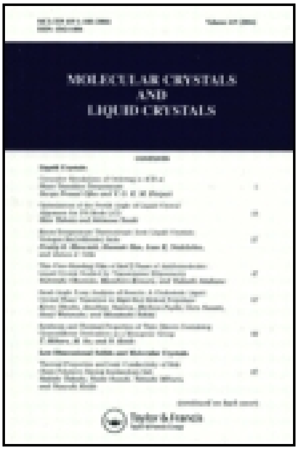

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Photochromic Materials for Reversible Switching of Second Order Nonlinear Optical Properties

Frederic Poineau [a] , Keitaro Nakatani [a] & Jacques A. Delaire [a]

[a] Lab. de Photophysique et de Photochimie Supramoléculaires et Macromoléculaires (PPSM, CNRS UMR 8531), Ecole Normale Supérieure de Cachan, 61 avenue du Président Wilson, 94235, Cachan, Cedex, (FRANCE)

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Photochromic Materials for Reversible Switching of Second Order Nonlinear Optical Properties

FREDERIC POINEAU, KEITARO NAKATANI
and JACQUES A. DELAIRE

*Lab. de Photophysique et de Photochimie Supramoléculaires et Macromoléculaires (PPSM, CNRS UMR 8531), Ecole Normale Supérieure de Cachan,
61 avenue du Président Wilson, 94235 Cachan Cedex (FRANCE)*

This paper reports on materials whose second order nonlinear optical (NLO) properties can be switched by light. We synthesized and studied the properties of a series of substituted N-salicylidene anilines which are noncentrosymmetric and photochromic crystals. All compounds exhibit second harmonic generation (SHG). One of the compounds exists in two different cristalline forms, one being photochromic and the other thermochromic. Photoswitching of SHG was performed : irradiation by UV light lead to a decrease of SHG up to 60 % of the SHG signal at 1064 nm and 10 % at 1907 nm.

Keywords: nonlinear optics; second harmonic generation; photochromism; salicylidene aniline; photoswitching; tautomerism

INTRODUCTION

Organic molecules and materials show promising properties for NLO applications, due to their instrinsically high nonlinear susceptibilities[1,2]. However, they are reactive and lack in stability, and this avoids them to compete with the more classical inorganic materials used for the same purpose. During the past years, taking advantage of reactions occuring in organics instead of avoiding them is a new prospective field of research, and the final goal is to get smart, switchable materials. Since the work by

Krongauz et al.[3], a growing number of photochromic molecules exhibiting high values of hyperpolarizability, particularly β (quadratic polarizability related to second order effects) and/or showing difference of NLO properties between the two photoisomers have been studied[4-7].

Concerning materials, the possibility to switch second order NLO by means of light have been shown in Langmuir films by ground to excited state excitation[8] and by trans-cis isomerization[9,10]. In "bulkier" materials, this cannot be performed easily in polymers. In fact, a prerequisite for having second order NLO properties on a macroscopic scale is the noncentrosymmetry (NC) of the material as a whole, and usually, NC configuration in polymer is metastable. As a consequence, repetitive photoswitching of photochromic polymers leads eventually to an inactive material[11].

In this paper, we present the investigation of a series of N-salicylidene aniline (SA) derivatives (Figure 1). Some of these molecules are known for yielding photochromic crystals for many years[12-15]. Among them, those which crystallize in a NC space group were selected, the NLO properties of the most stable isomer (usually "OH") were studied by SHG, along with the effect of photochromism on this property[16].

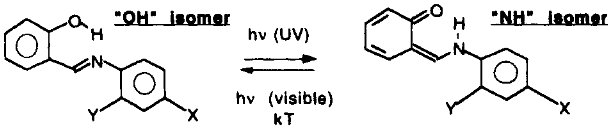

FIGURE 1 : N-salicylidene aniline derivatives.
N-salicylidene 2-chloro-aniline (2-Cl, X=H, Y=Cl), N-salicylidene 2-bromo-aniline (2-Br, X=H, Y=Br), N-salicylidene 4-bromo-aniline (4-Br, X=Br, Y=H), and N-salicylidene 2-methyl-4-nitro-aniline (2-Me-4-NO_2, X=NO_2, Y=CH_3).

EXPERIMENTAL SECTION [16]

Synthesis and sample preparation

Four compounds N-salicylidene 2-chloro-aniline (2-Cl), N-salicylidene 2-

bromo-aniline (2-Br), N-salicylidene 4-bromo-aniline (4-Br), and N-salicylidene 2-methyl-4-nitro-aniline (2-Me-4-NO_2) were prepared according to a straight forward procedure, by reaction of salicylaldehyde and the appropriate aniline derivative. mp (2-Cl : 82°C, 2-Br : 92°C, 4-Br : 109°C, 2-Me-4-NO_2 : see Results and Discussion) and IR spectra are in good agreement with literature[14-17]. For further studies, samples were heated up to mp between two glass plates, and allowed to crystallize as a polycristalline " thin film" (around 100 µm).

SHG measurements

The fundamental beam (1064 nm) of a Nd:YAG pico- or nanosecond laser was used. Measurements at 1907 nm were performed by shifting the wavelength by a H_2 cell. The SHG beam was passed through a narrow band filter and detected by a photomultiplier linked to an oscilloscope. Samples were irradiated (in most cases in situ) by the third harmonics of the Nd:YAG laser (355 nm, ca. 1 $mW.cm^{-2}$) for the UV and by the 514 nm beam of an argon ion laser (ca. 20 $mW.cm^{-2}$) for the visible.

Photochromism

The absorption spectra were taken on a Varian Cary 5E spectrophotometer. Irradiations were performed with a Xe/Hg lamp (450 W) with appropriate band-pass filters. Temperature dependent temperature was performed in a thermally regulated cryostat.

RESULTS AND DISCUSSION

2-Me-4-NO_2 compound

This compound is found in two different forms, according to the preparation method. When the melt is cooled down rapidly, a thermochromic red compound (R) is obtained, whereas for slow cooling rates, a photochromic yellow crystal (Y) is obtained. To the best of our knowledge, only one paper mentions this compound, and reports it a as a thermochrome[18]. The two forms differ from mp values (134.4°C for Y and 132.1°C for R, by DSC) and by the powder X-ray patterns. It is possible to switch from R to Y and vice-versa via the melt, and scratching Y leads irreversibly to R. Besides the characteristic red color, R shows an additional IR band at 1630 cm^{-1} compared to J, and we may conclude that R is at least partially in the "NH" form, whereas J is in "OH" form.

SHG properties and switching

All compounds showed SHG activity as polycristalline powder (Table I). Though the values of SHG are not very high, they are significant enough to confirm the NC structure for the "OH" isomer of 2-Cl, 2-Br and 4-Br[14,19,20]. In fact, the halogen substitution is not expected to yield a very important charge transfer. To understand the properties of 2-Me-4-NO_2 species, which has a significant electron attracting substituent, it is necessary to investigate the cristalline structure.

TABLE I : Powder SHG efficiencies at 1064 nm and 1907 nm fundamental beams (unit : urea reference powder).

	2-Cl	2-Br	4-Br	2-Me-4-NO_2 (Y)	2-Me-4-NO_2 (R)
1064 nm	1.2	1.5	0.7	1.1	0.7
1907 nm	1.2	1.3	2.2	0.2	0.6

SHG intensity change at 1064 nm could be observed for the three halogenated compounds, with a relative variation of SHG around 0.6 for the two bromine compounds (Table II, Figures 2 and 3).

TABLE II : SHG intensity change after UV irradiation. Relative variation of SHG between "high" and "low" states.

	2-Cl	2-Br	4-Br
1064 nm	0.15	0.55	0.64
1907 nm	not observed	not observed	0.10

However, this observed difference might arise at least partially from the re-absorption of the second harmonic beam (532 nm), and not from the difference of β values itself. At 1907 nm (SHG at 954 nm), absorption does not interfere, and switching could be performed for 4-Br (Figure 3). According to theoretical calculations ($\beta = 2.3\times10^{-30}$ esu for the "OH" isomer and 1.3×10^{-30} esu for the "NH" isomer)[16], there should be some significant difference of properties between the two isomers, but the low difference observed might arise from a low conversion ratio.

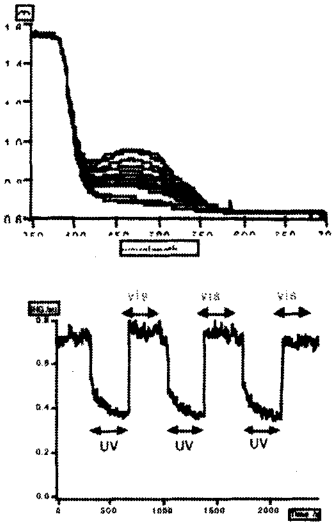

FIGURE 2 : Absorption change during color fading for 2-Br (during 3 h), and SHG change at 1064 nm (UV 355 nm 5 mW, vis 514 nm 19 mW)

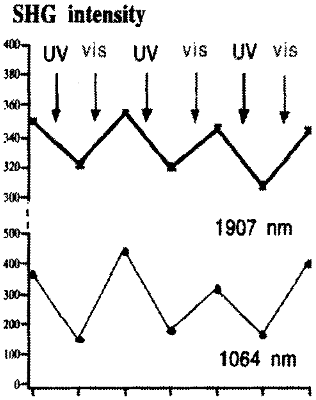

FIGURE 3 : SHG switching of 4-Br at 1064 nm and 1907 nm (UV 365 nm, vis 490 nm) [17]

CONCLUSION

Possibility to photoswitch NLO properties has been demonstrated. This could find some applications in optical switches and in the patterning of alternate structures for quasi phase matching. The advantage of photochromism in crystals is that NC configuration is kept, and that anisotropic effects can be used. However, extended and thorougher investigations are needed : these include theoretical and structural studies, as well as the design of more efficient polarizable molecules.

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References

[1] D.M. Burland, R.D. Miller, C.A. Walsh, *Chem. Rev.* **94,** 31 (1994).

[2] *Nonlinear Optics of Organic Molecules and Polymers,* H.S. Nalwa and S. Miyata Eds., CRC Press, Boca Raton, 1997.

[3] G.R. Meredith, V. Krongauz, D.J. Williams, *Chem. Phys. Lett.* **87,** 289 (1982).

[4] R. Loucif-Saïbi, K. Nakatani, J.A. Delaire, M. Dumont, Z. Sekkat, *Chem. Mater.* **5,** 229 (1993).

[5] J.A. Delaire, Y. Atassi, I. Maltey, K. Nakatani, *Pure Appl. Chem.* **5,** 529 (1996).

[6] S.L. Gilat, S.H. Kawai, J.M. Lehn, *Chem. Eur. J.* **1,** 275 (1995).

[7] S. Houbrechts, K. Clays, A. Persoons, Z. Pikramenou, J.M. Lehn, *Chem. Phys. Lett.* **258,** 485 (1996).

[8] H. Sakaguchi, L.A. Gomez-Jahn, M. Prichard, T.L. Penner, D.G. Whitten, T. Nagamura, *J. Phys. Chem.* **97,** 1474 (1993).

[9] K. Yamada, H. Otsubo, H. Yonemura, S. Yamada, T. Matsuo, *Chem. Lett.,* 451 (1997).

[10] O. Sato, R. Baba, K. Hashimoto, A. Fujishima, *Denki Kagaku* **62,** 530 (1994).

[11] K. Nakatani, Y. Atassi, J.A. Delaire, *Nonlinear Optics* **15,** 351 (1996).

[12] A. Senier, F.G. Shephard, *J. Chem. Soc.* **95,** 1943 (1909).

[13] A. Senier, F.G. Shephard, R. Clarke, *J. Chem. Soc.* **101,** 1952 (1912).

[14] M.D. Cohen, G.M.J. Schmidt, S. Flavian, *J. Chem. Soc.,* 2041 (1964).

[15] E. Hadjoudis, *Photochromism : Molecules and Systems,* H. Dürr and H. Bouas-Laurent Eds., Elsevier Publishers B. V., Amsterdam, 1990.

[16] K. Nakatani, J.A. Delaire, *Chem. Mater.* **9,** 2682 (1997).

[17] M. Carles, D. Eloy, L. Pujol, H. Bodot, *J. Molec. Struct.* **156,** 43 (1987).

[18] P. Gallagher, *Bull. Soc. Chim. Fr.,* 683 (1921).

[19] J. Bregman, L. Leiserowitz, K. Osaki, *J. Chem. Soc.,* 2086 (1964).

[20] S.V. Lindeman, V.E. Shklover, Yu.T. Struchkov, S.G. Kravcheny, V.M. Potapov, *Cryst. Struct. Commun.* **11,** 49 (1982).