Persistent Spectral Hole Burning of Resazurin Sodium Salt in Glassy Polymer Matrices

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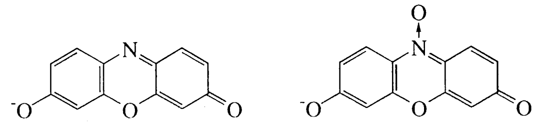
The first persistent spectral hole burning is reported for an acidic dye, resazurin anion (sodium salt), containing N-oxide moiety. The spectral hole was measured in three polymer matrices. The temperature dependence of holewidth for resazurin and the thermal stability of the burnt hole were measured and compared with those of a similar dye, resorufin.

Persistent spectral hole burning (PSHB) of dye molecules dispersed in amorphous solid is a useful method to study the relaxation processes in glasses at low temperatures with high resolution[1]. PSHB is also useful to study the change of the excited states of dye molecules which reflects their microenvironment. Ionic dyes are interesting for investigators of various fields in physics and chemistry because of their sensitivity to their environments. Especially, the dyes which have both electron-donating and electron-withdrawing moieties in its structure[2] such as Nile Red or pyridinium N-phenoxide derivatives are known to be good solvatochromic compounds and good probe to their environment. The most widely studied chromophore in PSHB is porphyrin and the studies of other dyes are not so much. Resorufin anion (**1**) has also been studied by PSHB[3-7]. The important role of the hydrogen bond between **1** and matrix was also suggested from the result that the hole formation efficiency was decreased by the addition of hydrogen-bond inhibitor in alcoholic glasses.[7b]



1 **2**

Figure 1. The structures of resorufin (**1**) and resazurin (**2**)

In this letter, the hole formation is reported using another anionic dye, resazurin anion (**2**). This contains N-oxide moiety which is a good probe to the microenvironment. And the present letter is the first PSHB report for resazurin to our knowledge. Though **1** is used frequently, **2** is seldom used for the studies of their photophysical properties, since the N-oxide moiety is reduced quite easily. So **2** is not so popularly studied by photochemists as **1**, and is mainly used for biological detection[8] or pH indicator.[8b,9] N-oxide moiety is thought to be solvatochromic, as it is ionized in highly polar media and is neutralized in nonpolar media. The possibility of **2** to be more sensitive probe to its microenvironment than **1** is an important factor for us to study their microenvironment at low temperatures.

Resazurin(3H-phenoxazin-3-one, 7-hydroxy, 10-oxide) sodium salt (Aldrich Chemical), resorufin(3H-phenoxazin-3-one, 7-hydroxy,) sodium salt (Aldrich Chemical) and UV spectral grade solvents, acetone and methanol(Dojin) were used as supplied. As polymeric matrices, poly(methyl methacrylate) (PMMA), poly(vinyl acetate) (PVAc) and poly(vinyl alcohol) (PVA) were used after reprecipitation. The samples were prepared by the solvent casting method. The dye solution (aqueous solution for PVA, and basic acetone:methanol = 1:1 (v/v) solution for other polymers as Ref. 3 but without hexafluoro-2-propanol) was added to polymer solution (aqueous solution for PVA, methanol solution for PVAc, and acetone solution for PMMA) and dried at 40~45 °C.

Each polymer film was set in a cryostat (Sumitomo, SRD204) and cooled to 20 K, or in a continuous flow type cryostat (Oxford, CF1204) and cooled to 3.6~17 K. The spectral holes were burnt by the irradiation with tunable He-Ne laser (Electro Optics, LSTP-1010) or Ar$^+$-laser (Coherent, Innova 70)-pumped ring dye laser (Coherent, 699-01) with DCM. Hole spectra were measured as the intensity change of the transmittance light with a 1m monochromator (Jasco, CT-100C) detected by a photomultiplier (Hamamatsu, R943-02) and a lock-in amplifier (Jasco, LA126W). The details were described elsewhere.[10] Absorption spectra at room temperature were also measured (Jasco, UVIDEC-660). Absorption spectrum at room temperature and the hole spectrum at 20 K of **2**/PMMA are shown in Figure 2.

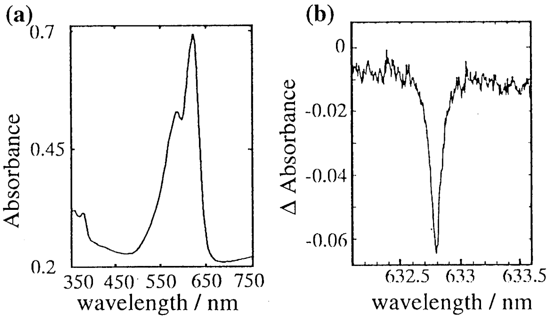


Figure 2 **(a)** Absorption spectrum at room temperature of **2**/PMMA and **(b)** Hole spectrum of **2**/PMMA irradiated at 632.8 nm with 200 μW•cm^{-2} power for 20 min at 20 K.

The absorption band of **2** had its maximum at ~620 nm in PVAc and in PMMA, but at ~600 nm in PVA. This is probably due to hydrogen-bond formation between **2** and PVA, as N-oxide formation[11] and/or the increase of the solvent polarity[12] as solvatochromic moiety. The peak around 580 nm in absorption spectrum of **2** in Figure 2(a) was assigned to be due to **1** which was at first **2** but lost its oxygen atom from the N-oxide during film preparation. This was confirmed from fluorescence excitation and emission spectra of **1** and **2**.

The dye concentration, the irradiated wavelength and holewidth are summarized in Table 1.

Table 1. The irradiated wavelength, concentration of **2** and holewidth in each polymer at 20 K

	PVA	PVAc	PMMA
Laser wavelength (nm)	611.9	632.8	632.8
concentration of **2** (mol·kg^{-1})	3.4×10^{-4}	1.2×10^{-4}	2.8×10^{-4}
holewidth Γ_{hole} (cm^{-1})	3.0	4.3	2.6

The real holewidth, Γ_{hole}, which is obtained by subtracting the apparatus limit due to the monochromator, Γ_l, from the apparent holewidth, $\Gamma_{obs.}$, is equal to twice of the homogenous width, Γ_h, of the dye molecule.

$$\Gamma_{hole} = \Gamma_{obs.} - \Gamma_l = 2\Gamma_h \qquad (1)$$

The Γ_h is proportional to the reciprocal of total relaxation time, T_{total}, which consists of excited state lifetime, T_1, and pure dephasing time, T_2.

$$\Gamma_h = 1/(\pi c T_{total}) \qquad (2)$$

$$1/T_{total} = 1/(2T_1)+1/T_2 \qquad (3)$$

As T_2 becomes infinite at 0 K, T_1 can be estimated from the extrapolated value of T_{total} when temperature, T, approaches zero. The temperature dependence of $1/T_{total}$ can be described as follows,

$$1/T_{total} = a + b\,T^n \qquad \text{(a,b,n: constants)} \qquad (4)$$

Table 1 shows that the holewidth depends on the kinds of matrix. This means that the total relaxation time of **2** is affected by the microenvironment which consists of polymer chains and residual solvents. Matrix-dependent holewidth were also observed for **1**.[7b] This should be a common characteristic of ionic dyes. The temperature dependence experiments of Γ_{hole} for **2** were carried out from 3.6 to 17 K. The homogeneous width Γ_h are estimated as is shown in Figure 3(a). From the result, $n = 1.5 \pm 0.5$ and $T_1 = 16.6$ ps were obtained by fitting the data with the equations (2)~(4). The temperature dependence of Γ_h could be compared with the values for **1** obtained by PSHB for similar system obtained by other groups. Völker *et al.* found that the Γ_h of **1** follows a $T^{1.3}$ law between 0.3 K and 10 K in PMMA or alcohol glasses.[7a,b] In general, the value of n in equation (4) is about 1.3 in glassy matrices and it becomes larger when the degree of the orderliness of the matrix increases. So the obtained value $n = 1.5 \pm 0.5$ was little larger, but it seemed to be in the usual range for glassy systems. The extrapolated value of Γ_h for **2** (0.32 ± 0.20 cm^{-1}) was different from those for **1** obtained by other groups[7c](T_1= 8 ns, and Γ_h = 0.043 cm^{-1} at 4.2 K). As we have no data of **2** below 3.6 K because of our apparatus condition and the influence of Γ_l on Γ_h becomes large at low temperatures, the accurate comparison could not be done between our data for **2** and other groups' data for **1**. However this difference might be due to the difference in the preparation method because our data of Γ_{hole} for **1**/PMMA(data is not shown, but measured under the conditions same as that of **2**/PMMA) at 20 K was a little broader than that for **2**/PMMA. Another possible reason is the existence of the fast charge transfer process which occurs for the structure involving N-oxide moiety.

To compare the thermal stability of the spectral holes for **1** and **2**, temperature excursion experiments were performed. The holes were burnt and measured at 20 K after the temperature excursion with increasing excursion temperature. The results are shown in Figure 3(b). Though the hole for **1**/PMMA was kept even at 60 K in part, the hole for **2**/PMMA could not remain at 50 K. Hole area for such an ionic dye is reported to decrease with timecourse[13] at 1.9 K. But in our case, the time-dependent decrease was not observed. Further, as the sample **1**/PMMA was kept longer time at excursion temperatures than the case of **2**/PMMA (15min), the difference between them are obvious.

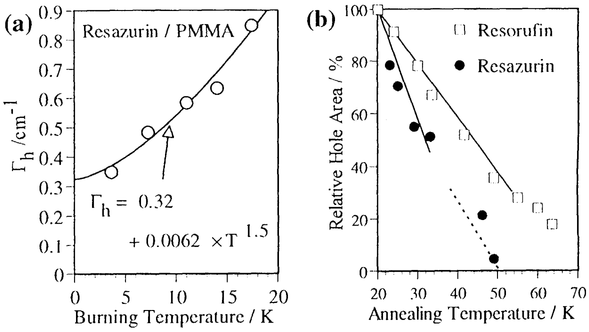


Figure 3. (a) Temperature dependence of the homogeneous width of **2**/PMMA. **(b)** Thermal stability of holes for **1**/PMMA and **2**/PMMA burnt at 20 K.

Therefore the spectral holes for **2**/PMMA were concluded to be thermally less stable than **1**/PMMA. The irreversible decrease in hole area for these ionic dyes might be caused by the backward reaction of nonphotochemical hole burning or by the change in hydrogen-bonding structure induced by thermal activation. This lower thermal stability of the holes for **2** than those for **1** would be due to the occurrence of some relaxation process around the N-O bonds even at low temperatures. This would be caused by the fact that the N-oxide moiety is not much ionized in PMMA (20 nm red shift in absorption band compared to that in PVA) resulting in its weak interaction with the matrix.

References and Notes

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