

SHORT COMMUNICATIONS

Photon-Gated Persistent Spectral Hole-Burning of Zinc-Tetrabenzoporphin with Crotonic Acid in Phenoxy Resin

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Persistent spectral hole-burning (PHB) is a phenomenon in which site-selective and persistent decrease in absorption or a hole is created in the absorption band of molecularly dispersed photoreactive guests in host matrices at low temperatures. The PHB has been attracting considerable interests as a tool for high-resolution spectroscopy as well as means for frequency-domain high-density optical storage.^{1,2} Recently hole formation above liquid-nitrogen temperature for meso-tetra-phenylporphin (TPP) in phenoxy resin,^{3,4} epoxy resin⁵ and for a sulfonated TPP in poly(vinyl alcohol)⁶ has been realized, and the temperature dependence of the quantum efficiency of hole formation has been explained based on the temperature dependence of Debye-Waller factor,⁴ low-energy excitation modes,⁷ laser-induced hole filling,⁸ and molecular relaxation of the matrix polymers.

Photon-gated PHB is another important topic in PHB, where one photon, λ_1 , excites the electronic state in the burning frequency and another photon, λ_2 , gives rise to photochemistry leading to hole creation. When only the λ_1 is irradiated for detection of a hole, no hole is created owing to the absence of the λ_2 and this enables us to make non-destructive

reading. The mechanisms of previously reported photon-gated PHB systems are two-color photoionization,⁹⁻¹¹ two-color photodecomposition^{12,13} and two-color photo-induced donor-acceptor electron transfer reactions.^{14,15} Recently we have found two new types of photon-gated PHB, *i.e.*, two-color photosensitization of a photoreactive polymer¹⁶ and two-color excited non-photochemical hole burning in the presence of carboxylic acid. In this letter the effect of two-color excitation on the PHB of zinc-tetrabenzoporphin (ZnTBP) in the presence of carboxylic acid is firstly reported.

Phenoxy resin (aromatic polyhydroxyether) films containing $2.4 \times 10^{-3} \text{ mol l}^{-1}$ of ZnTBP and 0.96 mol l^{-1} of crotonic acid were prepared by solvent-cast method. The addition of crotonic acid as a mild electron acceptor with the reduction potential of -1.9 eV was attempted in order to realize electron transfer from the higher excited triplet state T_n ($n \geq 2$) of ZnTBP to crotonic acid but not to realize the electron transfer from the lowest excited triplet state T_1 of ZnTBP.

The samples were set in a cryostat with a cryogenic refrigerator (Sumitomo, SRD 204) and irradiated at 20 K by an Ar⁺-laser-pumped

single-mode CW ring dye laser (Coherent, 699-01) with $0.038\text{--}15\text{ mW cm}^{-2}$ laser power around 635 nm for λ_1 and the Ar^+ laser (Coherent I-70) itself with $3.75\text{--}9\text{ mW cm}^{-2}$ laser at 488 and 514 nm as a gating light (λ_2). Holes were detected by the change in transmittance with a 1 m monochromator (Jasco, CT100C), a photomultiplier (Hamamatsu, R943-02), and a lock-in amplifier (Jasco, LA126W). Details of the apparatus were given previously.⁴

The typical changes in hole depth, $\Delta A/A_0$, during one-color (λ_1 only) and two-color (λ_1 and λ_2) irradiations at 20 K are shown in Figure 1 against irradiation energy, where ΔA is the difference in absorbance produced by hole formation and A_0 is the absorbance before irradiation. The results of one-color and two-color hole burnings for ZnTBP in the phenoxy resin without crotonic acid¹⁷ are also given in Figure 1 as a reference. The quantum efficiency of hole formation⁴ based on the laser power of λ_1 for two-color hole burning in the presence of crotonic acid was estimated to be about 3×10^{-5} from the initial slope in Figure 1, which is twice as large as that for the one-color irradiation. Since the one-color irradiation of the sample with crotonic acid

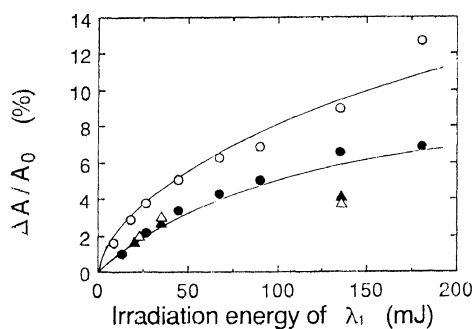


Figure 1. Changes in hole depth, $\Delta A/A_0$, for PHB of ZnTBP in phenoxy resin with 0.96 mol l^{-1} of crotonic acid (\circ , \bullet) and without crotonic acid (\triangle , \blacktriangle) at 20 K during two-color irradiation with $75\text{ }\mu\text{W cm}^{-2}$ dye laser and 3.75 mW cm^{-2} Ar^+ laser (\circ) or $38\text{ }\mu\text{W cm}^{-2}$ dye laser and 10 mW cm^{-2} Ar^+ laser (\triangle), and during one-color irradiation with $75\text{ }\mu\text{W cm}^{-2}$ (\bullet) or $38\text{ }\mu\text{W cm}^{-2}$ (\blacktriangle) dye laser.

fits to the same curve as one-color and two-color irradiations of the sample without crotonic acid, it is obvious that crotonic acid contributes to the enhancement of hole formation by two-color excitation.

The temperature-cycle experiments for the holes burnt at 20 K by one-color and two-color irradiations for ZnTBP and crotonic acid system in phenoxy resin (Figure 2) have revealed the marked thermal stability of the hole formed by two-color excitation compared to the hole formed by one-color excitation. Thus, in contrast to the fact that the hole

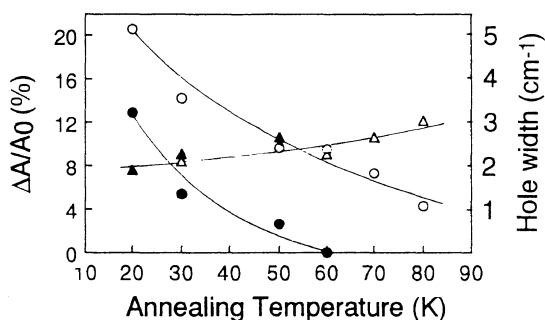


Figure 2. Changes in hole depth, $\Delta A/A_0$, (\circ , \bullet) and hole width (\triangle , \blacktriangle) after cycle annealing experiments for ZnTBP with crotonic acid in phenoxy resin burnt at 20 K by two-color irradiation for 30 min with $94\text{ }\mu\text{W cm}^{-2}$ dye laser and 7.5 mW cm^{-2} Ar^+ laser (\circ , \triangle) and by one-color irradiation for 30 min with $94\text{ }\mu\text{W cm}^{-2}$ dye laser (\bullet , \blacktriangle).

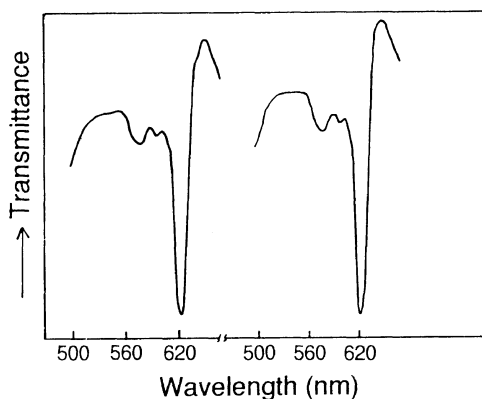


Figure 3. Absorption spectra for ZnTBP with crotonic acid in phenoxy resin before (left) and after (right) two-color irradiation of 15 mW cm^{-2} dye laser and 9 mW cm^{-2} Ar^+ laser for 30 min at 20 K .

formed by one-color excitation at 20 K disappears after temperature cycle to 60 K and being cooled again to 20 K, the hole formed by two-color excitation restores 20% of its depth at 20 K after temperature cycle up to 80 K. The higher temperature stability of the holes burnt by two-color irradiation is also reported for ZnTBP/halomethane system in PMMA.¹⁵

Figure 3 shows that absorption spectrum of the Q band of ZnTBP hardly changes after 30 min irradiation with a 15 mW cm^{-2} dye laser (λ_1) and 9 mW cm^{-2} Ar^+ laser (λ_2), suggesting the absence of irreversible photoionization of ZnTBP but the occurrence of non-photochemical hole burning (NPHB)¹⁸ due to the rearrangement of hydrogen bonds in the carboxylic acid. The NPHB due to the hydrogen-bond rearrangements of phenoxy resin is also supposed to be a reason for one-color hole formation in the presence of crotonic acid as well as that for one-color and two-color hole formation of the sample without crotonic acid, since no hole was observed for one-color or two-color irradiation of ZnTBP in poly(vinyl acetate) which has no hydrogen bonding.

Well-known acceptor materials for the photon-gated hole burning due to donor-acceptor electron transfer with ZnTBP are halomethanes^{14,15} in PMMA, where the electron transfer is followed by a spontaneous irreversible bond cleavage forming halogen anion and substituted alkyl radical which prevents a backward electron transfer. No hole formation has been reported so far to our knowledge for reversible (non-destructive) donor-acceptor systems except for TPP/*p*-benzoquinone system.¹⁹ It is not obvious whether electron transfer occurs in the present ZnTBP/crotonic acid system. But even if it occurs, rapid backward electron transfer regenerates ZnTBP molecule, leading to no change in absorption spectrum of ZnTBP as is shown in Figure 3. So, the rearrangement of hydrogen bonding in crotonic acid would be

the main reason of photon-gated hole formation. This is ascertained by the large shift energy of pseudo-phonon side hole from a zero-phonon hole, E_s , of 17.1 cm^{-1} for the present ZnTBP/crotonic acid system in the phenoxy resin compared to 15.1 cm^{-1} for TPP in phenoxy resin without crotonic acid.⁷ The value of E_s reflecting a peak energy of low-energy excitation modes is a measure of a kind of stiffness of the lattice around the chromophore and becomes large in the presence of dense hydrogen bonds.⁷ The further elucidations of the effect of hydrogen bonds in carboxylic acids on the photon-gated PHB and the reality of electron-phonon interaction are being continued in the laboratory of the present authors.

In conclusion, persistent spectral hole-burning (PHB) with two-color excitation was performed at 20 K for zinc-tetrabenzoporphin with crotonic acid in phenoxy resin. The presence of carboxylic acid provides the enhancement of hole formation by two-color excitation and the thermal stability of the resulting holes, raising a non-photochemical hole burning with the rearrangement of strong hydrogen bonds in the carboxylic acid. This is supported by the large value of E_s reflecting a large peak energy of low-energy excitation modes (17.1 cm^{-1}) compared to the case without crotonic acid (15.1 cm^{-1}).

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