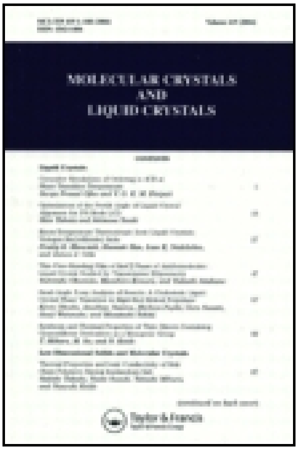

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006.

To cite this article: Indrek Renge & Urs P. Weld (1996): Gated Spectral Hole Burning of Zn-Tetrabenzoporphine in the Presence of Various Organic Activators, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 283:1, 265-270

To link to this article: http://dx.doi.org/10.1080/10587259608037898

Mol. Cryst. Liq. Cryst., 1996, Vol. 283, pp. 265–270
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GATED SPECTRAL HOLE BURNING OF Zn-TETRABENZOPORPHINE IN THE PRESENCE OF VARIOUS ORGANIC ACTIVATORS

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Abstract The influence of a broad range of solid and liquid additives on the photon-gated hole burning has been investigated in toluene-benzene solvent glass containing Zn-tetrabenzoporphine(ZnTBP) at 8K. Two different mechanisms of gated spectral hole burning have been observed. Photoisomerization of olefines, sensitized by means of energy transfer from the highly excited triplet level of ZnTBP can lead to the hole formation with the efficiency as high as $\Phi_2=5\times10^{-3}$ per absorbed gating light quantum. Electron transfer processes in the presence of most favourable acceptors (C_2Cl_6, DDT) and donors (triethylamine) can be realized with the efficiency $\Phi_2=1\times10^{-3}$. The quantum yield of the one-color process is relatively independent on the composition of the system ($\Phi_1\sim10^{-5}$). Polymer films activated with the same additives display comparable hole-burning properties.

INTRODUCTION

Most of the optical experiments using spectrally highly selective photochromism have been performed on the photoactive solids which are based on one-quantum processes. The destructive readout sets severe limits to the possible applications of the organic hole-burning materials for optical data processing, such as octaethylporphine[1] and chlorin[2] doped into polymer matrices.

Two-color gated hole burning was first realized for a derivative of zinc tetrabenzoporphine (ZnTBP) in poly(methyl methacrylate) (PMMA) film.[3] The hole-burning efficiency increased at least by a factor of 100 when the selective radiation of the He-Ne laser was combined with pulsed UV excitation of a N_2 laser.[3] A detailed study of the same system with halocarbon additives (CH_2Cl_2, CH_2Br_2, $CHCl_3$) has confirmed that the triplet state is involved in the phototransformation process.[4] It probably donates an electron to the halocarbon acceptor after the excitation by a second (gating) quantum.[4] Later, the ability to support the two-color hole burning in ZnTBP complexes have been reported for a variety of compounds.[5-9] In general, little correlation was observed between the efficiency and the characteristics of the activators. Therefore it is difficult to optimize the properties of photoactive materials for gated hole burning.

The present study was undertaken with the aim to establish relationships between the structure of potential activators and their efficiency in supporting the two-color hole burning. Frozen solvent glasses have been used as their composition can be varied more easily than that of the polymers.

EXPERIMENTAL

A 0.1ml aliquot of ZnTBP (7×10^{-4}M) in pyridine and 1mmol of the activator were dissolved in toluene-benzene mixture (2:1 v/v) and diluted to the final volume of 1ml. The solution in a 1mm glass cuvette was quenched in liquid N_2 and loaded to the continous flow cryostat (CF1204, Oxford) where the temperature 8K was maintained. Holes were burned at ~630nm with Lambda Physik dye laser (LPD 3002E) pumped with an LPX 100 excimer laser. A 500W incandecent lamp coupled to a fiber bundle and supplied with a combination of color glass filters (transmission maximum 490nm, 10% transmission cut-off limits at 450 and 580nm) was used as a gating source. The detection of the burned holes was accomplished by scanning the dye laser and by measuring the transmitted intensity with a sensitive photodiode (Molectron J3S-10). A less sensitive photodiode J3-09 monitored the intensity of laser output pulses. The signals were averaged and divided by using Molectron JD2000 Joulemeter Ratiometer.

RESULTS AND DISCUSSION

Figure 1 shows one- and two-color holes burned in the presence of styrene and two of its β-methyl substituted derivatives. Both holes can be recorded in a single scan as the red-light exposure during the one-color hole burning has negligible influence on the already existing two-color hole. For styrene, anethole (*trans*-β-methyl-4-methoxystyrene) and asarone (β-methyl-2,4,5-trimethoxystyrene, 70% *cis*) the one-color process occurs with the yield of $\Phi_1=(0.8\text{-}1.8)\times10^{-5}$.

Only about 0.11 quanta pass the triplet cross-section area (2.8Å^2 [10]) during the average triplet-state lifetime of 40ms[11] at the green light intensity of 4mW/cm^2. Because the

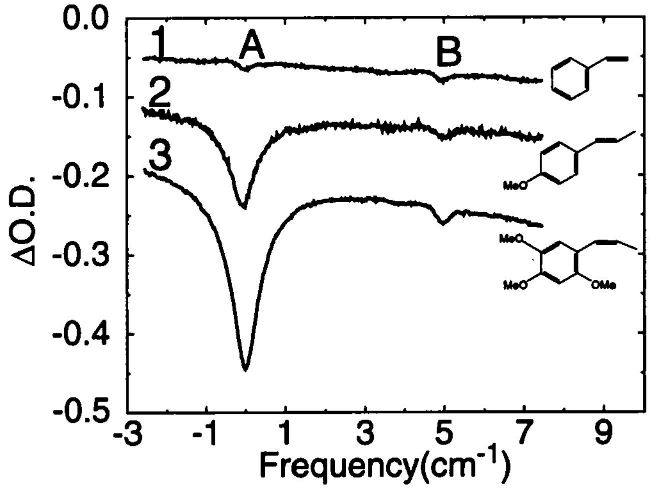

FIGURE 1 Spectral holes in ZnTBP/toluene-benzene glass containing 1.3M of activators: 1 - styrene, 2 - *trans*-anethole, 3 - *cis*-asarone. Holes were burned at (A) 15873cm^{-1}(630nm) and (B) 15868cm^{-1} (630.2nm) during 100s with 5mJ/cm^2 of pulsed (20Hz) light. The gated hole (left) was burned first with simultaneous exposure to 4mW/cm^2 of continuous green light.

triplet quantum yield is close to unity (~0.85[11]), one can easily estimate the phototransformation probability after the triplet molecule has absorbed a gating quantum(Φ_2). The gating ratio(G) was defined as a ratio of areas of the holes burned under identical conditions, with and without the gating light incident on the sample, respectively. The triplet-state phototransformation probability increases from $\Phi_2 < 2\times10^{-5}$ in styrene to 2×10^{-3} in anethole and further up to 5×10^{-3} in *cis*-asarone. The respective gating ratios are 1.4, 18 and 30.

The most efficient additives contain one or two double (>C=O) or triple (-C≡N) bonded heteroatomic substituents conjugated with a single ethylenic fragment: *trans*-butenal or croton aldehyde ($\Phi_2 = 5\times10^{-3}$; G=70), a mixture of *cis*- and *trans*-dimethyl-2,6-octadienal or citral (5×10^{-3}; 40), *trans*-cinnamaldehyde (2×10^{-3}; 40), 2-methyl-2-penten-4-one or mesityl oxide (6×10^{-4}; 9), diethyl maleate (6×10^{-4}; 15), cinnamonitrile (5×10^{-4}; 9) and fumaronitrile (1.5×10^{-4}; 10).

Both the high activity of *cis*-alkenes and the spectral distribution of the product within the inhomogeneously broadened band contour (data not shown) can be rationalized in terms of the isomerization of the alkene sensitized by highly excited triplet porphyrin. The structural change in a co-dopant molecule produces a shift of the 0-0 transition frequency of the pigment which, of cause, remains intact.

Figure 2 shows the data on the quantum yield of one-color burning (Φ_1), the triplet phototransformation (ionization) probability Φ_2 and the gating ratios G of the halogenated hydrocarbons as a function of the irreversible reduction potential values (E_{red}) taken from refs 12 and 13. The one-color burning yield remais approximately constant [$\Phi_1=(8\pm4)\times10^{-6}$] for all the acceptors with $-E_{red}$ values (*vs* SCE) ranging from 0.3V (CBr_4) to >2.6V ($C_2H_2Cl_2$). The gating effect appears first for the activators with $-E_{red}<2V$ and increases with increasing the electron affinity of the acceptor. The gating ratio is also quite well correlated with the magnitude of relative free energy of intermolecular electron transfer (Figure 2C).

At room temperature the solution of ZnTBP changes color from bright green to olive-green in some minutes upon addition of CCl_3CN, CBr_4, allyl chloride and hexachlorobutadiene. Fortunately, the pigment is very stabile with respect to other efficient activators, such as C_2Cl_6, 1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane(DDT) and γ-hexachlorane. These additives can be doped easily in polystyrene at the concentrations as high as 1M. The photon-gated hole-burning characteristics of polymer films are similar to those of frozen solvent glasses.

A two-quantum mechanism was suggested for the photoinduced charge separation at 77K in the Zn-etioporphyrin-triethylamine(TEA) system, where TEA acts as an electron donor.[14] A considerable gating effect is also observed for ZnTBP/TEA (1.3M) system (G=5; $\Phi_1=2.5\times10^{-5}$). Larger effect appears in the presence of N,N'-dimethylpiperazine (8; 1.5×10^{-5}) and in neat $CH_2[N(CH_3)_2]_2$ (27; 1.3×10^{-5} at T=18K) which has the highest density of electon-donating *tert*-amino groups. The influence of much stronger π-electronic donors N,N,N'N'-tetramethyl-*p*-phenylenediamine (G=3) and tetrathiafulvalene (G=2.7) is rather small. Quinuclidine, 1,4-diazabicyclo[2.2.2]octane, N.N-dimethylaniline and β-carotene were found to be completely inert. Concerning the inefficiency of some good donors in supporting the gated hole-burning process, it is conceivable that extensive structural relaxation of the cation radical is necessary in order to prevent recombination of the initial ion pair.

Burning of permanent holes obviously requires irreversible structural changes in the

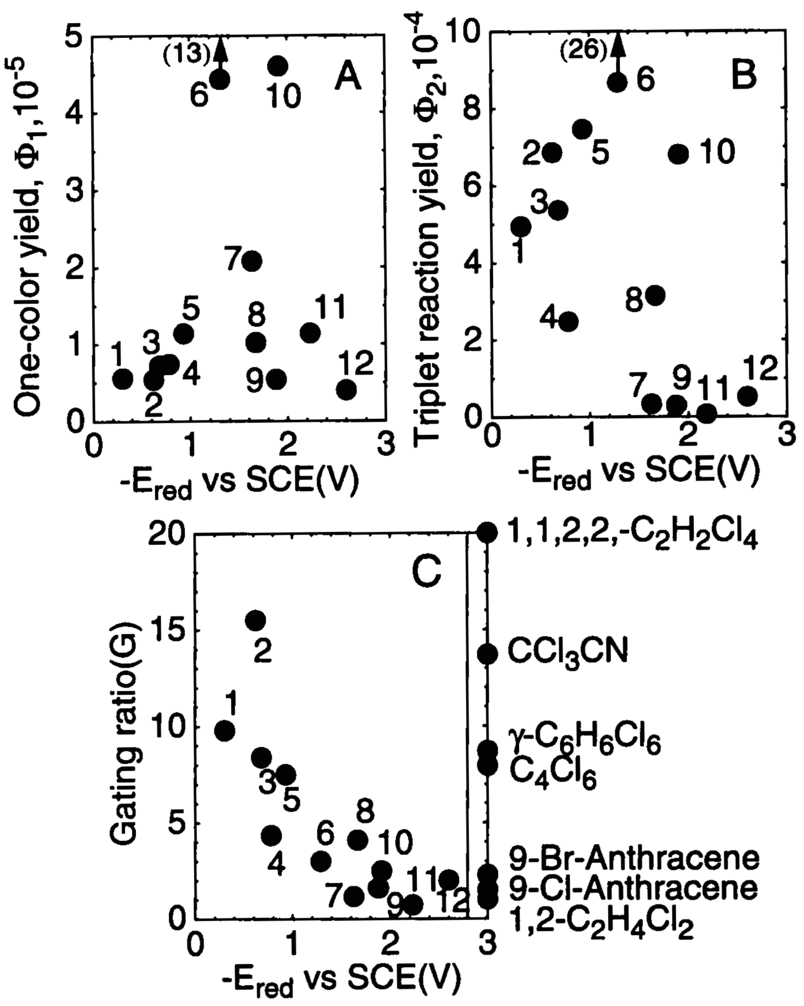

FIGURE 2 One- and two-color hole-burning parameters of ZnTBP/toluene-benzene glass in the presence of 1.3M of halocarbons as a function of irreversible reduction potential of the acceptor (from refs 12 and 13): 1 - CBr_4, 2 - C_2Cl_6, 3 - $C_6H_5CCl_3$, 4 - CCl_4, 5 - DDT, 6 - allyl bromide, 7 - CH_3I, 8 - $CHCl_3$, 9 - C_2Cl_4, 10 - allyl chloride, 11 - CH_2Cl_2, 12 - *cis*-$C_2H_2Cl_2$. G values for substances with unknown E_{red} are depicted on the right-side panel of C.

system. For example, 1.3M of "inert" compounds, nitrobenzene and benzophenone, can quench the gated hole burning in the presence of 1.3M croton aldehyde by~50% by means of energy (or electron) transfer. Dicyanobenzenes (*o*- and *m*-) and 4-hydroxybenzaldehyde used as activators in refs 5 and 6, respectively, have negligible influence on hole burning in solvent glass matrix. Also, no additives have been reported to be introduced to the PMMA film which showed a good gating effect in ref 3. The residual solvents ($CHCl_3$, CCl_4) may be responsible for the gating observed in these studies.

CONCLUSIONS

Gated hole burning of ZnTBP with more than 100 different activators have been examined in toluene-benzene solvent glass under identical conditions. Because of the high energy of the T_n state (~4eV above S_0[10]) both electron and energy transfer processes are possible. *cis-trans*-Isomerization of the ethylenic compounds can lead to remarkable gating when relatively small groups that can be displaced in solid environment are available. Halocarbons with reduction potential below -2V vs SCE (after refs 13 and 14) are inefficient. The same is true for planar acceptor molecules (quinones, substituted nitrobenzenes, aromatic anhydrides) forming charge-transfer complexes with ZnTBP. Extensive structural relaxation of redox products (anion radicals of alkyl halogenides or cation radicals of tertiary aliphatic amines) is a necessary precondition of permanent gated hole burning.

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