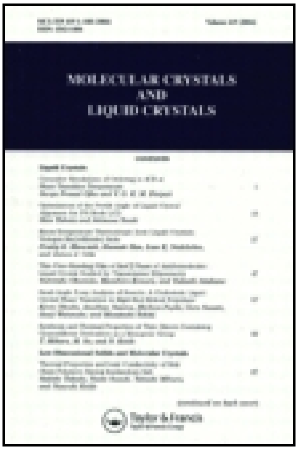

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EXCITED STATE PROTON TRANSFER AND PERSISTENT HOLE FORMATION PROCESSES IN HYDROXYANTHRAQUINONE DERIVATIVES

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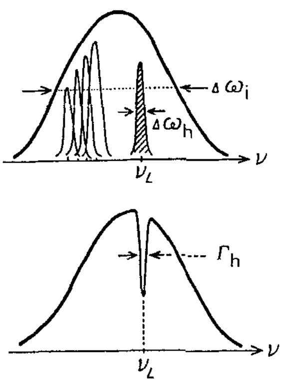
Abstract Persistent spectral hole burning properties of ten kinds of hydroxyanthraquinone derivatives are investigated. Possible photo-reaction process for the hole formation will be discussed on the basis of the observed electronic structures of these molecular systems in relation to hydrogen bonds and excited-state proton transfer.

INTRODUCTION

Persistent spectral hole burning (PSHB) is a kind of site-selective saturation spectroscopy which utilizes photochemical and/or photophysical process to get population redistribution in the ground state (Fig.1). Observation of the hole spectra bring us information such as electron-phonon interaction, microscopic structural relaxation in matrices and so on. Though it requires basically cryogenic temperatures, its characteristic is the persistency of hole fairly



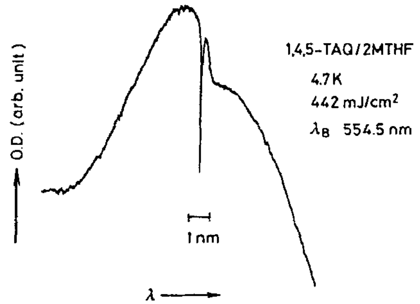


FIGURE 1 Implication of PSHB process and example of hole spectrum. $\Delta\omega_h$: homogeneous width, $\Delta\omega_i$: inhomogeneous width, Γ_h: hole width ($=2\Delta\omega_h$ in simple case).

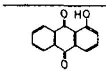
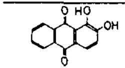
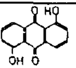
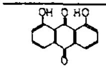
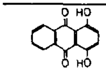
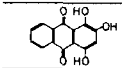
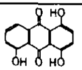
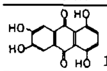
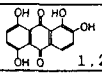
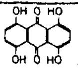
long after shutting off the laser illumination. To be able to form many holes independently within one absorption band is another feature if laser wavelength is tuned for each irradiation. These two features provide us also a possibility towards high density optical memory in the future.[1]

For the formation of holes, the existence of both photoactive centers and solid matrix suspending them is essential. Thus the comprehension of the molecular interaction in these molecular system is significant. Using quinizarin and free-base porphyrin derivatives, we have been investigating various properties of dye-doped glass systems by modifying the structure of both matrix and dye molecules.[2-7] Glassy matrices are surveyed from organic solvents[8] through modified polymers[2,10] to inorganic sol-gel a-SiO_2[5] and recently extended to some biological systems such as intercalated DNA and protonated heme proteins.[6,7] These investigations have revealed that the electron-phonon interaction between dye-matrix system should be basically weak for the efficient hole formation. This constitutes a major notion of our working hypothesis for optimizing the memory materials, in which we should consider some mesoscopic size of guest-host complex as a functional unit of the materials.

As for the hole formation process, detailed understanding of intramolecular electron-phonon interaction and photochemical reaction scheme should be required. 1,4-dihydroxyanthraquinone (1,4-DAQ) and metal-free porphyrin (H_2P) are the most extensively studied dye molecules in PSHB, both of which relate to photo-induced proton transfers. We have already been investigating the former and its related derivatives in this respect and obtained some notable features.[9,10] In this paper we present our recent results on the PSHB properties of ten kinds of hydroxyanthraquinone derivatives including three newly synthesized ones. Typical molecules are 1,4-DAQ and 1,5-DAQ. If doped in polymers or organic glasses, the former gives sufficiently narrow persistent zero-phonon holes by irradiating laser light at liquid helium temperature whereas the latter does not within our experimental conditions. Evident correlation has found between the appearance of narrow hole and the molecular structures. Possible photo-induced reaction scheme and related electronic structures of these molecules will be discussed based also on the observation of absorption and emission spectra: diabatic crossing of the ground state and role of nonbonding electrons.

RESULTS and DISCUSSION

TABLE I Burning wavelength (λ_B) and efficiency (Φ).

Molecule	λ_B (nm)	ϕ
 1-HAQ	420.0	----
 1,2-DAQ	472.7 476.5	---- ----
 1,5-DAQ	457.9	----
 1,8-DAQ	457.9	----
 1,4-DAQ	520.8	3.7×10^{-4}
 1,2,4-TAQ	520.8	2.2×10^{-4}
 1,4,5-TAQ	525.3 554.5	3.0×10^{-4} 1.4×10^{-3}
 1,4,6,7-TAQ	514.5	2.1×10^{-3}
 1,2,5,8-TAQ	520.8 530.9	5.3×10^{-7} 2.6×10^{-4}
 1,4,5,8-TAQ	514.5 541.8 554.6	5.4×10^{-6} 1.1×10^{-4} 3.7×10^{-4}

Molecular structures dealt with in this study and their abbreviations are shown in Table I. They possess anthraquinone skeleton in common and the number and position of hydroxy group(s) are systematically changed which bear the holeburning photochemistey as well as characterizing the nature of each π electron system. They are solved into EtOH:MeOH mixed solvent or 2MTHF with concentration from 10^{-4} to 10^{-3} M/l and sealed into 1.0 mm^t optical cell. Hole burnings were carried out with tunable pulsed dye lasers excited with N_2 or Nd:YAG in 2nd or 3rd harmonics lasers and cw Ar^+ or Kr^+ laser with solid etalon. Spectral observation was carried out with high resolution monochromator (~0.03cm^{-1}).

Low temperature absorption spectra are shown in Fig. 2. There are two notable features: differences of vibro-electronic structure and bathochromic shift. From the absorption profiles the molecules

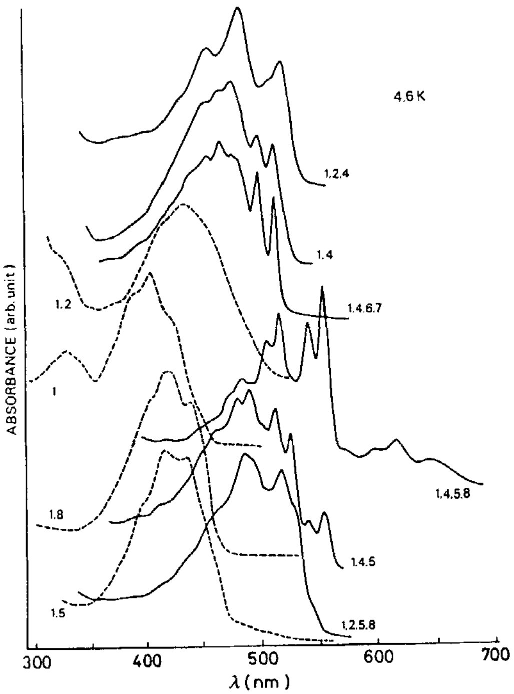


FIGURE 2
Absorption spectra at 4.6K.

are classified into two groups A and B; A contains 1-, 1,2-, 1,8- and 1,5-derivatives and B the remainders. The vibronic structures in group A is not so clear as in group B and the quantity of red shift from the spectrum of anthraquinone skeleton is much larger in B than in A. As is summarized in Table I, the derivatives in group B give clear 0-phonon hole formation while no hole was observed in group A within our experimental conditions. Example of hole formation is shown in Fig. 1. It should be noted that in the molecular structures in group B there are at least two OH-groups at 1 and 4 positions simultaneously with distinguished contrast with those in A.

In Fig. 3, fluorescence emission spectra observed at 4.6K are presented in 1,4-DAQ and 1,5-DAQ as prototype of two groups compared with each absorption band. It is readily discernible that in case of 1,5-DAQ the Stokes shift is as large as 7000cm^{-1} and there is no sufficient overlapping which indicates the 0-0 transition. Observed dual fluorescence character, the short wavelength fluorescence (500-550nm), is attributed to the excited-state proton transfer (ESPT)[11] which occurs even at liquid He temperature. We conclude therefore that in case of 1,5-DAQ rather strong linear electron-phonon coupling is realized and almost no 0-0 transition component is contained in the absorption band. On the other hand in case of 1,4-DAQ, Stokes shift is about 2400cm^{-1} and sufficient overlapping around 520nm. As is seen in the figure no evidence for the ESPT is

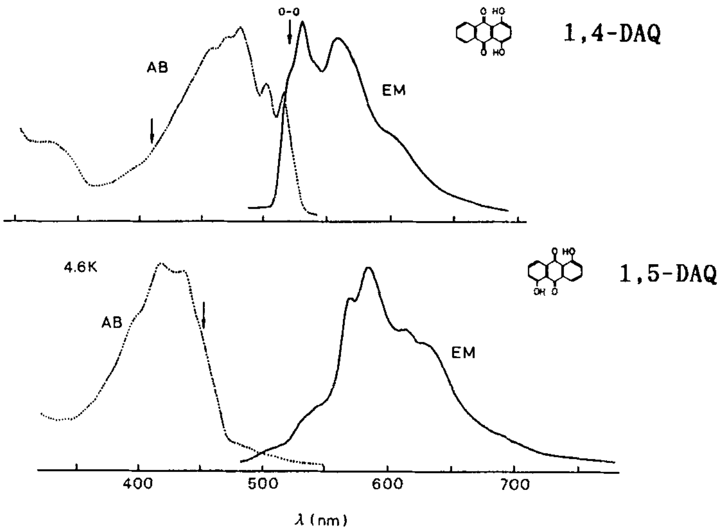


FIGURE 3 Fluorescence and absorption spectra of 1,4-DAQ and 1,5-DAQ.

observed. Thus it is readily concluded that in case of 1,4-DAQ the absorption band in which the burning are performed contains sufficient amount of 0-0 transition component which appears as sharp 0-phonon hole.

Then the basic question arises; What is the photochemical reaction scheme of 1,4-DAQ and what electronic structures drive it? As for the former the breakage of an internal hydrogen bond and subsequent formation of an external bond to the solvent has been suggested (Fig.4).[12,8-10] Based on the hole burning properties of group B molecules and absorption (see Fig. 2) and fluorescence (not shown here) spectra, we consider so far the possibility of the photoreaction through low-lying excited singlet state. In Fig. 5, the possibility of diabatic crossing[13] of the ground state is described. Our data based on the systematic modification of molecular structures indicate that this low-lying excited state (S_0') may be related to the non-bonding state(s) at oxygen(s). In case of 1,4-DAQ it is believed that n-π^* transition is pushed up higher than π-π^* transition due to its intramolecular hydrogen bond(s). If for instance the π electron system becomes as large as anthraquinone, however, $E(n-\pi^*)<E(\pi-\pi^*)$ could be realized.

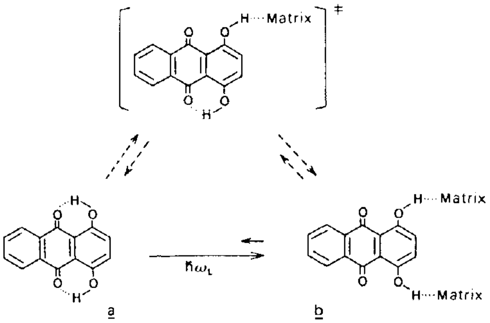


FIGURE 4
Photoreaction scheme of 1,4-DAQ for PSHB.

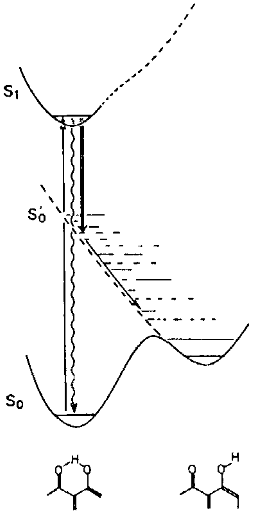


FIGURE 5 Possible electronic states related to PSHB process.

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