (DWF), α_0, as

$$\alpha_0 = I_{ZPH} / (I_{ZPH} + I_{SBH}) = \exp(-S_0), \qquad (1)$$

where I_{ZPH} and I_{SBH} correspond to the hole area of a ZPH and a SBH, respectively. In order to avoid saturation, extrapolating to zero burning-time is necessary[19]. The measurement of DWFs of acridine, proflavine and 9AA are summarized in Table I. We suggest that the absence of a sharp ZPH can be attributed to strong electron-phonon coupling.

TABLE I. DWF and Δμ of acridines.

Samples	DWF	Δμ (D)[21]
acridine	0.25	0.77
9AA	0.75	0.60
proflavine	~ 0	4.36

Renge[20] found that electron-phonon coupling increases, as the difference of the dipole moments between ground and excited states (Δμ) increases. The Δμ values of the three acridine derivatives (see Table I) were calculated by using the PPP method[21]. We found that 9AA has the smallest Δμ and the largest DWF; while proflavine has the largest Δμ and the smallest DWF. Knowing that the width of the phonon sideband is approximately one third of the width of the inhomogeneous band, as shown in figure 2b, most of the proflavine molecules can be excited via the phonon sideband. As a result, no sharp hole is produced. On the other hand, the amino group on the C(9) position of 9AA reduces the electron-phonon coupling, as the 9AA molecules can be excited site-selectively. Consequently, narrower holes can be observed. We conclude that the substitution of amino groups in different positions of 9AA and proflavine critically effects DWF.

In summary, we have described that the proton transfer between the chromophores and the matrix, triggered by electronic excitation, is the mechanism for the HB spectra of protonated acridine, proflavine, and 9AA. Our measurements of the DWF values of the acridines confirm that the electron-phonon coupling increases as $\Delta\mu$ increases. Substituting the C(9) position of 9AA with an amino group reduces its $\Delta\mu$, while substituting with two amino groups on the C(3) and C(6) positions increase its $\Delta\mu$ significantly for proflavine. In addition, our results demonstrated that only molecules with low electron-phonon coupling can produce high-resolution site-selective satellite holes.

ACKNOWLEDGMENTS

This work was supported by the Academia Sinica and the NSC of the Republic of China (Grant NO. NSC-85-2113-M001-025).

REFERENCES

1. W. E. Moerner, ed., Topics in Current Physics 44, Persistent Spectral Hole Burning: Science and Applications (Springer, Berlin, 1988).
2. J. Friedrich and D. Haarer, Angew. Chem. Intern. Ed. Engl., 23, 113 (1984).
3. S. Volker, in Relaxation Processes in Molecular Excited States, edited by J. Funfschilling (Kluwer, Dordrecht, 1989); Ann. Rev. Phys. Chem., 40, 499 (1989).
4. L. R. Narasimhan, K. A. Littau, D. W. Pack, Y. S. Bai, A. Elschner, and M. D. Fayer, Chem. Rev., 90, 439 (1990).
5. R. Jankowiak, J. M. Hays, and G. J. Small, Chem. Rev., 93, 1471 (1993).
6. S. Volker and J. H. van der Waals, Mol. Phys., 32, 1703 (1976).
7. F. Drissler, F. Graf, and D. Haarer, J. Chem. Phys., 72, 4996 (1980).
8. Y. Iino, T. Tani, M. Sakuda, H. Nakahara, and K. Fukuda, Chem Phys. Lett., 140, 76 (1987).
9. R. van den Berg and S. Volker, Chem. Phys., 128, 257 (1988).
10. L. Shu and G. J. Small, Chem. Phys., 141, 447 (1990); J. Opt. Soc. Am., B9, 724 (1992).

11. J. M. Hayes and G. J. Small, Chem. Phys., 27, 151 (1978).
12. C. C. Chiang, B. C. Hwang, J. Yu, J. Y. Cheng, C. Y. Mou, S. H. Lin, and T.-C. Chang, J. Chem. Soc. Faraday Trans., submitted (1996).
13. T.-C. Chang, C. C. Chiang, G. J. Small, and S. H. Chou, Chem. Phys. Lett., 223, 190 (1994).
14. R. M. Acheson, Acridines (Interscience, New York, 1956).
15. C. C. Chiang, J. Y. Cheng, and T.-C. Chang, unpublished data.
16. A. Gafni and L. Brand, Chem. Phys. Lett., 58, 346 (1978).
17. J. Rak and J. Blazejowski, J. Photochem. Photobiol. A: Chem., 67, 287 (1992).
18. N. Mataga, Y. Kaifu, and M. Koizumi, Bull. Chem. Soc. Japan, 29, 373 (1956).
19. J. Friedrich, J. D. Swalen, and D. Haarer, J. Chem. Phys., 73, 705 (1980).
20. I. Renge, J. Opt. Soc. Am. B9, 719 (1992).
21. J. J. Aaron, M. Maafi, C. Parkanyi, and C. Boniface, Spectrochimica Acta, 51A, 603 (1995).