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Relationship between Spectral Hole Burning and Stokes Shift of Organic Dyes in Polymer Systems

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Several organic dyes were studied both by fluorescence spectroscopy and by persistent spectral hole burning spectroscopy. The chromophores realizing spectral hole formation at 20 K have small Stokes shift approximately less than 10^3 cm^{-1}. It ascertains that the small Stokes shift related to the existence of appreciable zero-phonon line would be a requisite for the spectral hole formation of the chromophore. The realization of hole formation by using poly(vinyl alcohol) or photoreactive matrices for the chromophores which have appreciable zero-phonon line but don't undergo light-induced chemical or conformational change is also discussed.

Since a persistent spectral hole burning (PSHB) was realized by two Russian groups in 1974, a variety of PSHB materials have been found out and studied for these twenty years.1-3) Hole burning is a powerful technique for scientific research on solid materials as well as for application to optical frequency-domain information storage. Zero-phonon line (ZPL) of the chromophores is indispensable to PSHB.2) Debye-Waller factor (DWF) is defined as the relative ratio of ZPL intensity to the whole absorption intensity including phonon side bands. The DWF and spectral hole widths for organic dyes imbedded in amorphous hosts were reviewed by Renge, emphasizing that the DWFs and spectral hole widths are strongly correlated with the changes in molecular dipole moments between the lowest singlet excited state (S_1) and the ground state.4) The relationship of quantum efficiency for hole formation with chemical structure and absorption spectra of quinizarin and its 1,4-substituted analogues were reported by Tani et al.5) They also reported that the quinizarin and its derivatives capable of hole burning have small Stokes shift with a overlap of absorption and fluorescence spectra.6)

Only a few reports about the general characteristics of hole burning materials have been published as shown above. The amount of data is, however, not enough in the present. Much more chromophores should be studied from a variety of viewpoints. We report in the present letter quantum efficiency for hole formation with regard to several hole burning materials together with their fluorescence spectroscopy. It ascertains that the Stokes shift of chromophores is strongly related to the spectral hole formation not only for the quinizarin derivatives but also for a wide range of organic dyes.

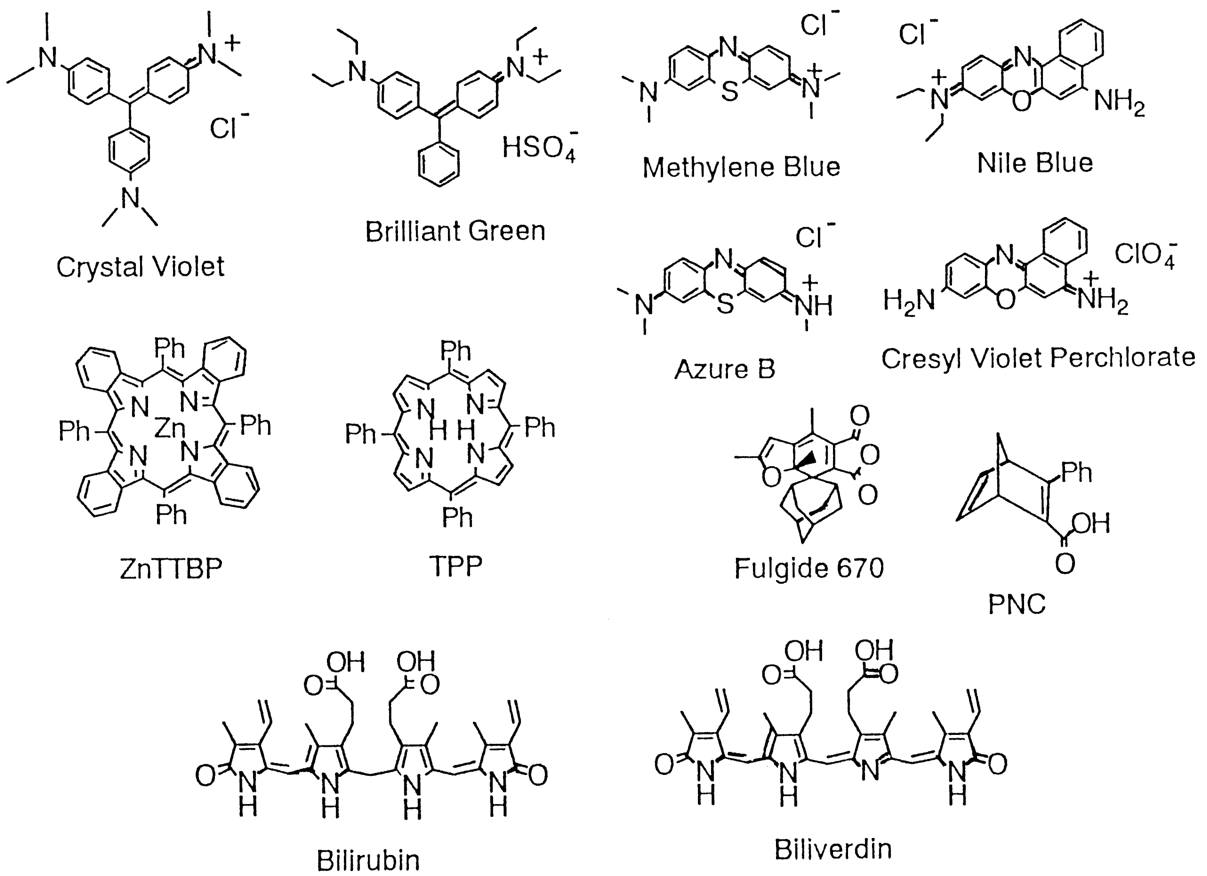

Fig. 1. The chemical structure of the chromophores in Table 1.

The 3-phenyl-2,5-norbornadiene-2-carboxylic acid (PNC) was synthesized and given by Nishikubo et al.7) The other dyes used in the present work are commercial products. The chemical structure of the dyes is shown in Fig. 1. The polymers used for the matrices were poly(vinyl alcohol) (PVA), poly(methyl methacrylate) (PMMA), and phenoxy resin (PhR). Sample preparation and apparatus for hole burning measurement were depicted in the previous papers.8) The fluorescence measurement was performed at room temperature with a Hitachi 850 fluorescence spectrophotometer.

All the hole burning experiments were performed at 20 K. The quantum efficiency for hole formation, Φ_{HF}, calculated from the slopes of hole depth against absorbed energy,8) absorption and fluorescence peak wavelengths, and Stokes shifts are shown in Table 1. It is obvious that all the chromophores having the Stokes shift smaller than 680 cm^{-1} in Table 1 showed spectral hole formation at 20 K. Among them, not only Φ_{HF} but also hole formation itself are first reported here for Brilliant Green, Nile Blue, and Azure B. No hole formation was observed for the Crystal Violet sample, whose hole formation is already reported in PVA at 2 K.9) The PVA is an excellent matrix for high temperature hole burning. So, no hole formation for the Crystal Violet sample at 20 K should not be ascribed to the structural relaxation of the dye-matrix system, but to a small value of DWF at 20 K. It shows that the DWF of this system is strongly temperature-dependent.

The Φ_{HF} of TPP is much higher than that of the other chromophores in the present work. This is because the mechanism of spectral hole formation for TPP, tautomerism of central protons of free base porphyrins, is of high quantum efficiency compared to that for the other systems. The PVA matrix is supposed to make possible the spectral hole formation with a non-photochemical process, so PVA is a convenient matrix polymer for examining the existence of appreciable ZPL of chromophores which seem to induce no photochemical reactions. The hole formation of the other chromophores than TPP and zinc tetratolyltetrabenzporphine (ZnTTBP) in Table 1 should be regarded as non-photochemical hole burning (NPHB). Another method of forming spectral holes for molecules having ZPL but not undergoing photochemical reactions is the use of triplet energy transfer to photoreactive matrices. One of the examples is ZnTTBP in the glycidylazide polymer (GAP).10)

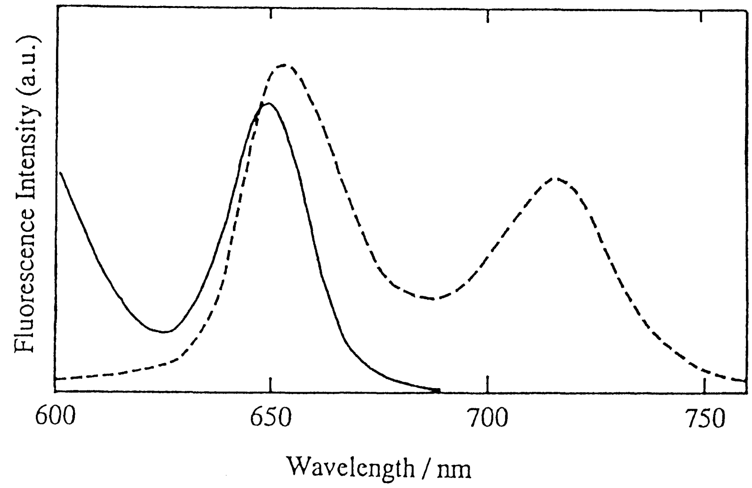

Fig. 2. Fluorescence spectrum (- - -) excited at 590 nm and fluorescence excitation spectrum (——) monitored at 720 nm for TPP in PhR at room temperature. The Stokes shift of this system is as small as 95 cm^{-1}.

No spectral hole formation was observed for PNC / PMMA at 20 K. It is known that norbornadiene derivatives in PMMA are transformed into the corresponding quadricyclene derivatives by light even at 77 K as efficient as at room temperature.11) The transformation of PNC into the corresponding product must have occurred by irradiation with UV light, suggesting no appreciable ZPL in the absorption profile of PNC at 20 K.

The closed-ring form of Fulgide Aberchrome 670 / PMMA exhibited *no* spectral hole at 20 K. Excitation light induced the photochromic reaction of the closed-ring form of Fulgide 670 at 20 K, because the sample was decolorized only at a part where the light was irradiated. The fluorescence of the closed-ring form of Fulgide 670 is too weak to determine the peak of fluorescence spectrum.

The merocyanine form of spiropyran, another famous photochromic material, has never been reported as a hole burning chromophore. The merocyanine form of spiropyran fluoresces strongly, however, the Stokes shift is no less than 1260 cm^{-1}.12) The value of 1260 cm^{-1} is larger than those of

Table 1. Qauntum efficiency for hole formation at 20 K (Φ_{HF}), absorption (λ_a) and fluorescence (λ_f) peak wavelength, and Stokes shift ($\Delta\lambda$) of organic chromophores

Chromophore	Matrix	Φ_{HF}	λ_a/nm	λ_f/nm	$\Delta\lambda/cm^{-1}$
Fulgide 670	PMMA	n.o.*a*)	524	n.o.*a*)	-
PNC	PMMA	n.o.*a*)	290	n.o.*a*)	-
Bilirubin	PhR	n.o.*a*)	460	520	2510
Crystal Violet	PVA	n.o.*a*)	597	637	1020
Cresyl Violet	PVA	5.0×10^{-5}	606	632	679
Azure B	PVA	1.6×10^{-5}	631	656	604
Brilliant Green	PVA	5.5×10^{-7}	634	659	598
Methylene Blue	PVA	8.0×10^{-6}	658	682	535
Nile Blue	PVA	6.1×10^{-7}	642	664	516
ZnTTBP (S_2)	PCMS	1.4×10^{-5}	427	430*b*)	163
ZnTTBP (S_1)	GAP	1.0×10^{-3}	634	638	99
TPP	PhR	1.5×10^{-3}	648	652	95

a) Not observed. *b*) In cyclohexane.

the hole burning dyes.

Bilirubin / PhR, bilirubin bound to HSA / PVA, and biliverdin / PVA did not show any hole formation at 20 K. Antenna pigments of photosynthetic system are known to be PSHB materials. The chemical structure of biliverdin bears great resemblance to those of the antenna pigments, however, no spectral hole was observed for biliverdin / PVA.

Recently Soret band (excited to the second-lowest singlet state, S_2) of ZnTTBP which fluoresces with a Stokes shift of 160 cm^{-1} in cyclohexane has been shown to form a spectral hole at 20 K in poly(*p*-chloromethylstyrene) (PCMS) with a photon-gating technique in our laboratory.13) The present results that chromophores with Stokes shift smaller than 680 cm^{-1} show hole burning at 20 K while chromophores with Stokes shift larger than 1000 cm^{-1} did not show hole burning are also consistent with the fluorescence measurements of quinizarin and its derivatives.6)

It would be concluded that the hole burning materials have comparatively small Stokes shift, less than 1000 cm^{-1}, and it ascertains that the small Stokes shift of chromophores is related to the existence of appreciable ZPL. The hole formation of chromophores which have very small Stokes shift but don't undergo chemical reaction themselves can be realized by the introduction of either non-photochemical hole burning (NPHB) technique with PVA or the sensitization technique to photoreactive matrix polymers.

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