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PERSISTENT SPECTRAL HOLES AND INHOMOGENEOUS BROADENING OBSERVED IN BIOLOGICAL SYSTEMS WITH MESOSCOPIC STRUCTURES

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Abstract Persistent spectral holes and absorption spectra are observed in two biological systems; daunomycin/adriamycin intercalated in DNA and DNA-oligomer and protonated cytochrome-c both are doped in buffer glass. They possess similar mesoscopic structures. Their relations to the hole widths and inhomogeneous band widths are discussed.

INTRODUCTION

For the formation of persistent holes, the existence of photoactive centers and solid matrix suspending them is both significant. Thus, to make clear the role of electron-phonon coupling is essential not only for the comprehension of phenomena but also for the construction of guiding principle for designing future optical memory materials.

Using quinizarin and free-base porphyrin derivatives, we have been investigating various spectroscopic properties of persistent holes in dye-doped glass systems by modifying the structures of matrix and dye molecules.[1] Glass matrices are surveyed from organic solvents through modified polymers to inorganic sol-gel glasses.[2,3] We have been trying to classify and understand the observed spectroscopic and persistent hole properties and also photochemical ones in relation to the local structures of materials.[4,5] Our tentative viewpoint obtained in the course of these investigations is that the possible formation of guest-host complex which includes some intermediate range of matrix molecules around the photoactive center should be consciously taken into consideration. This range or size of the complex has multiplexed structure and should depend upon the nature of the interaction which dominates the phenomena. We would like to propose this viewpoint, a possibility of

controlling their mesoscopic structures of matters, as a working hypothesis for optimizing the materials.

We present our recent results of some biological materials as prototypes of such mesoscopic systems stated above. Materials to be discussed are daunomycin/adriamycin doped in glassy solvents and polymers. Daunomycin(Da) or adriamycin(Ad) is known as anticancer antibiotics and can be considered as quinizarin derivatives. It is said that their physiological activity appears through intercalation between base pairs of DNAs. Therefore, Da intercalated in DNA and oligo-DNA/buffer glass systems have also be examined and compared.

Another material to be described is related to porphyrin; iron-free cytochrome c in buffer glass. Cytochrome c (Cyt-c) contains a heme moiety, held through two thioether linkages to cysteines 14 and 17, which is surrounded by the folded polypeptide chain. Local structure of iron-free Cyt-c doped in buffer glass possesses at least three-fold hierarchy; central free-base porphyrin derivative, protein cage next and buffer molecules, which should be different from the porphyrin simply doped in buffer glass. It is expected for example the protein cage should provide fairly ordered surrounding for the porphyrin molecule in comparison with otherwise. The observed results seem to support these predictions.

EXPERIMENTS and RESULTS

DNA from salmon testes (Wako) was used as purchased without further treatments. The form of the oligo-DNA is the double helix of 5'-CGTACG-3'[6] (Toray Res). DNA and oligo-DNA were solved in Tris buffer, pH 7.5. Da and Ad were also solved in the same buffer solution and then mixed with the DNA or oligo-DNA solution to form intercalated complex at room temperature. The ratio of Da or Ad/DNA is 0.2mM/4mM-nucleotide and that of Da/oligo-DNA is 0.4mM/8mM-nucleotide.[7] Glycerol and methanol were then mixed with the solution to form glass at low temperatures. Final volume ratio of Tris buffer : glycerol : methanol is 1:1:2.

Iron-free porphyrin Cyt-c from that from bovine heart was prepared in accordance with the method by Vanderkooi and Erecinska.[8] It is obtained as the solution with 0.5M PO_4 buffer, pH 7.4. Three times of glycerol in volume was mixed. They were degassed and sealed in the

glass cells with 1 to 3 mm optical path length. For the formation of holes in the latter case, light from single-mode dye laser were irradiated into the $Q_x(0\text{-}0)$ band. Hole spectra were observed both by scanning the dye laser and by high resolution monochromator (0.04 cm^{-1}).

Fig. 1 shows the observed absorption spectra of Da, Da/DNA and Da/oligo-DNA doped in the buffer glasses. Inhomogeneous band widths of lowest 0-0 transition, zero-phonon hole widths and quantum yields of hole burning in these systems are summarized in Table I.

Fig. 2(a) shows the absorption spectrum of $Q_x(0\text{-}0)$ band in Cyt-c:H_2. By irradiating the laser light (615.3 nm, 0.03 mW/cm^2, 60"), we obtained deep 0-phonon hole of FWHM=0.043 cm^{-1} at 4.4 K. Quantum yield of hole formation is about 0.005, which is roughly equal to other porphyrin derivatives. Burning profiles of width, depth and area of 0-phonon hole and their temperature properties are also observed. In Figs. 3 and 4, the burning dose dependence of the hole width and the cycle temperature dependence of the hole area are shown, respectively. The behavior of the hole area indicates that Cyt-c:H_2/buffer glass system possesses fairly ordered structures around each porphrin moiety; it is quite different from the $1\text{-}\sqrt{(T/T^{\ddagger})}$ dependence[9] observed in more randomized system. To compare the effect of the ordered structures with the disordered one, we also measured H_2-octaethylporphyrin(OEP) doped in PMMA system as a randomized case. In Figs. 2, 3 and 4, the results of OEP/PMMA are also shown, respectively. The behavior of the area of OEP /PMMA resembles the $1\text{-}\sqrt{(T/T^{\ddagger})}$ dependence, indicating rather strong coupling between the dye and the two-level systems (TLS) in the buffer glass. In the case of Cyt-c:H_2/glass system, this coupling seems to become weak because TLSs are kept away from the dye by "introducing" the armor of the Cyt-protain. As can be seen in Fig. 3, the hole width becomes smaller and hard to be broadened in Cyt-c:H_2. We consider this is due to the decrease of spectral diffusion originated from the TLSs. The inhomogeneous width $\Delta\omega_i$ is mainly dominated by the nearest neighbor structures and the decrease of their fluctuation will reflect itself to the decrease of $\Delta\omega_i$ as can be seen in Fig. 2.

The behaviors of both Da/DNA systems and Cyt-c:H_2 related are consistent with each other. Therefore, we conclude that $\Delta\omega_i$ should be dominated by the nearest structures of moiety and the hole width should be originated from the distant TLSs in the glass.

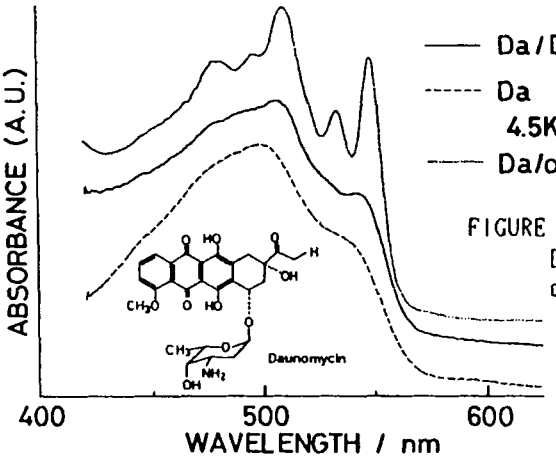

FIGURE 1 Absorption spectra of Da, Da/DNA and Da/oligo-DNA doped in buffer glasses.

TABLE 1 0-0 band widths, hole widths and burning yields of Ad and Da systems.

SAMPLES	$\Delta\omega_i(cm^{-1})$	$\Gamma_h(cm^{-1})$	η
Ad/DNA	950	1.3	4.9×10^{-7}
Ad	1150	~ 3	1.5×10^{-7}
Da/DNA	800	1.45	2.0×10^{-7}
Da	1050	~ 3.7	$<10^{-8}$
Da/oligo-DNA	400	1.25	9.1×10^{-8}

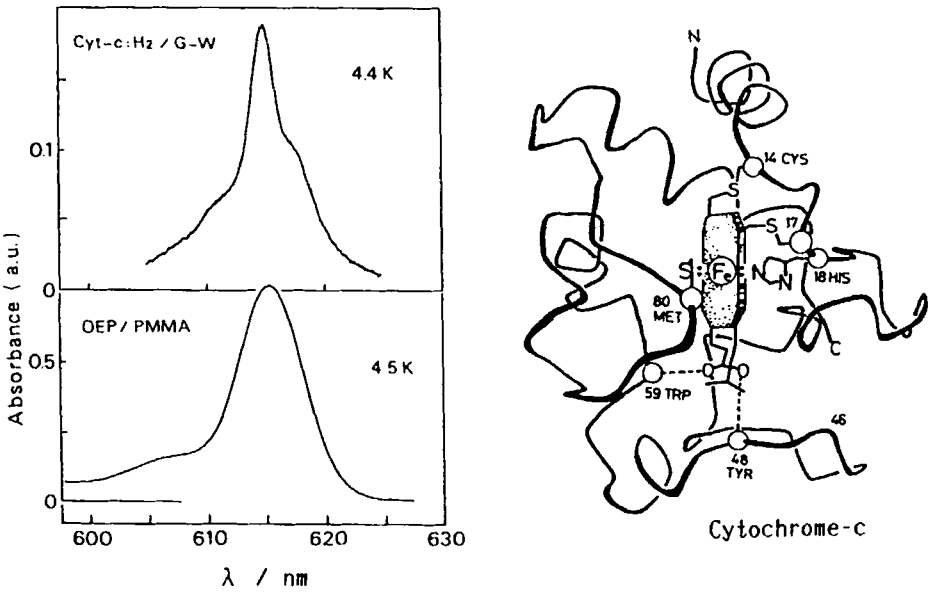

FIGURE 2 Absorption spectra of $Q_X(0\text{-}0)$ band observed in H_2 cytochrome-c/buffer glass and OEP/PMMA systems.

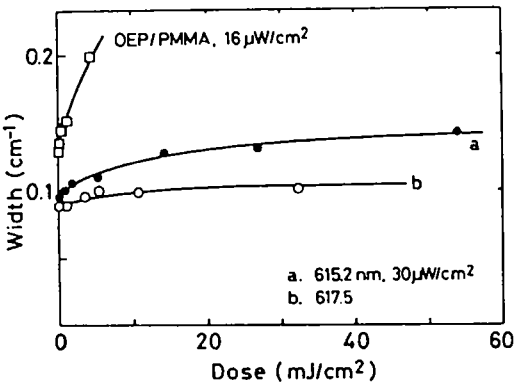

FIGURE 3 Dose dependences of hole width in Cyt-c:H_2/glass (a, b) and OEP/PMMA.

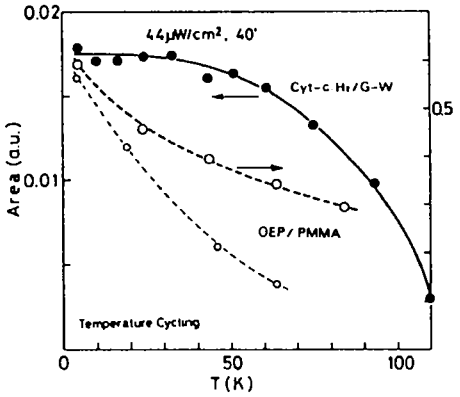

FIGURE 4 Cycle temperature dependences of hole area in Cyt-c:H_2/glass(●) and OEP/PMMA(○, smaller ones were burnt by single-mode laser)

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