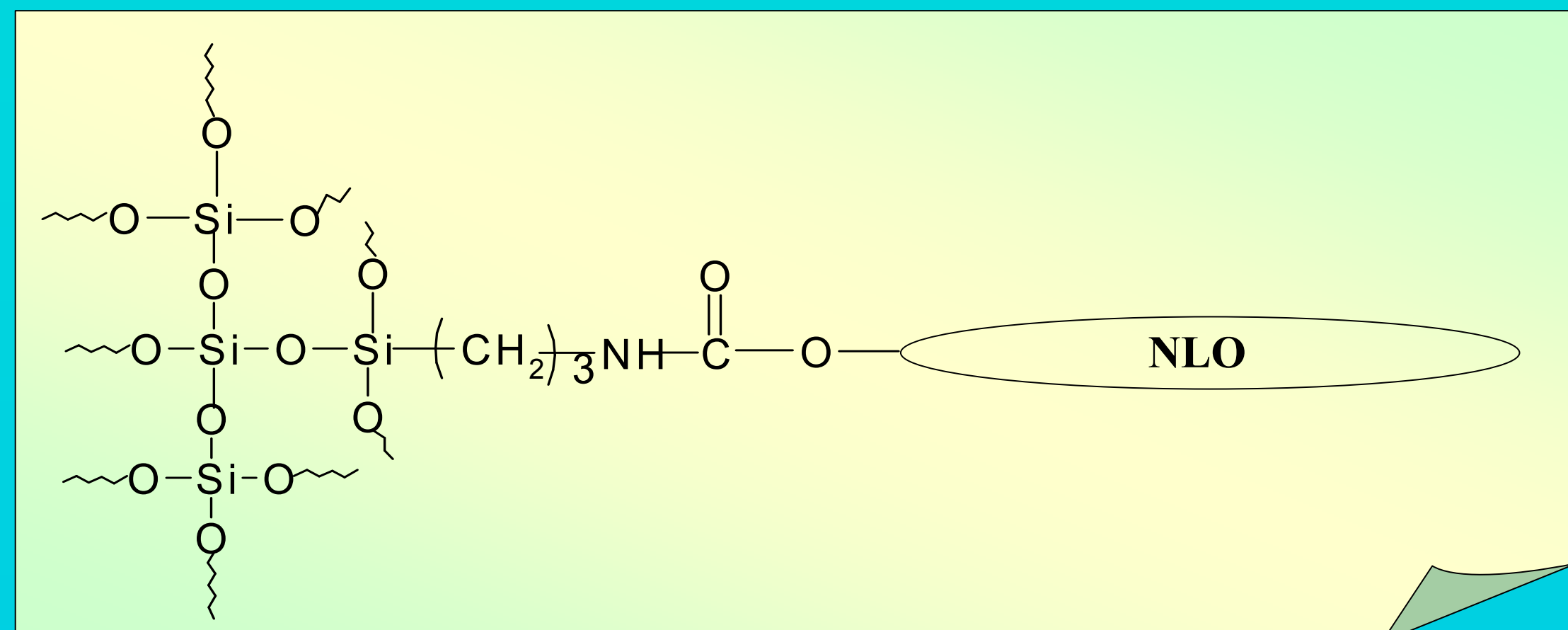


## INTRODUCTION

Photoresponsive materials are unique since the properties of these materials can be manipulated by light. Incorporating photochromic functionalities, such as chromophores, into organic systems lead to photoresponsive materials. Organic molecules can also be embedded in silica network by the sol-gel process for making non linear thin films. In this work we have prepared a new photochromic sol-gel silica hybrid materials in which the optically non linear units ( azo chromophore groups: nitrothiazole and nitrile derivatives, Figure 1.) were covalently linked to the silica matrix. These photochromic materials have potential applications as active materials in information storage devices: optical data storage and holographic applications.



## MATERIAL PROCSSING

The materials were prepared through sol-gel process using functionalized silanes. The chromophores were attached to a sol-gel precursor ICPTEOS (3-(triethoxysilyl)propyl isocyanate) by simple reaction between alcohol and isocyanate. Synthetic approach is simply illustrated in Figure 2.

Sol-gel hybrid materials were obtained by copolycondensation of the second order NLO active triethoxysilane and tetraethoxysilane (TEOS) precursor. The concentration of chromophore group was 10% (mol.). These materials were deposited on glass substrates via spin-coating and casting technique to provide thin transparent films. The thin films were fabricated using the sol after hydrolysis and condensation. The sol was filtered using 0,2 um filter.

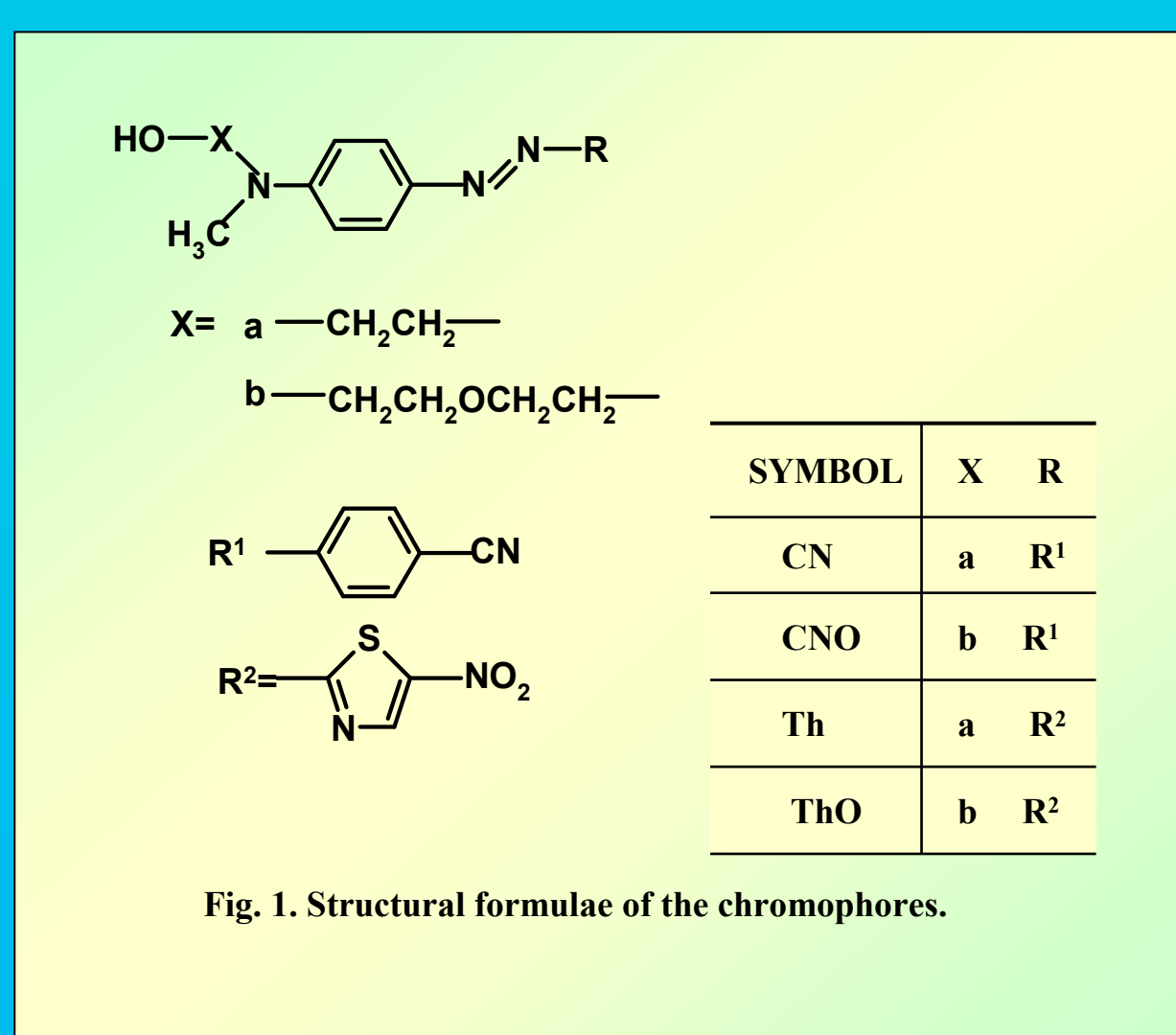


Fig. 1. Structural formulae of the chromophores.

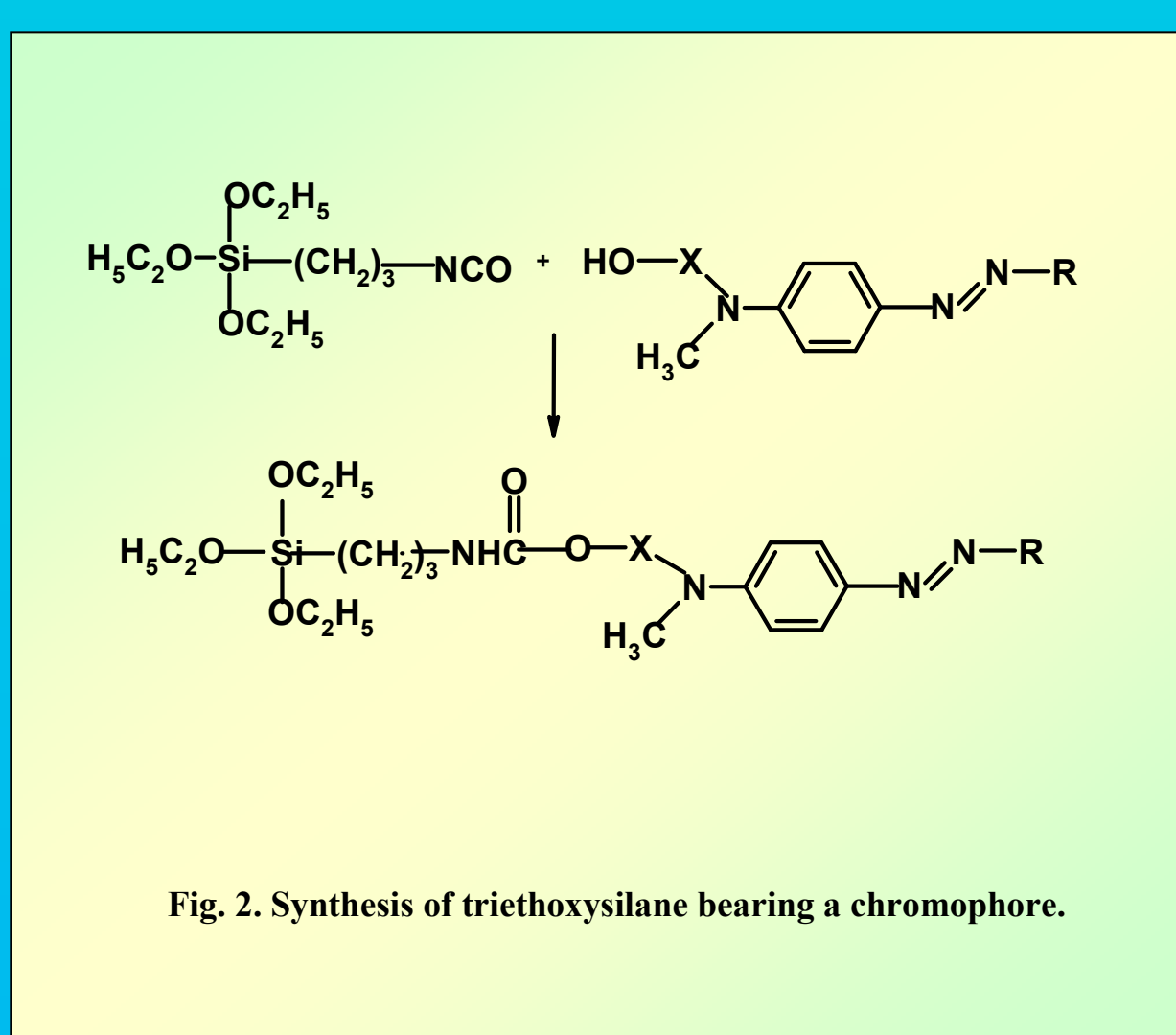


Fig. 2. Synthesis of triethoxysilane bearing a chromophore.

## UV-VIS ABSORPTION SPECTROSCOPY

*Trans-cis* photoisomerization was observed under the exposure of light with UV-VIS absorption spectroscopy. Investigated materials showed a strong absorption band in the visible region with maximum at ca. 450 nm for nitrile derivatives and 570 nm for nitrothiazole derivatives. On illumination with light chromophore groups underwent reversible *trans-cis* isomerization, which was manifested by a drop in the absorbance of the maximum absorption peak (Figure 3.). The rate of *cis-trans* thermal back reaction was relatively fast for sol-gel hybrid materials containing nitrothiazole derivatives as a chromophore. This indicates that the chromophore fragment have enough free space in the cross-networked gel structure to change configuration upon illumination and thermal relaxation. This photoinduced transformation results in changes of physicochemical properties, such as dipole moment, polarizability and refractive index.

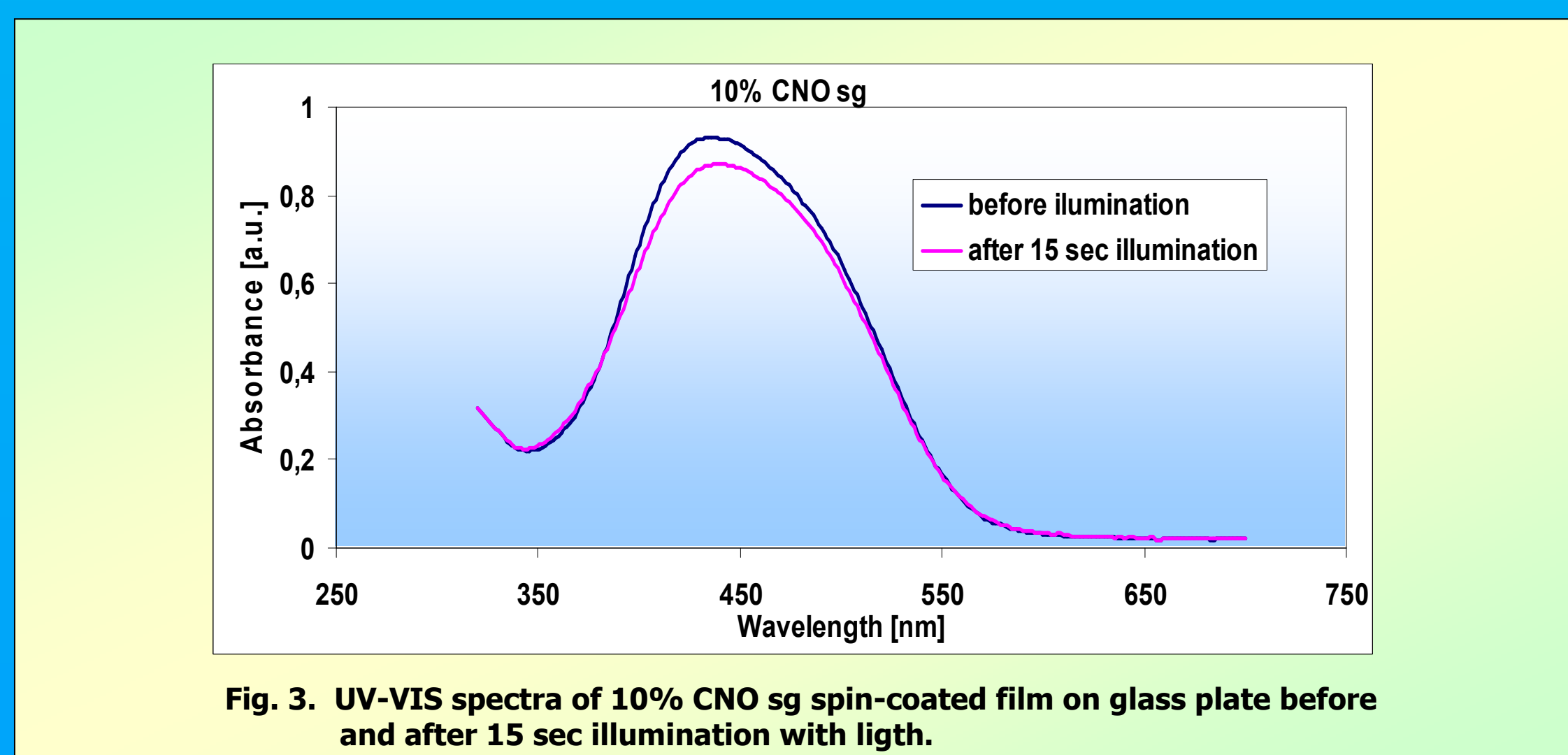


Fig. 3. UV-VIS spectra of 10% CNO sg spin-coated film on glass plate before and after 15 sec illumination with light.

## ELIPSOMETRIC MEASUREMENTS

The changes of refractive index of the materials were carried out by ellipsometry technique. Results of measurements showed the ability of the investigated materials to reversible changes of refractive index in repeated illumination cycles with unpolarized white light. As a results of measurements the ellipsometric parameters  $\Delta$  and  $\Psi$  before and after illumination were obtained. From this parameters the film thickness and complex refractive index:  $n = n_r + ik$  ( $n_r$  –real part,  $k$ –imaginary part) were calculated. The change of real part of refractive index caused by illumination was in the range of 0,003-0,007 ( Table 1.) and the typical average of film thickness was ca. 0,2  $\mu$ m. The network of the materials showed enough free space to reversible *trans-cis-trans* isomerization of the chromophore groups.

TABLE 1. Changes of real part of the refractive index of spin – coated films after 1 min. irradiation with white light.

material	$\Delta n$
CN sg	0,0029
CNO sg	0,0071
Th sg	0,0023

## CONCLUSIONS

- A series of new photochromic materials were synthesized by sol-gel technique. The materials showed ability to formation of diffraction grating.
- Chromophore groups had enough free space in the material network to undergo *trans-cis* isomerization upon illumination and thermal relaxation.
- In investigated systems, the spacer length between the dye and matrix backbone could optimize the rate of photochromic reactions.
- All results indicate that investigated photochromic hybrid siloxane materials posses attractive properties for such photonic applications as optical switches and holographic storage media.

## QUANTUM CHEMICAL CALCULATION

The aim of calculation was to:

- propose the suitable chromophore as promising NLO units;
  - determine differences between *trans* and *cis* form and relationship between structure and photochromic properties of selected chromophores.
- The first step was an optimisation of the geometrical structures of the isolated molecules of the chromophores with GAUSSIAN 98 program using *ab initio* calculations RHF ( restricted Hartree-Fock) with a split-valence 3-21G basis set. Next, the optimised geometry was used to calculate dipole moment ( $\mu$ ), polarizability ( $\alpha$ ) and first hyperpolarizability ( $\beta$ ), for both *trans* and *cis* form of the chromophores and potential energy difference ( $\Delta E$ ) between them. Quantum chemical methods showed significant differences in dipole moments, polarizability and first hyperpolarizability between both isomers ( Table 2.). The differences in dipole moment, polarizability and first hyperpolarizability depend on the length of spacer joining nitrogen atom with siloxane functional group. In both of the homologous series of the chromophores difference between dipole moments, polarizability and first hyperpolarizability of *cis* and *trans* isomers increased with increasing length of spacer.

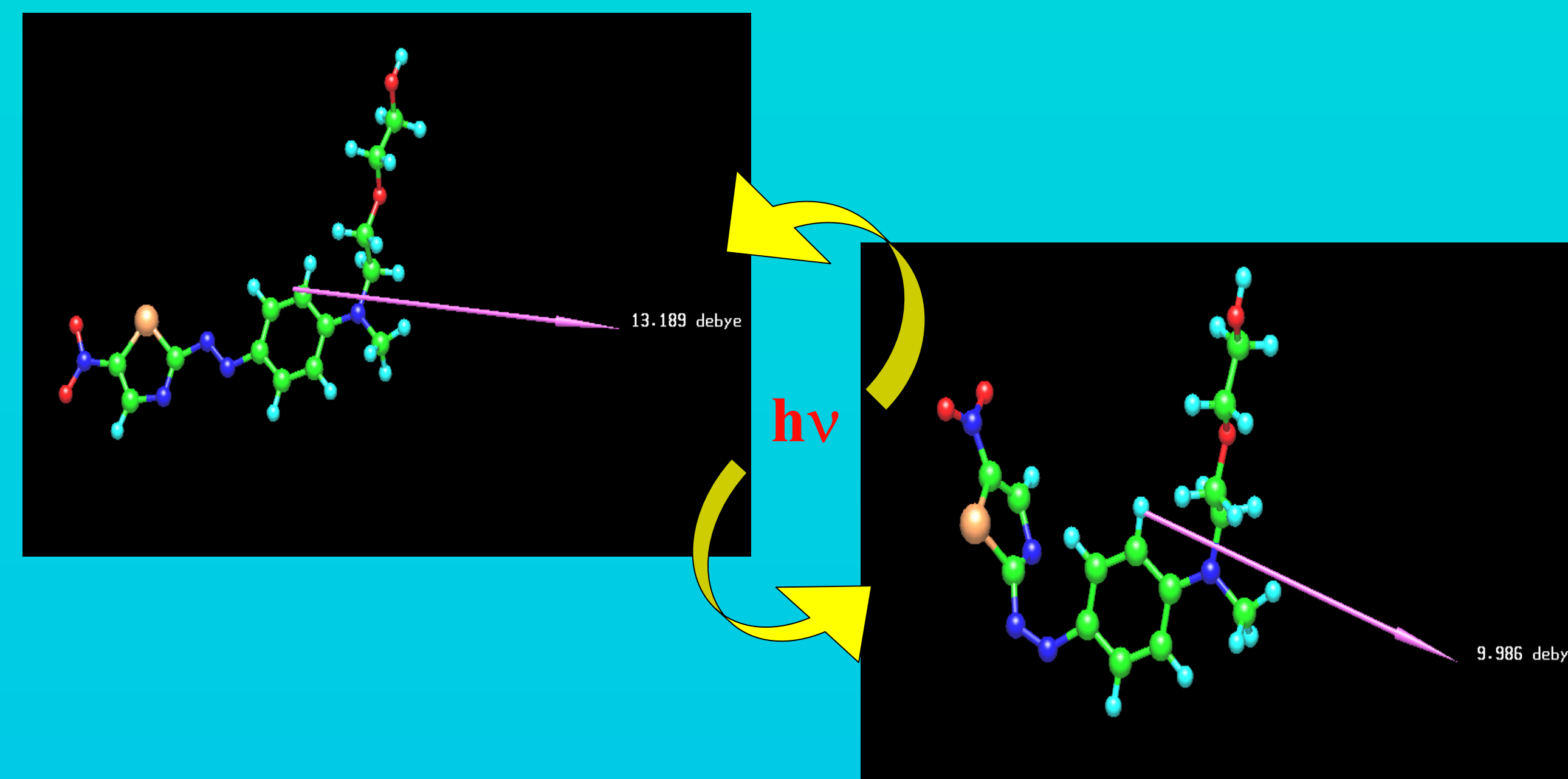


TABLE 2. Dipole moments, polarizability, first hyperpolarizability and potential energy difference of *trans* and *cis* structures as calculated by GAUSSIAN .\*

Compound	$\mu/10^{-30}$ (C m)		$\alpha/10^{-24}$ (cm <sup>3</sup> )		$\beta^0/10^{-30}$ (esu)		$\Delta E$ (kJ/mol)
	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>	
CN	22,37	28,67	26,56	29,95	15,45	41,13	83,23
CNO	23,72	31,49	29,95	33,50	14,78	41,28	84,54
Th	24,52	42,16	26,48	30,77	28,22	78,14	57,63
ThO	29,94	36,69	30,24	34,19	28,95	79,96	74,09

\* Quantum chemical calculations were carried out at Wrocław Supercomputer Centre using GAUSSIAN 98 program.

## TWO BEAM COUPLING

Formation of diffraction grating was achieved by a Two Beam Coupling (TBC) technique. Crossed 532 nm p-polarized laser beams, each of 10 mW power, were coupled on the sample, to write diffraction grating. On switching the laser beams on, symmetrical diffraction spots appeared. The diffraction efficiency for first order diffraction was ca. 6,25% and the value of refractive index modulation was 0,005. Figure 5. shows dynamics of growing and decay of the diffraction signal. The growing period of the signal is relatively short. The time needed to reach maximum intensity of diffraction signal was only 5-10 seconds. This means that this process in our material is faster as compared with that of polymeric methacrylate film [3].

The geometry used in our experiment ( Figure 4.) determines the grating period of  $\Lambda = 1,65 \mu$ m.

$$\eta = \frac{I_d}{I_d + I_t} = \sin^2 \left( \frac{\pi d \Delta n}{\lambda \cos \theta} \right) \quad \Lambda = \frac{\lambda}{2n \sin \left( \frac{\theta}{2} \right)}$$

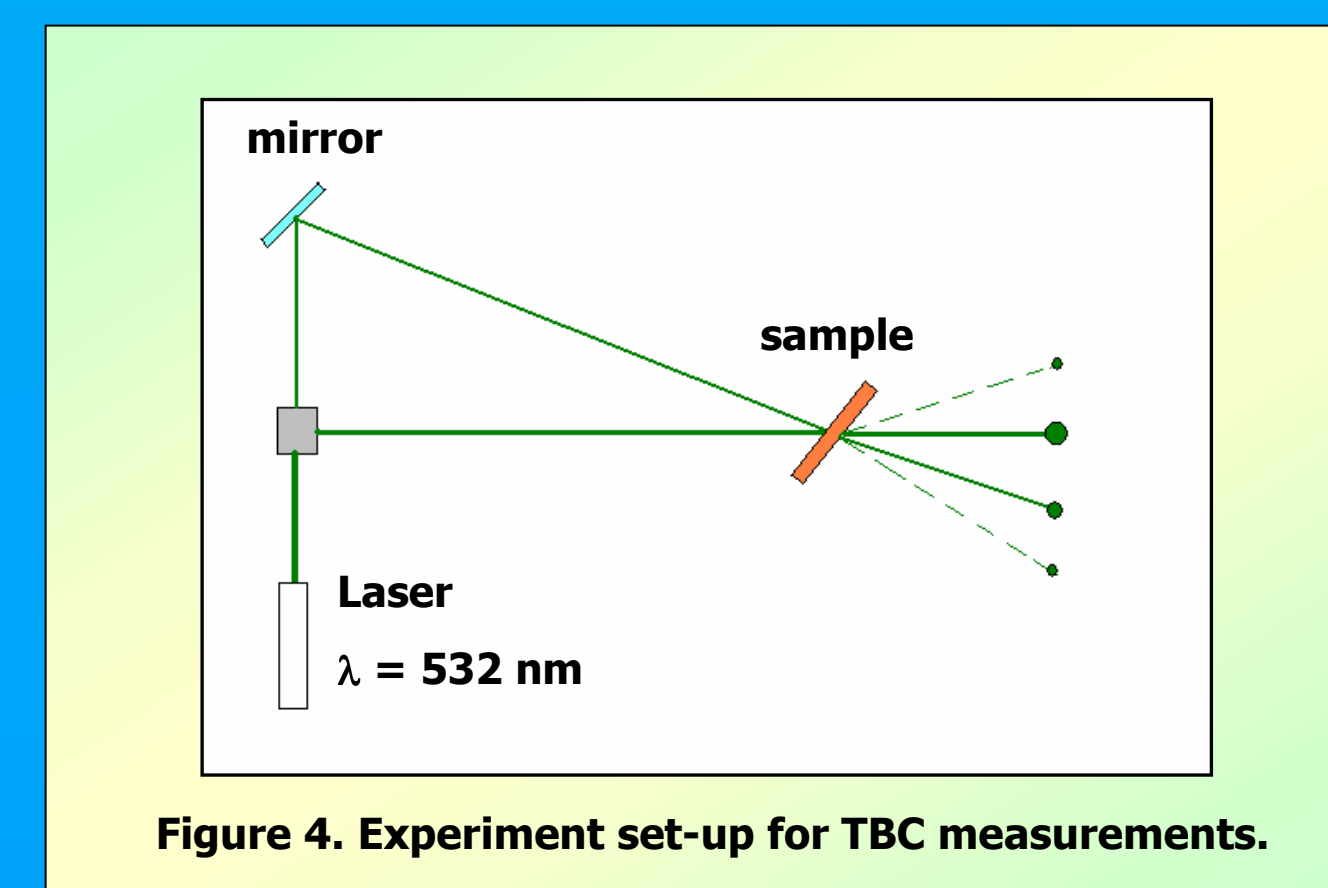


Figure 4. Experiment set-up for TBC measurements.

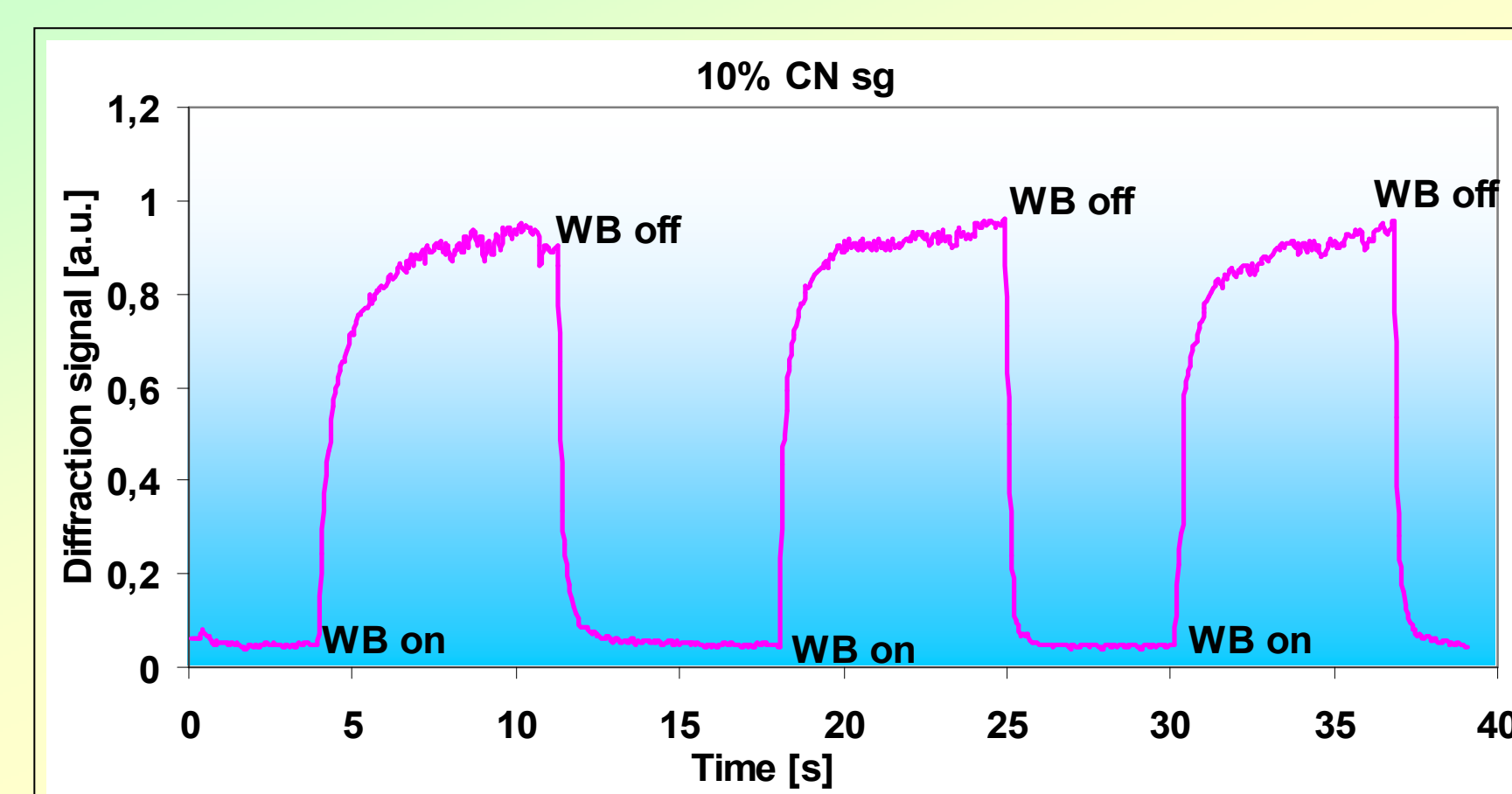


Fig. 5. Diffraction signal vs. time in TBC. WB on – writing beams on, WB off – writing beams off

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