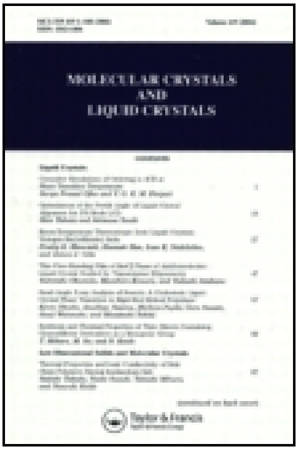

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 04 Oct 2006.

To cite this article: Indrek Renge & Urs P. Wild (1996): Activators of Spectral Hole Burning, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 291:1, 257-268

To link to this article: http://dx.doi.org/10.1080/10587259608042755

Mol. Cryst. Liq. Cryst., 1996, Vol. 291, pp. 257–268
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ACTIVATORS OF SPECTRAL HOLE BURNING

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Abstract The effect of different additives on the one-color and two-color hole burning in the S_1 bands of zinc tetrabenzoporphine and 1,2-benzanthracene has been investigated in solvent glasses at 7-9 K. Two different mechanisms of activated hole burning have been observed: electron transfer to the acceptors and triplet energy transfer to the olefins followed by *cis-trans* isomerization. The decomposition rate of 1-azidopyrene was determined from the hole width to be as fast as 130 fs.

INTRODUCTION

A large variety of the transformations of molecules embedded in solid cryogenic matrices can be triggered by light. The biphotonic photochemistry in solid solutions is predominately based on electron transfer (photoionization) processes.[1,2] Several monomolecular reactions, such as photodissociation and -isomerisation occur in cryogenic environment, despite the restricted molecular mobility and the absence of thermal activation.[3,4] The formation of metalloporphyrin cation radicals under illumination of frozen solvent glasses containing large amounts of polychlorinated alkanes at 77 K was investigated by Khairutdinov *et al.*[5] and Stillman *et al.*[6] Following these studies, Zn and Mg-tetrabenzoporphyrins codoped with several halogenomethanes in poly(methyl methacrylate) thin films have been shown to display promising characteristics of photon-gated hole burning (HB).[7] Large gating ratios have been achieved by using the photodecomposition of an azide polymer which can be sensitized with a Zn porphyrin.[8] However, the wealth of data accumulated in solid-state photochemistry has not been fully used in the field of spectral HB.

The reasons to carry out phototransformations at low temperatures with high spectral selectivity by using monochromatic light are three-fold. First, spectral HB enables one to follow the kinetics of both extremely fast and very inefficient reactions. The rate of a fast process can be obtained from the hole width according to the relation:[9]

$$\Gamma_{\text{hom}} = 1/2\Gamma_{\text{hole}} = 1/2(\pi T_1)^{-1} + (\pi T_2^*)^{-1}, \tag{1}$$

where Γ_{hom} is the homogeneous line width, T_1 is the lifetime of the excited state and T_2^* is the pure optical dephasing time. On the other hand, photoinduced changes with quantum yields of 10^{-6}-10^{-8} can be easily detected by means of HB, because a small number of molecules can be excited with a monochromatic laser via their zero-phonon lines having very large absorption cross section. Second, the presence of narrow holes greatly facilitates the characterization of the electronic transition as well as the matrix properties by applying relatively small electric fields and pressures. Last but not least, better understanding of photoprocesses in amorphous solids at liquid helium temperatures can lead to a considerable diversification and improvement of organic HB materials.

In the present work the influence of various activators on the HB behaviour of several metalloporphyrins, polycyclic hydrocarbons and fullerene C_{70} was studied. Different electron and excitation energy acceptors were used as activators. The efficiency and mechanism of both one-color and two-color HB will be discussed.

EXPERIMENTAL

Frozen solvent glasses were utilised as matrices because their composition can be varied more easily than that of the polymers. Typically, an aliquot of 0.1 ml Zn-tetrabenzoporphine (ZnTBP) (7×10^{-4} M) in pyridine and 1 mmol of the activator were dissolved in toluene-benzene mixture (2:1 v/v) and diluted to the final volume of 1 ml. The solution was placed in a 1 mm glass cell, quenched in liquid N_2 and loaded to the CF1204 continous flow cryostat (Oxford Instruments) where the temperature 7-9 K was maintained. Holes were burned with a Lambda Physik dye laser (LPD 3002E) pumped with an excimer laser (LPX 100). A 500 W incandescent lamp supplied with a combination of filters (ZhS-12+M575, transmission maximum 490 nm, 10% transmission cut-off limits at 450 and 580 nm) was used as a gating source. The detection of holes was accomplished in a two-channel set-up using Molectron JD2000 Joulemeter Ratiometer. The transmission signal was converted to logarithmic units and fitted with the Lorentzian function.

The quantum yield of one-quantum process (Φ_1) was calculated by dividing the number of out-burned molecules by the amount of absorbed quanta. Bearing in mind that the Q band consists of two transitions with equal intensities and the Debye-Waller factor is about 0.7 and the extinction coefficient of ZnTBP in pyridine at room temperature equals to $\varepsilon=1.3\times10^5$ $M^{-1}cm^{-1}$,[10] it was found that the unit hole area ($\Delta D\times nm$) corresponds to 9.1×10^{14} molecules per cm^2. The triplet-triplet absorption cross section calculated from the ε value at 490 nm (7.4×10^4 $M^{-1}cm^{-1}$ [11]) equals to 2.8 $Å^2$. On the other hand, during the average triplet-state lifetime of 40 ms[12], only about 0.11 quanta pass this area at the green light intensity of 4 mW/cm^2. Because the triplet quantum yield is close to unity (~0.85 [12]), one can estimate the phototransformation probability, if 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.

ACTIVATORS OF HOLE BURNING IN ZnTBP

The influence of various additives on the quantum efficiency of HB was studied in the vitreous toluene-benzene mixture at 7-9 K. ZnTBP was chosen as a model sensitizer, because its meso-phenyl substituted derivatives have been already widely studied in connection with photon-gated HB.[7] ZnTBP has a small absorption coefficient ($\varepsilon<3\times10^3$ M^{-1} cm^{-1}) in the spectral window between 460 and 560 nm[10] where its long-lived triplet state has strong $T_n\leftarrow T_1$ transitions. Large gating effect can be achieved with 0.1 W/cm^2 of green light of an Ar^+ laser.[7] Even a relatively weak gating light (4 mW/cm^2) can lead to a considerable enhancement of the HB rate (holes on the left side in Figures 1a and 1b). With the aim of optimizing the composition of gated HB materials we started the measurements with halocarbons, since their photoreactivity relative to metalloporphyrins has been already demonstrated, both under broad-band excitation[5,6] and in the hole burning regime.[7] As expected, both the efficiency of two-color HB and the gating ratio increases with increasing the electron affinity of halocarbon (see our previous paper, Reference 13). The phototransformation probability of the ZnTBP triplet (Φ_2) can be as high as 0.5%

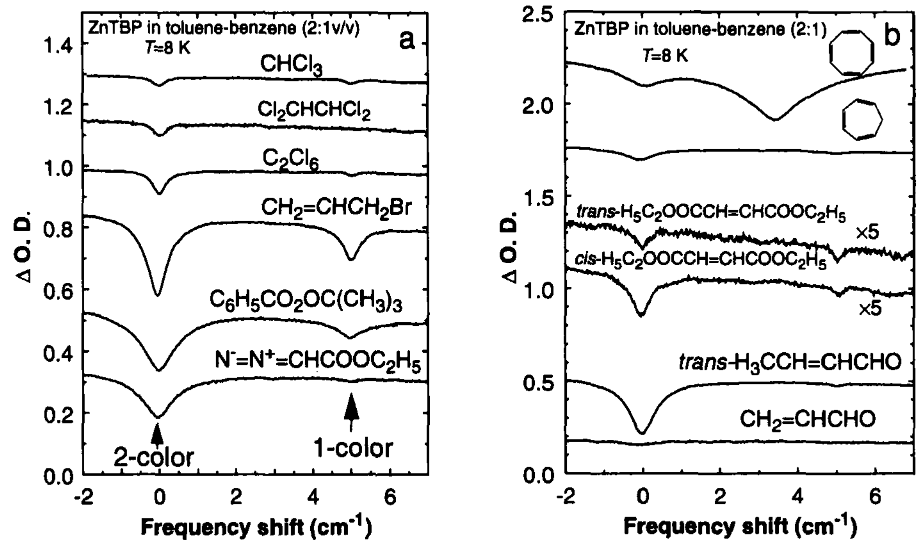


FIGURE 1 One-color and two-color holes burned in the S_1 band of ZnTBP (7×10^{-5} M) in toluene-benzene glass containing 1.3 M of electron acceptors (a) and olefins (b). Holes were burned at 628-630 nm during 100 s with 5 mJ/cm^2 of pulsed (20 Hz) light. First the gated hole at the origin of frequency scale was burned with simultaneous exposure to 4 mW/cm^2 of continuous green light. The curves are shifted arbitrarily in the optical density scale.

when the environment contains 1.3 M of allyl bromide, *tert*-butyl peroxybenzoate and ethyl diazoacetate (Figure 1a). The one-color process is also efficient in case of best activators and the resulting gating ratio is small.

A peculiar behavior was observed in presence of cyclooctatetraene (COT) which was first considered as a weak electron acceptor. For COT the one-color bleaching occurs with high quantum yield of Φ_1=0.7% (Figure 1b). As a result of extensive hole filling under the green light exposure, the gating ratio is less than unity (G=0.15). It was found that numerous olefinic compounds devoid of appreciable electron affinity can also induce HB.[13] Consequently, a process different from electron transfer can be also responsible for permanent HB.

MECHANISMS OF PERMANENT HOLE BURNING IN ZnTBP

In Figure 2 the spectral changes after extensive burning are displayed in a large wavelength interval. In neat glassy olefin, *cis*-asarone, the accumulation of the photoproduct can be clearly seen, in particular, in the short-wavelength side of the hole where there is no overlap with the broad pseudo hole. In contrary, *trans*-1,4-dibromo-2-butene obviously reacts as an electron acceptor relative to the pigment molecule, because the S_1 band of the ZnTBP is bleached.

Olefins which can undergo *cis-trans* isomerism, such as cycloheptatriene ($\Phi_2=1.3\times10^{-3}$; G=11) (in propylene carbonate-toluene-benzene 3:2:1 mixture) and *trans*-butenal (croton aldehyde) (6×10^{-3}; 70) support the gating effect more strongly than those without isomers: 2-methyl-1,3-butadiene (isoprene) (2×10^{-4}; 2.5), 1,6-dimethyl-2,4-hexadiene (1×10^{-5}; 1.4) and acrolein (6×10^{-4}; 10). Diethyl maleate (*cis*) is four times more active than diethylfumarate (*trans*) ($\Phi_2=6\times10^{-4}$ and 1.5×10^{-4}; G=15 and 2, respectively) (Figure 1b)

The most efficient additives contain one or two double (>C=O) or triple (-C≡N) bonded heteroatomic substituents conjugated with a single ethylenic fragment: croton aldehyde, *trans*-dimethyl-2,6-octadienal (citral) (5×10^{-3}; 35), cinnamaldehyde (2×10^{-3}; 40) and diethyl maleate. Large π-electronic system seems to suppress HB in 1,3,5-hexatriene (~0; 0.7), 2,4-pentadienal (sorbic aldehyde) (3×10^{-4}; 6) and *trans*-1-phenyl-1-buten-3-one ($<1\times10^{-4}$; 1.2). *cis*-Dichloroethylene and *cis*-1,4-dihydroxy-2-butene are inactive because the triplet level of compounds with only one double bond is probably too high to accept energy from the T_n level of ZnTBP.

Both the high activity of *cis*-alkenes and the spectral distribution of the product within the inhomogeneously broadened band contour can be rationalized in terms of isomerization of alkenes sensitized by highly excited triplet porphyrin:

$$\mathrm{ZnTBP(T_1)+h\nu(490\ nm)\rightarrow ZnTBP(T_n)}$$
$$\mathrm{ZnTBP(T_n)+}\textit{cis}\mathrm{\text{-}alkene(S_0)\rightarrow ZnTBP(S_0)+}\textit{cis}\mathrm{\text{-}alkene(T_1)}$$
$$\textit{cis}\mathrm{\text{-}alkene(T_1)\rightarrow}\textit{trans}\mathrm{\text{-}alkene(T_1)}$$
$$\textit{trans}\mathrm{\text{-}alkene(T_1)\rightarrow}\textit{trans}\mathrm{\text{-}alkene(S_0)}.$$

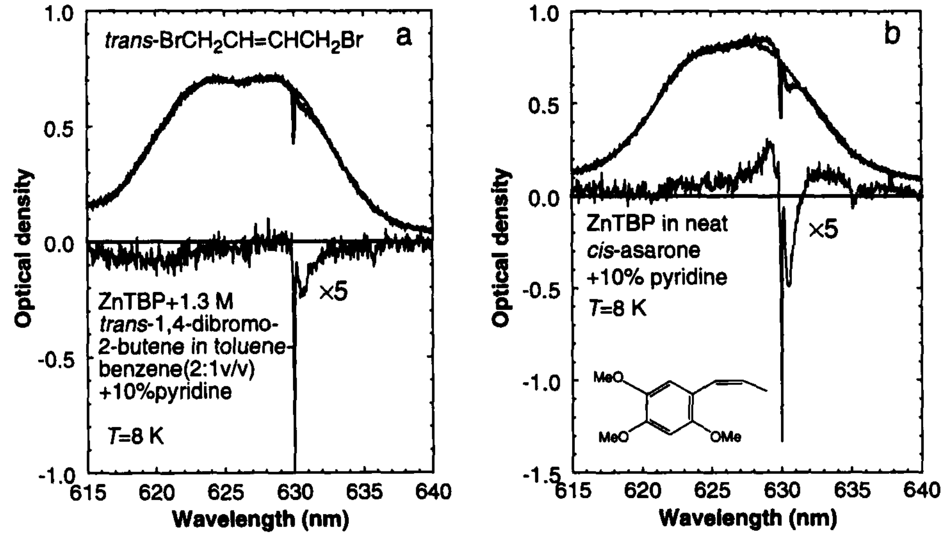


FIGURE 2 Absorption spectra of ZnTBP in toluene-benzene mixture containing 1.3 M *trans*-1,4-dibromo-2-butene (a) and neat *cis*-asarone (+10% v/v of pyridine) (b) before (thin line) and after extensive burning during 200 s with simultaneous exposure to 630 nm laser pulses (40 Hz, 0.2 J/cm^2) and continous green light (0.8 J/cm^2). The difference of two curves is shown below.

The structural rearrangement of alkene molecule in the close vicinity of pigment molecule can give rise to a solvent shift of zero-phonon transition frequency of the latter and create a resonant hole.

Remarkably efficient one-colour hole burning in the presence of COT may arise as a result of triplet energy transfer (or electron transfer, see below) from the T_1 level of ZnTBP followed by the isomerization of polyene.

Interestingly, it has been already observed that naphthalene-D_8 can sensitize the conversion of matrix molecules to the *trans* form in neat glassy *cis*-2-pentene at 77 K as a result of energy transfer from the higher triplet level of naphthalene.[4]

The activators which form transparent glasses on cooling, such as 1,1,2,2-tetrachloroethane can be mixed with a neutral diluent, and the influence of the concentration of activator can be studied in a broad range (Figure 3). It turns out that the gating sets in at

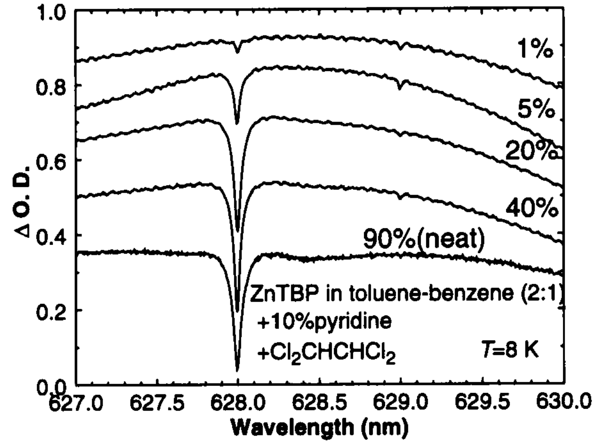


FIGURE 3 One-color and two-color holes burned in the S_1 band of ZnTBP (7×10^{-5} M) in toluene-benzene glass containing various amounts of 1,1,2,2-tetrachloroethane (in volume%). Holes were burned at 628 and 629 nm during 120 s with 50 mJ/cm^2 of pulsed (100 Hz) light. First the gated hole was burned at 628 nm with simultaneous exposure to 4 mW/cm^2 of continuous green light. All curves, except the upper one, are shifted downwards in the optical density scale.

the concentration of 2% and its efficiency increases rapidly up to 20% (1 M) of the reactant and then reaches practically a limiting value. Therefore, the two-color HB cannot be regarded as a photoionization reaction followed by electron capture at some distant acceptor molecule. Also, as a result of fast relaxation of the T_n state (probably several ps or less) the electron transfer by means of long-range (~15 nm) tunnelling in the sense expressed in Reference 5 has no time to occur. Evidently both exchange processes, the triplet-triplet energy transfer and the electron transfer require nearly van der Waals contact between the pigment and activator molecules. However, in case of electron transfer mechanism, the yield of permanent hole formation is not further increased when the pigment becomes fully surrounded by acceptor molecules. Possibly, a very fast recombination of the contact ion-radical pair may compete with the structural changes in the halocarbon anion radical (e. g. the halogen ion detachment) which are needed to render the process irreversible.

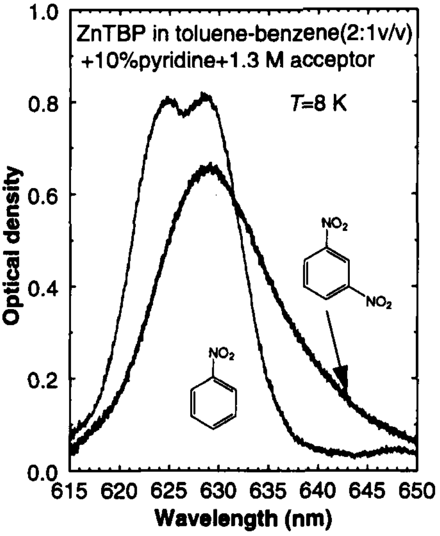
The reversible π-electronic acceptors (nitrobenzene, phthalonitrile, isophthalonitrile) as well as aromatic donors (anilines)[13] fail to induce any HB. The triplet energies of these compounds are also well below the T_n (~4 eV) of ZnTBP. Thus both the electron and triplet energy transfer to these additives is possible. There is practically no permanent change in the system capable of leading to the HB because of rapid charge recombination and the absence of isomerisation. The broadening and bathochromic shift of the Q band of ZnTBP in the presence of stronger π-acceptors (1,3-dinitrobenzene, benzoquinone, 1,4-naphthoquinone, maleic anhydride) indicates that a charge-transfer complex is formed (Figure 4).

It is worth noting that the same HB activators can be also used with Mg and Zn-octaethylporphines. It is, however, of interest to extend the measurements to the other π-electronic chromophores.

ACTIVATED HOLE BURNING IN 1,2-BENZANTHRACENE AND C_{70}

The α (^1L_b) transitions in polycyclic hydrocarbons are known to be relatively weakly coupled to low-energy matrix vibrations. In glassy hosts they are characterized by Debye-Waller factors (DWF) about 0.7-0.8.[14] However, no detectable hole is formed after the irradiation of the 1,2-benzanthracene solution (10^{-2} M) in ethanol-benzyl alcohol (2:1 v/v) glass at 384.6 nm with the light dose of 20 mJ/cm^2 during 150 s (pulse frequency 40 Hz). Thus the HB quantum yield (Φ_1) ought to be less than 10^{-4}, despite the protic nature of the matrix.

Fairly efficient HB in this system can be initiated by adding 1.3 M of different activators (Figure 5). By taking the extinction coefficient (ε) equal to 10^{-3} M^{-1}cm^{-1}, the HB yields amounting to 1.0% and 0.6% were obtained for *tert*-butyl peroxybenzoate and CHT, respectively. In the former system the HB yield remains relatively independent on the hole depth, i. e. the HB kinetics is not very dispersive, and the hole depth of 50% can be easily reached. Saturated holes are accompanied by a pseudo wing displaced by 17±1 cm^{-1} from the burning frequency. The effect of halogenated electron acceptors is less pronounced with Φ_1 values about 0.2%. The isomerization of CHT can be sensitized by the energy transfer from the T_1 level of arene, because its triplet energy (13300 cm^{-1}) is much



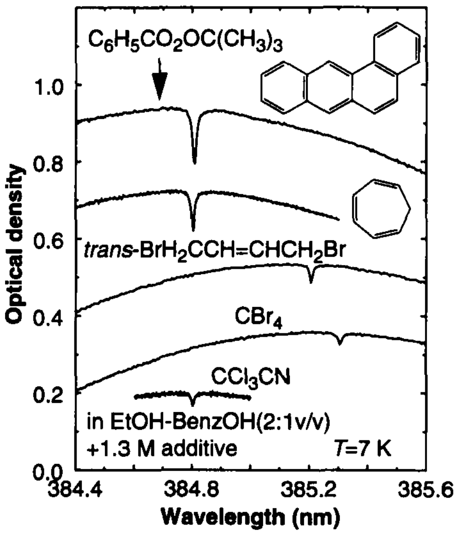


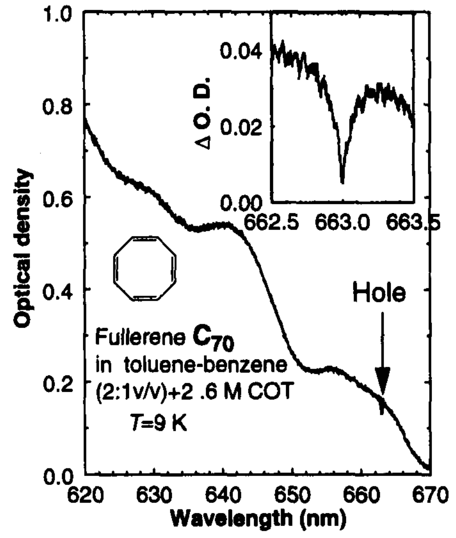
FIGURE 4 (left) Absorption spectra of ZnTBP (7×10^{-5} M) in toluene-benzene mixture containing 1.3 M of nitrobenzene and 1,3-dinitrobenzene.

FIGURE 5 (right) One-color holes burned in the S_1 band of 1,2-benzanthracene (10^{-2} M) in ethanol-benzyl alcohol glass containing 1.3 M of activators. The light dose was 20 mJ/cm^2 (150 s, 40 Hz, 3 μJ/cm^2 per pulse). All curves, except the upper one, are shifted downwards in the optical density scale.

lower than that of the 1,2-benzanthracene (16500 cm^{-1}).[15]

Addition of 2.6 M of another cycloolefin, COT, to the toluene-benzene host was utilised to sensitize HB in the lowest singlet absorption band of fullerene C_{70} (Figure 6). The T_1 energy of the fullerene C_{70} lies at 12373 cm^{-1}.[15] On basis of a triplet quenching study at room temperature the T_1 level of COT can be located at 14000-17500 cm^{-1} (40-50 kcal/mol), depending on the degree of planarity of the molecule.[16] Therefore the triplet energy transfer from C_{70} to COT is improbable. The HB mechanism in ZnTBP (E_T=12450 cm^{-1} [12]) and C_{70} in the presence of COT needs further studies.

The DWFs of the S_1 transitions of fullerenes appear to similar to those for α bands of polycyclic arenes, in accordance with similar polarizability density changes upon excitation or dispersive solvent shifts (~1000 cm^{-1} per unity Lorentz-Lorenz function[17]).[18]



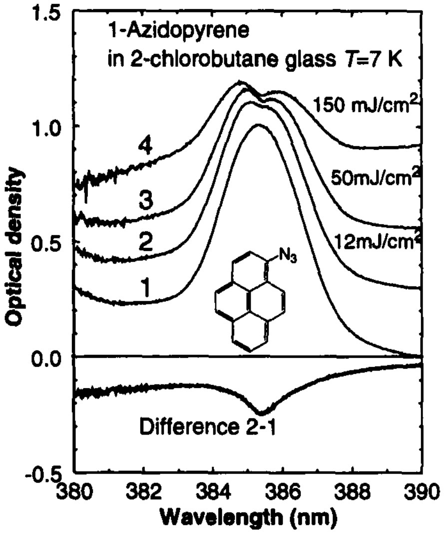


FIGURE 6 (left) Absorption spectrum of fullerene C_{70} in toluene-benzene glass containing 2.6 M of cyclooctatetraene. The insert shows a hole burned at 663 nm with the light dose of 0.1 J/cm^2 during 200 s (100 Hz, 5 μJ/cm^2 per pulse).

FIGURE 7 (right) Absorption spectra of 1-azidopyrene (~10^{-2} M) in 2-chlorobutane glass in a 0.5 mm cell before (1) and after the irradiation with increasing doses of pulsed light (40-100 Hz) at 385.4 nm (2-4).

PHOTODISSOCIATION OF 1-AZIDOPYRENE

In previous sections the activation of HB by adding reactive compounds has been discussed. An alternative way to induce the photoactivity is attaching a photosensitive group directly to the chromophore molecule. The azido substituent is well suited for this purpose because organic azides are known to produce nitrene and N_2 with high efficiency in solid matrices at 77 K.[3]

1-Azidopyrene shows a typical α transition with relatively narrow (195±5 cm^{-1}) 0-0 band peaking at 385.3 nm in vitreous 2-chlorobutane (Figure 7). At 7 K a very broad and shallow hole can be burned in this band with quantum efficiency close to unity, Φ_1=1.2±0.2

(assuming $\varepsilon=10^3\ M^{-1}cm^{-1}$). The full width at half maximum (FWHM) of the Lorentzian contour of the difference spectrum before and after burning with the light dose of 12 mJ/ cm^2 equals to 80 cm^{-1}. From Equation (1) the monomolecular decomposition rate as fast as 130 fs can be obtained. The rise of the background occurs as a result of very strong absorption of the nitrenopyrene overlapping with the 0-0 band of 1-azidopyrene.[3] Too fast phototransformation resulting in lifetime-broadening of spectral holes is clearly unfavourable for practical applications. Fortunately, not all aromatic azides possess such a high reactivity and the selection of derivatives decomposing with yields 0.5-0.9 seems to be possible.[3]

CONCLUSIONS

In this study the possibilities to induce persistent spectral HB in non-photoreactive organic impurity systems were considered. The methods of adding a reactive codopant to the matrix and the binding of a photolabile group directly to the chromophore molecule were investigated. As far as bimolecular processes are concerned, both the one- and two-quantum versions of the electron transfer and sensitized photoisomerization were realized.

It was observed that *cis-trans* isomerization of olefins in glassy hosts at 7-9 K can be sensitized by means of triplet energy transfer from the T_1 or T_n levels of polycyclic arenes and metalloporphyrins. The hole is formed as a result of the solvent shift accompanying the structural change of the nearby olefin molecule.

A monomolecular process, the photodissociation of azido-arenes appears to be a promising HB reaction in the short-wavelength region.[3] For 1-azidopyrene the photodecomposition yield is unity and it proceeds with the rate as fast as 130 fs. Obviously less reactive azides should be used to achieve still the 50-90% burning yield without sacrificing the spectral selectivity of the HB material.

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