Determination of third-order nonlinear optical properties of ABI derivatives

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Abstract: In this paper we studied linear and nonlinear optical properties of novel organic materials MeSBI and MeOBI in form of solution with chloroform as solvent. For experimental measurements we implemented Z-scan method as it is one of the most widely used methods for nonlinear optical studies and can simultaneously measure two-photon absorption and Kerr effects. 1064 nm Nd:YAG laser with 30 ps pulse duration and 10 Hz repetition rate was used to avoid any thermal contribution to changes of optical properties and correctly evaluate magnitude of third-order nonlinear optical effects. Using acquired values we also calculated third-order susceptibility and second-order hyperpolarizability, as these coefficients are more appropriate for properties comparison on molecular level. Both materials possess insignificant absorption over 500 nm which makes them applicable for all-optical devices in infra-red spectrum. Acquired data for MeSBI and MeOBI were compared with data for previously studied ABI derivative DMABI to better understand how different structural configuration influence third-order nonlinear optical properties.

Keywords: Nonlinear optics, Kerr effect, Two-photon absorption, Organic materials, All-optical switching

1. Introduction

In last decade the demand for bandwidth increase in telecommunication sector has grown significantly. This has turned scientific group interest towards new technologies for telecommunication systems that could resolve this problem. One solution would be moving towards an all-optical communication system, but to do this it is necessary to first design devices for optical information transfer, processing and storage. While former of these devices has already been implemented for practical applications in form of optical fibers and waveguides, the later ones are still in development phase and at this stage has only been demonstrated in scientific papers[1], [2]. The key elements for optical data storage and processing are third-order nonlinear optical (NLO) materials that can work as media for light interaction. Mainly these can be done through two-photon absorption (TPA) and Kerr effect[3]. Both effects characterize optical property dependence on optical intensity, where TPA effect characterizes absorption changes and Kerr effect – refractive index changes. While these effects have been widely studied, appropriate materials with strong NLO properties are yet to be presented. Material selection process for these applications is based on various aspects[4]: i) molecular third-order NLO efficiency, ii) ultrafast NLO response time for higher bandwidth all-optical signal processing, iii) low optical losses due to unwanted absorption or scattering, iv) the possibility to retain microscopic NLO properties in macroscopic material forms v) Ability to process material in macroscopic form for device manufacturing. Both organic and inorganic materials have been studied for NLO applications and both classes possess their own advantages and disadvantages. Main reasons why to choose organic materials for NLO applications are the possibility to tune the material properties by varying the molecular structure and cheap device manufacturing. Although tunability is a significant advantage and has already been widely studied in form of structure-property relations of NLO properties[5]–[7], there is still not enough understanding for theoretical designing of efficient NLO materials without experimental verification.

For NLO properties studies we used Z-scan method[8]. Compared to other NLO methods (Mach-Zehnder interferometer[9], degenerate four wave mixing[10] and others), Z-scan has a very simple experimental setup and allows to simultaneously measure TPA and Kerr effect. It is also important to emphasize that with Z-scan method it is possible to determine the sign of Kerr effect. To correctly evaluate Kerr effect contribution to nonlinear refractive index changes, it is important to separate it from thermal[11], free carrier[12] and other effects contribution. Each effect is characterized by specific time constant and can be separated by using different pulse lasers. In literature it has been demonstrated that ps range lasers are appropriate for Kerr effect studies[11].

In this work we studied linear and non-linear optical properties of two different aminobenzylidene-1,3-indandiones (ABI) derivatives *2*-(4-methylsulfanylbenzylidene)-1*H*-indene-1,3-dione MeSBI and *2*-(4-methoxybenzylidene)-1*H*-indene-1,3-dione MeOBI. Materials were studied in form of solutions, where organic compounds were dissolved in chloroform. Acquired results were compared to reference material *2*-[4-(*N*,N-dimethylamino)-benzylidene]-1*H*-indene-1,3-dione (DMABI)[11]. Materials were studied using 1064 nm Nd:YAG laser with 30 ps pulses at 10 Hz repetition rate (EKSPLA PL2140 Nd:YAG laser).

2. Experimental part

Names and structural formulas of studied materials are shown in Fig. 1. Samples were prepared in form of solutions where organic compounds were dissolved in chloroform and contained in 2 mm thick optical quartz cells. Sample with concentration from 0.1 to 1 wt% of selected compounds mass in solution were studied. Organic compounds concentration was kept low to avoid any aggregation or crystallization effects. Selected materials possess the same acceptor group (indane-1;3-dione) but have different donor groups.

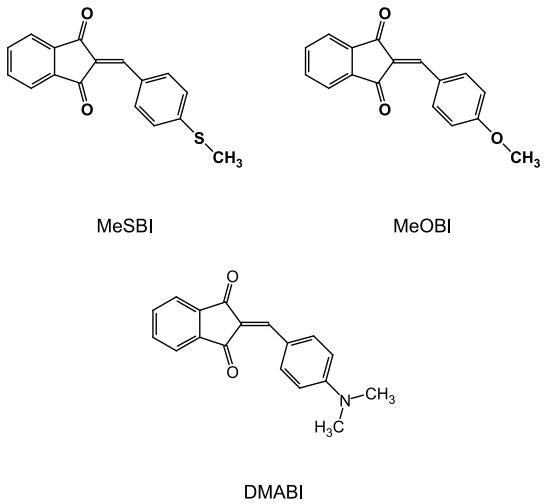

Fig. 1. Names and structural formulas of studied materials.

Absorption spectrum for both compounds and reference material in chloroform can be seen in Fig. 2, with absorption peaks at 390 nm for MeOBI, 420 nm for MeSBI and 483 nm for DMABI. Dashed line indicates absorption at 532 nm. As experimental measurements are carried out using a 1064 nm laser, materials should possess significant absorption at half-wavelength (532 nm) for this wavelength to induce TPA effect. From absorption spectrum we can see that none of the materials shows considerable absorption at 532 nm. Also, MeSBI and MeOBI absorption spectrums starts under 500 nm, which indicates that these materials should not possess any significant TPA in infra-red spectrum.

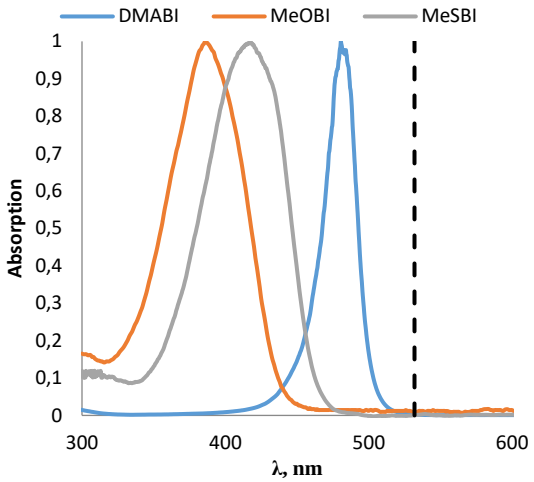

Fig. 2. Absorption spectrum of studied materials.

To determine refractive index of selected materials we used attenuated total reflection measured with metricon (Metricon 2010 Prism coupler). First, guest-host thin films with studied compounds as guest materials and polystyrene as hoast materials were prepared using spin coatting method. Polystyrene was chossen as it has relatively small refractive index value at 1064 nm. Both materials were dissolved in chlorform and then spin coatted (Laurell-650 spin coatter) onto 1-inch square glass slide. Samples with different guest material wt% from 2 to 25 were prepared. Higher concnetrations was not used to avoid crystalization of organic compounds. Sample thicknes was mesured to be around 2 μm. Experimental resaults for refractive index of thin films with different concentrations are shown in Fig 3. Acquiered data was extropolated with linear fit to calculate refractive indexes for pure material. From experimental measurments we calculated refractive index for pure MeOBI to be n=1.7105 and for MeSBI – n=1.7687.

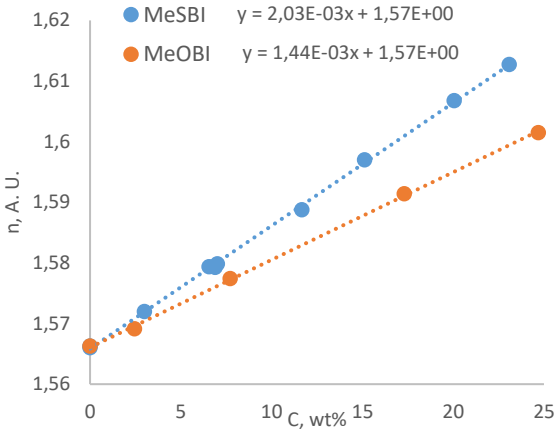

Fig. 3. Refractive index measurments for MeSBI and MeOBI.

For our experimental Z-scan setup 1064 nm laser beam was focused using an 11 cm focusing lens. Waist radius at focus was calculated to be w_0=26 μm. As for this setup Rayleigh length is comparable to sample thickness we can implement thin sample approximation for data processing[8]. Precise description of Z-scan experimental setup can be found in our previous paper[11].

For description of Kerr we used the following formalism. Refractive index *n* changes due to Kerr effect can be expressed in the following way:

$$n=n_0+n_2 \cdot I, \quad (1)$$

where n_0 is linear refractive index of the material, n_2 is nonlinear refractive index and I is incident light intensity. In case of TPA we study how materials absorption α changes due to incident light intensity:

$$\alpha=\alpha_0+\alpha_2\cdot I, \tag{2}$$

where α_0 is linear absorption coefficient and α_2 is nonlinear absorption coefficients.

One of the most essential aspects of Z-scan method is that one can study Kerr and TPA effects at the same time. This is done by measuring sample transmittance as function from sample position using two detectors – open aperture and closed aperture detectors. Open aperture measurement detects only TPA effect influence, while closed aperture detector measures both Kerr and TPA effects. If both of these effects are present in media, Kerr effect can be separated by dividing closed aperture data with open aperture data. If Kerr effect is present in NLO media, then sample transmittance can be expressed as follows:

$$T(z)=1+\frac{4\cdot\Delta\Phi\cdot\frac{z}{z_0}}{\left(\frac{z^2}{{z_0}^2}+9\right)\left(\frac{z^2}{{z_0}^2}+1\right)}, \tag{3}$$

where z is sample position relative to focal point and phase change $\Delta\Phi$, and z_0 is parameters defined by following relations:

$$\begin{cases}\Delta\Phi=k\cdot n_2\cdot I\cdot L_{eff}\\ L_{eff}=\frac{1-e^{-\alpha L}}{\alpha}\\ z_0=\frac{k\cdot {w_0}^2}{2}\end{cases}, \tag{4}$$

where w_0 is beam waist radius at focal point, L is sample thickness and k is the wave number. This theoretical model can be applied for case of weak nonlinear media, for which $|\Delta\Phi|<\pi$. In experimental setup we used 1 mm aperture that transmitted roughly 1 % of incident light. If TPA is present in NLO media, then sample transmittance can be expressed as follows:

$$T(z)=\sum_{i=0}^{\infty}\frac{\left[\frac{\alpha_2\cdot L_{eff}\cdot I}{\left(1+\frac{z^2}{{z_0}^2}\right)}\right]^m}{(m+1)^{\frac{3}{2}}}, \tag{5}$$

Similar to Kerr effect this theoretical model can be used when weak nonlinear media criteria are meet - $|\alpha_2 L_{eff} I|<1$. This is essential for correct evaluation of NLO coefficients[13]. For casses where media does not exhibit any TPA effect, open aperture measurment can be used as reference measurment to separate any power fluctotions or other effects not connected with Kerr effect that influences transmiteed intensity from closed aperture measurment. Laser intensity at focal point was varied in range from 10 to 100 GW/cm^2. Usage of higher laser intensities was limited by conditions for weak nonlinear media as well as to avoid sample degradation.

3. Results and Discussion

Experimental Z-scan setup was calibrated using pure chloroform and CS_2 solutions. Both solutions have been widely used as reference solutions for calibration of NLO experiments. Acquired values of Kerr coefficient was $n_2=3.10\pm0.25\cdot10^{-14}$ cm^2/W for CS_2 and $n_2=1.88\pm0.12\cdot10^{-15}$ cm^2/W for chloroform. Both values fit the ones given in literature[8], [14]. Example of experimental measurement (closed-aperture measurement) for MeSBI dissolved in chloroform can be seen in Fig. 4. For both compounds no significant changes in absorption (open aperture measurement) were detected. This confirms previously stated fact about TPA correlation with absorption at half-wavelength. As solutions and solutes contribution to NLO properties of sample depends on their weight fraction, Kerr coefficient of organic compounds can be calculated by expression[15]:

$$n_{2;solute} = \frac{n_{2;Sample} - (1-\rho) n_{2;CHCl_3}}{\rho}, \quad (6)$$

where ρ is weight fraction of organic compound in sample, $n_{2;Sample}$ is sample Kerr coefficient and $n_{2;CHCl3}$ is Kerr coefficient of chloroform.

Experimentaly measured phase changes as function from organic compound concentration is shown in Fig. 5. As concentration is increased, phase change increases. This means, that organic compounds have the same sign for Kerr coeficient as chloroform – positive. Experimental data fits linear aproximation very well, that allows us to use equation 6 to calculate Kerr coefficient.

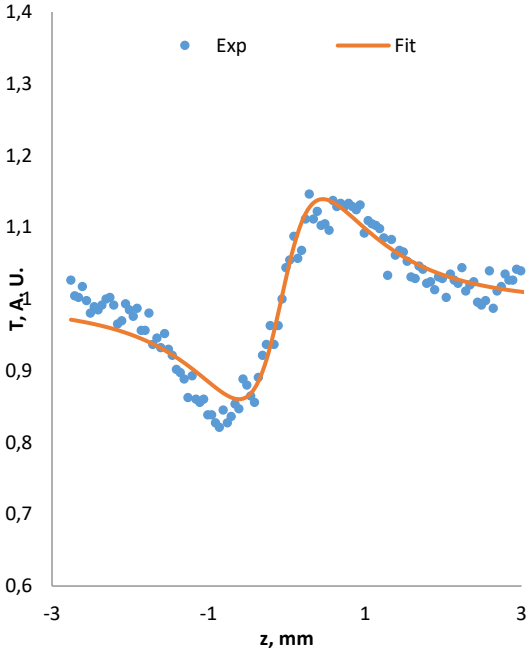

Fig. 4. Closed-aperture measurement for MeSBI dissolved in chloroform.

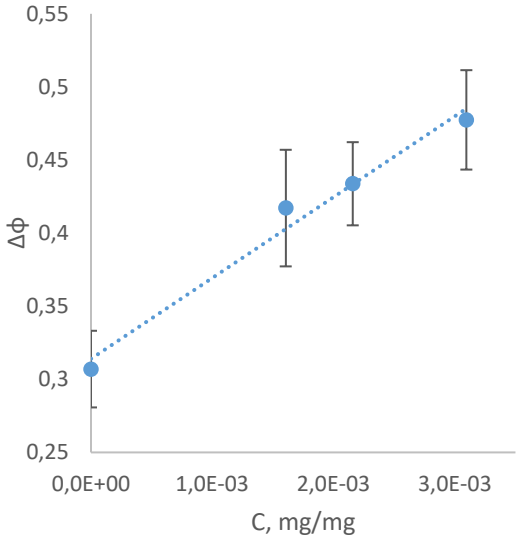

Fig. 5. Phase change as function of organic compounds concentration.

Using experimentally acquired values for Kerr coefficient, we calculated the real part of third-order susceptibility using equation[16]:

$$\chi_{Re}^{(3)} = \left(4 \cdot \frac{\varepsilon_0 \cdot c \cdot {n_0}^2}{3}\right) \cdot n_2 \left(\frac{m^2}{W}\right), \quad (7)$$

where ε_0 is vacuum dielectric constant, c is speed of light in vacuum and λ is laser wavelength. Third-order susceptibility characterizes materials NLO properties on macroscopic scale. To study and compare NLO properties on molecular scale, we need to compare values of second-order hyperpolarizability. In case of solutions where we can assume that we have an isotropic media, second-order hyperpolarizability can be calculated as[17]:

$$\gamma = \frac{\chi^{(3)}}{\left[\frac{1}{3}({n_0}^2+2)\right]^4 N}, \quad (8)$$

where N is molecule concentration per cm^3. Values of all calculated coefficients are shown in table 1.

Table 1. Nonlinear optical coefficients

Compound	$n_{2;Kerr}$ ($cm^2/W \cdot 10^{-12}$)	χ_{Re} ($m^2/V^2 \cdot 10^{-19}$)	γ ($esu \cdot 10^{-34}$)
MeSBI	0.252±0.062	2.79±0.69	8.1±2.0
MeOBI	0.220±0.054	2.28±0.56	7.4±1.8
DMABI[6]	0.249±0.022	2.59±0.23	7.83±0.69

From acquired values we can conclude that selected materials have similar values of third-order nonlinear susceptibility. While this conclusion does not make specific materials more efficient than parent compound DMABI, considering that absorption spectrum of MeSBI and MeOBI is more blue-shifted compared to DMABI, makes them more applicable for infra-red all-optical applications. Also compared to DMABI, it was possible to fabricate higher concentration homogeneous guest-host thin films which is essential for fabricating devices with high NLO efficiency.

4. Conclusions

In this work we studied linear and nonlinear optical properties of two novel organic compounds (MeSBI and MeOBI) in form of solutions, dissolved in chloroform and compared them to previously studied reference material (DMABI). Absorption spectrum of both materials was measured with corresponding peaks at 390 and 420 nm for MeOBI and MeSBI. Refractive indexes for materials was measured to be n=1.7105 and n=1.7687 for MeOBI and MeSBI, respectively. From experimental data it is evident that both materials have NLO properties of similar order as reference material. At the same time, both materials exhibit no significant absorption over 500 nm which is essential for infra-red optical devices, to avoid any unwanted TPA effects.

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