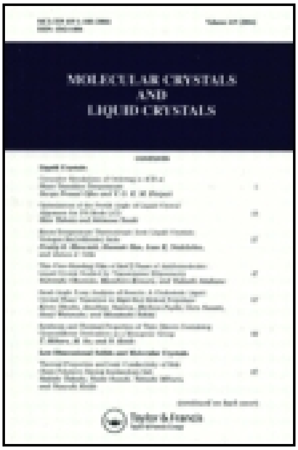

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

A Novel Material for Spectral Hole-Burning Applications: Photochemical Properties of meso-Diphenyl-Tribenzonaphtoporphine

Bernd Plagemann [a], Indrek Renge [a], Alois Renn [a] & Urs P. Wild [a]

[a] Physical Chemistry Laboratory, Swiss Federal Institute of Technology, ETH Zentrum, CH - 8092, Zurich, Switzerland

To cite this article: Bernd Plagemann, Indrek Renge, Alois Renn & Urs P. Wild (1998): A Novel Material for Spectral Hole-Burning Applications: Photochemical Properties of meso-Diphenyl-Tribenzonaphtoporphine, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 314:1, 137-142

To link to this article: http://dx.doi.org/10.1080/10587259808042469

Mol. Cryst. Liq. Cryst., 1998, Vol. 314, pp. 137–142
Reprints available directly from the publisher
Photocopying permitted by license only

A Novel Material for Spectral Hole-Burning Applications: Photochemical Properties of meso-Diphenyl-Tribenzonaphtoporphine

BERND PLAGEMANN, INDREK RENGE, ALOIS RENN, URS P.WILD
Physical Chemistry Laboratory, Swiss Federal Institute of Technology,
ETH Zentrum, CH - 8092 Zürich, Switzerland

We have studied the photochemical properties of meso-diphenyl-tribenzonaphtoporphine (P_2TriBNP) as a material exhibiting spectral hole-burning (SHB) that are important for its use in optical data storage and imaging spectroscopy. We measured the Debye-Waller factor, the hole-burning efficiency, the inhomogeneous and homogeneous line width, the back reaction rates of the photoproduct, and the dipole moment differences between ground and excited state of this compound at liquid helium temperatures. Poly(vinyl butyral) was used as the matrix. The hole-burning efficiency is higher by orders of magnitude compared with commonly used systems like chlorin (3.5 ± 1.5% vs. 0.03%) which brings about the possibility to perform storage experiments with much lower light levels and on shorter time scales than before.

Keywords: spectral hole-burning, quantum yield, optical data storage, imaging spectroscopy, porphyrins

INTRODUCTION

The requirements of materials exhibiting SHB for the use in optical data storage[1] and imaging spectroscopy[2] include a high photochemical quantum yield. We chose a new compound, P_2TriBNP, for our investigations. The molecule combines the advantages of chromophores like octaethylporphyrin which exhibit a high yield and possess an extended π-electronic system with the good spectral separation of the photoeduct and -product of non-centrosymmetric compounds like chlorin. We determined the photochemical parameters being important for the use in practical applications and compared it with other systems used so far.

SAMPLE PREPARATION AND ABSORPTION SPECTRA

A mixture of symmetric and non-symmetric meso-di- and meso-triphenylbenzoporphines was synthesized following Ref. [3], and separated chromatographically. The main asymmetric fraction was identified as meso-diphenyl-tribenzonaphtoporphine. Poly(vinyl butyral) (PVB) and an appropriate amount of the dye were dissolved in CH_2Cl_2 and the solvent was slowly evaporated, yielding a thin film with good optical quality and a thickness of 100-200 μm.

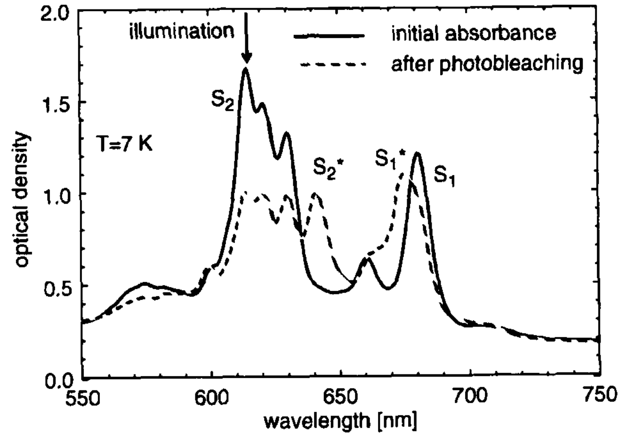

FIGURE 1 Absorption spectrum of P_2TriBNP before (straight line) and after (dotted) strong illumination of the S_2 band.

The absorption spectrum of the sample reveals a strong absorption around 683 nm, corresponding to the $S_1 \leftarrow S_0$ transition (S_1), and a structured band from 600-650 nm, which could be identified as the $S_2 \leftarrow S_0$ absorption (S_2). During strong illumination with broadband laser light, the photoproduct is accumulated, exhibiting a shift of the S_1^* band of 115 cm^{-1} (4.1 nm) compared with the S_1 transition.

PHOTOCHEMICAL PROPERTIES

The basic photochemical parameters that are important for practical applications were determined using SHB. The experiments were performed at 1.7 K and we used the background-free holographic detection method for the measurement of shallow signals.[4]

Hole-Burning Yield

The photochemical hole-burning yield Φ is the focus of this investigation. It can be defined as the ratio of the number of photoreactions leading to a shift of the absorption frequency to the number of photons absorbed by the sample. The number of photoreactions can be calculated by comparing the areas of small spectral holes with the overall absorption band. The number of absorbed photons is easily obtained from the irradiance I and the absorbance of the sample. Taking into account the Debye-Waller factor α_{DW}, the transmittance T and the reflectivity R of the sample, the quantum efficiency becomes

$$\Phi = \frac{h\nu_b\, A_{\lambda_{max}}}{(1-T)(1-R)\alpha_{DW}\, I\, \varepsilon_{\lambda_{max}}} \frac{1}{A_{total}} \frac{d}{dt}\left(\int_0^\infty L(\nu_b, \nu)d\nu\right) ,$$

where A_{total} is the integrated absorbance of the inhomogeneous band, assuming a Gaussian lineshape, and $L(\nu_b, \nu)$ is the Lorentzian absorption profile of the hole burned at the frequency ν_b. The molecule concentration and the sample thickness are expressed by the absorbance A and the molar extinction coefficient ε at the wavelength with maximum absorbance, denoted by the subscript λ_{max}.

Series of holes were burned with constant irradiance but increasing exposure times. The increase of the hole area with the increasing fluence yields the value for the hole-burning efficiency. We obtained values of 3.5 ± 1.5% at different positions of the inhomogeneous band, with a slight increase towards the long wavelength side. This value is among the highest burning yields measured so far for organic dye molecules. It is two orders of magnitude higher than in chlorin which has been widely used for SHB applications.

Homogeneous Linewidth

The ratio of the inhomogeneous to the homogeneous linewidth can be regarded as a figure of merit for the frequency selectivity of the examined system. For the determination of the homogeneous linewidth we burned a series of shallow holes with constant exposure times but increasing irradiance. The signals were detected holographically as this technique has a much better signal-to-noise ratio. Extrapolation to zero fluence and zero power yields the homogeneous hole width. One has to keep in mind that this width only excludes broadening caused by saturation of the involved states and photochemical depletion. The homogeneous width measured here is not only determined by the lifetime of the transition. Broadening caused by dephasing and frequency shifts taking place on shorter time scales than some seconds are included as well. The extrapolation gives a value of 235 ± 20 MHz. Together with the inhomogenous width of 9.9×10^6 MHz this yields a ratio of 4×10^4.

Debye-Waller Factor

The Debye-Waller factor α_{DW} is defined as the relative contribution of all zero phonon lines (ZPL) to the overall absorption band. To determine this parameter we monitor the absorbance of the sample while burning a deep spectral hole. From the time evolution of the optical density we can extrapolate to the contribution of the phonon wing which is undergoing a photoreaction with much slower kinetics. The difference of the absorbance before and after "infinitely" long burning is determined at several positions throughout the inhomogeneous band. This yields the ZPL contribution from which we calculate the Debye-Waller factor. The time evolution of the ZPL part of the absorbance A can be calculated from a convolution of the time dependent chromophore density $N(\nu,t)$ with the absorption cross section σ_{ZPL}, which has a Lorentzian lineshape:

$$A(\nu, t) = -A_0\, \sigma_{ZPL}(\nu_b, \nu) \otimes N(\nu, t) \ .$$

The chromophore density decays exponentially with time:

$$N(\nu, t) = N(\nu, t_0)\, \exp(-C\, \sigma_{ZPL}(\nu_b, \nu)\, t) \ ,$$

where C is a constant containing burn parameters like the photon energy, the hole-burning efficiency and the relative orientation of the laser polarization and the transition dipole moment. The time evolution is calculated at the burn frequency and fitted to the experimental data.

From the integrated areas of the ZPL contribution and the complete absorption we get a value for α_{DW} of 0.59. This is a lower limit for the true value since the baseline is not well defined due to the long ranging wings of the absorption bands further to the blue. The value is similar for chlorin (0.67).

Backreaction Rates

The time evolution of the hole area gives a quantitative measure for the stability of the photoproduct and the rate of the backreaction to the initial state. Monitoring a holographically detected hole over several days shows that he integrated area decays with a logarithmic time dependence. This corresponds to a backreaction of the photoproduct with a distribution of back transfer rates.[1] The decay of the hole area A, normalized with the initial value A_i, can be expressed as

$$\frac{A(t)}{A_i} = 1 - \frac{\ln(R_i\, t)}{\ln(R_i/R_{min})} ,$$

where R_{min} is the lower cutoff value of the rates occurring and R_i is the highest value that can be observed in the experiment. The slope of the area decay of an absorption hole had a value of 21.2 ± 0.6% per decade. The corresponding ratio of the rates (R_i/R_{min}) is approximately $5{\times}10^4$. This implies that the area of a spectral hole decays to half the value that it has one minute after burning in three to four hours. This has to be taken into consideration in practical applications.

Dipole Moment Differences

The dipole moment difference between the ground state and the first excited singlet state of the dye molecule can be determined by applying an electric field to the sample and observing the changes of the hole shapes. The linear Stark effect causes reversible shifts of the individual absorption frequencies which in turn leads to broadening or splitting of the spectral hole. We performed holographic measurements and determined the dipole moment differences according to Ref. [5]. The evaluation made the distinction of two contributions possible. We observed an absolute value of $|\Delta\mu_{fix}| = 0.29 \pm 0.03$ D for the fixed dipole moment difference which includes an angle of 90° with the transition dipole moment of the $S_1 \leftarrow S_0$ transition. Additionally, we observed a randomly oriented, matrix induced component with a root mean square value of $\overline{\Delta\mu_{ind}} = 0.15 \pm 0.02$ D. This makes it possible to use the electric field as an additional degree of freedom.

CONCLUSIONS

We investigated the fundamental photochemical properties of P_2TriBNP which are important for practical applications at low temperatures. The comparison with other systems shows that P_2TriBNP has one fundamental advantage, the much higher photochemical hole-burning yield, while many other properties remain unchanged. It may open the possibility for a new class of experiments. The imaging of spectrally structured objects with lower brightness than the so far used ones should be possible.[2] Although the backreaction of the photoproduct restricts the possible applications to finite times, one can perform optical data storage investigations on the time scale of some hours or use the system for time-domain applications of frequency-selective materials.

References:

[1] W. E. Moerner (Ed.), ***Persistent Spectral Hole Burning: Science and Applications***, (Springer, Berlin, 1988), and references therein.

[2] · C. U. Keller, W. Graff, A. Rosselet, R. Gschwind, U. P. Wild, *Astron. Astrophys.* **289**, 41 (1994).

[3] V. N. Kopranenkov, S. N. Dashkevich, E. Ya. Lukyanets, *Zh. Obshch. Khim.* **51**, 2513 (1981) [*J. Gen. Chem. USSR* **52**, 2165 (1982)].

[4] A. Renn, A. J. Meixner, U. P. Wild, F. A. Burkhalter, *Chem. Phys.* **93**, 157 (1985).

[5] A. J. Meixner, A. Renn, S. E. Bucher, U. P. Wild, *J. Phys. Chem.* **90**, 6777 (1986).