Toward device applicable second order NLO polymer materials: definition of the chromophore figure of merit.

M Rutkis1, A Jurgis2, V Kampars3, A Vembris4, A Tokmakovs1 and V Kokars3

1 Institute of Solid State Physics, University of Latvia, Riga, Latvia
2 Institute of Physical Energetic, LV 1006, Riga, Latvia
3 Riga Technical University, Riga, Latvia

Abstract. Maximal achieved second order non linear optical (NLO) efficiency of the PMMA based host – guest systems containing eight dimethylaminobenzylidene -1, 3 - indandione (DMABI) related chromophores have been analysed. Two contradicting sets of NLO chromophore figure of merit (FOM) equations were tested. One of them predicts that NLO efficiency of the poled polymer host - guest film is proportional to ground state dipole $d_{33} \sim \mu_g$, another to $d_{33} \sim 1/\mu_g$. The best correlations for the maximal achieved nonlinearity were obtained with second set of FOM, especially if high ground state dipole ($\mu_g>7D$) chromofores are included in analysis.

1. Introduction

Over last two decades there is an enduring interest to make use of organic molecular systems in the (NLO) devices [1]. The advancement in this field, are very much dependent on the development and characterization of new functional materials exhibiting high NLO efficiency and good long term stability. One of the possibilities to create such a material is poled polymer host – guest systems, where NLO active chromophore is dispersed in polymer matrix. Deliberate modification of the chromophore properties are one of the keystones for the design of highly effective and stable NLO material. There are several molecular properties of the chromophore, what have a high impact on NLO efficiency and stability of the host – guest system. Along with the first molecular hyperpolarizability ($\beta_0$) they are: ground state dipole moment ($\mu_g$), CT band wavelength, alignment of $\beta_0$ and $\mu_g$, aggregation in matrix etc. Tailoring of the structure to achieve best value of the particular molecular property usually results in some kind of trade-off in other properties. To compare chromophores and evaluate their perspectives it is very useful to have some kind of the figure of merit (FOM) for NLO chromophore. Since 90’s, when the active search for best chromophore begun, the product of the ground state dipole moment ($\mu_g$) and first molecular hyperpolarizability ($\beta_0$) is widely used as $FOM = \mu_g\beta_0$ (for example see [2,3]). That approach comes from the text book type expressions for macroscopic second harmonic coefficients $d_{33}(\sim \chi^{(2)}/2)$:

$$d_{33} = \frac{1}{2} \left( N \beta_0 F \langle \cos^3 \theta \rangle \right) = \frac{1}{2} \left( N \beta_0 F \frac{\mu_g E}{5kT} \right) = \frac{1}{2} \left( \mu_g \beta_0 N \frac{FE}{5kT} \right)$$

(1)
where $N$ is the number density of the chromophore, $F$ is the product of all local field factors, $<\cos^3 \theta>$ is electric field induced acentric order parameter, $E$ poling electrical field and $T$ poling temperature. As one can notice from expression (1) number density has a very high impact on NLO efficiency, so chromophores should be small to achieve high values of $N$. The expression (1) can be rewritten in form:

$$d_{33} = \frac{1}{2} \left( \mu_g \beta_0 \frac{w \rho N_A FE}{M_w} \right) = \frac{1}{2} \left( \mu_g \beta_0 \frac{w \rho N_A FE}{5kT} \right)$$  (2)

where $w$ is the weight fraction of the chromophore, $\rho$ density, $N_A$ Avogadro’s number and $M_w$ is chromophore molecular weight. Based on equation (2), it is obvious to define second order NLO chromophore $FOM = (\mu_g \times \beta_0)/M_w$ [4], that takes it to account size of molecule. Some times this $FOM$ is called “molecular nonlinearity” [5]. During the last decade of previous century best chromophore search paradigm was based on this expression. Chemists all over the world are searching for small highly polar molecules with high $\beta_0$ value, or so called “high $\mu\beta$” chromophores. Typical values of ground state dipole of such chromophores usually were over 10 D. In our attempts to search for new highly NLO active molecules within the class of indandion derivatives, we were in same race to create such “high $\mu\beta$” chromophores too. The potential of indandione derivatives, success in the synthetic strategy, results of quantum chemical calculations and experimental investigations has been described in several articles [6-12].

At the end of century this high $\mu\beta$ paradigm was revised by L. Dalton and co-workers [4], who droved attention to fact that macroscopic nonlinearity ($d_{33}$) – chromophore load ($w$) relation usually is not linear, as predicted by equation (2). It is worth to be mentioned, this equation is based on so called “free gas model” with an assumption of non-interacting chromophore molecules. This model looks like far-off reality, especially in cases of highly polar chromophore at high load. L. Dalton and co-workers have developed model, where electrostatic interactions of chromophores were taken into account [4]. According to this model electric field induced acentric order parameter is:

$$\langle \cos^3 \theta \rangle = \frac{\mu_g E}{5kT} \left[ 1 - L^2 \left( \frac{W}{kT} \right) \right]$$  (3)

were $L$ is the Langevin function and $W$ is chromophore - chromophore electrostatic interaction energy. As one could notice order parameter, and therefore nonlinearity is attenuated. Afterwards they developed model [1] and came up with equation for optimal (maximal nonlinearity) chromophore load:

$$N_{\text{max}} = 1.38 \frac{kT}{\mu_g}$$  (4)

Combining equations (1) and (4) we could came to equation for maximal achievable nonlinearity for particular chromophore:

$$d_{33}^{\text{max}} = \frac{1}{2} \left( N_{\text{max}} \beta_0 F \mu_g E \right) = \frac{1}{2} \left( 1.38 \mu_g \beta_0 \frac{kT FE}{5kT} \right) = 0.138 \frac{\beta_0 F E}{\mu_g}$$  (5)

This equation give us surprising result: maximal possible value of $d_{33}$ is proportional to $\beta_0/\mu_g$ instead of the proportionality to $\beta_0 \times \mu_g$ predicted by equation (2). As a result this best chromophore search paradigm must be revised - low $\mu_g$ and high $\beta_0$ molecule must be our search target. To be honest in early 90’s extreme case of this low $\mu_g$ approach was developed by J.Zyss - zero $\mu_g$ or so called “octupole” chromophore paradigm. Of course, for successful poling by electrical field chromophore must have nonzero $\mu_g$. This problem for “octupole” ($\mu_g = 0$) occasion was successfully solved by Fiorini et al. [13] by applying all optical poling procedure. In the case of electrical field poled polymer systems ($\mu_g \neq 0$) lower $\mu_g$ results in smaller orientation energy $\mu_g E$, that could be compensated by higher electrical field intensity. Coming back to L. Dalton and co-workers, it is worth to mentioned
that they have drawn also some conclusions about a shape [1] of chromophore – as close as possible to sphere is a best. To summarize, new century came with new best chromophore paradigm: small spherical molecule with low $\mu_g$ and high $\beta_0$.

Based of that approach we have targeted our attention to low $\mu_g$ indandione derivatives and in some of our host – guest films we have reached significant nonlinearities [14]. In this contribution we would like to analyse these results according to above mentioned new best chromophore paradigm.

Our search for the best NLO chromophore is based on workflow presented in Scheme 1.

Scheme 1. Workflow of best chromophore search

Involving ab initio calculations allows us to do initial screening of molecular structures and skip work consuming steps 3 & 4 for cases of inadequate ideas. For numerical evaluation, based on QC calculations there is high demand of a new FOM, what represents a new paradigm of the best NLO chromophore. We would like come forward with some equations for FOM and test them on our chromophore host – guest film data.

2. Results and Discussion

Structures of the eight indandione derivatives, which we have included in our analysis, are presented in scheme 2. Experimental conditions and more detailed results were published elsewhere [14].

Scheme 2. Molecular structures of investigated NLO chromophores

In the table 1 we have presented results of our [14] HF ab initio (6-31G) calculated molecular characteristics used for proposed FOM calculations, as well as our target parameter - maximal observed $d_{33}(0)$ value for chromophore / PMMA host – guest films. According to two level model
[15] frequency corrected values are used in correlation analysis, which allows us to exclude resonant effects on nonlinear efficiency. For some of the molecular parameters it will be useful to give an explanation and calculation methods. The hyperpolarizability \( \beta \) is calculated by applying so called finite field (FF) method [16]. The parameter \( C = \cos \mu^\beta \) characterize alignment of molecular hyperpolarizability with dipole moment. In electric field poled polymer films projection of \( \beta \) over \( \mu \) is a source of nonlinearity.

Table 1. Calculated molecular parameters of investigated chromophores and maximal obtained NLO efficiency in PMMA host – guest films.

| Compound   | \( M_w \) | \( \mu_g \) | \( \beta_{ff} \) | \( \cos \Psi \) | \( \Psi \) | \( SP \) | \( w \) | \( d_{13}^0 \) |
|------------|-----------|------------|----------------|--------------|---------|------|------|-------------|
| DD-DMABI   | 373.4     | 7.71       | 21.8           | 0.64         | 0.836   | 0.297| 25.0| 3.14        |
| D-DMABI    | 325.4     | 7.83       | 32.9           | 0.85         | 0.839   | 0.090| 9.0 | 0.46        |
| DMABI-Ju   | 329.4     | 3.70       | 22.5           | 0.98         | 0.849   | 0.168| 9.0 | 2.68        |
| DMABI-dPh  | 401.5     | 1.86       | 24.2           | 0.73         | 0.802   | 0.100| 9.0 | 6.28        |
| DMABI      | 277.3     | 3.74       | 19.1           | 0.99         | 0.856   | 0.117| 15.0| 5.20        |
| tB-DMABI   | 333.4     | 3.00       | 19.3           | 0.98         | 0.825   | 0.285| 15.0| 12.10       |
| DMABI-OH   | 250.2     | 2.16       | 7.4            | 0.21         | 0.881   | 0.037| 0.0 | 0.006       |
| DMABI-CN   | 259.3     | -5.90      | 1.2            | -0.50        | 0.865   | 0.035| 0.1 | 0.02        |

The last parameter is \( SP \) a shape parameter used to characterise how close to sphere our chromophore is. Particle sphericity \( \Psi (0<\Psi<1) \) was obvious starting point in our attempts to include some kind of shape parameter in FOM. Usual method to calculate sphericity is via use of the volume \( (V) \) and the surface area \( (A) \) of particle (in our case molecule) in equation \( \Psi = \frac{1}{\pi} \left( \frac{6V}{A} \right)^{\frac{2}{3}} \). These two characteristics of the molecule could be easily calculated by HyperChem software package and we have achieved some improvement in our correlations by including \( \Psi \) in FOM. Unfortunately, obtained by this calculation method \( \Psi \) values is not so sensitive to molecular overall shape. The source of such insensitivity lays in fact that atoms are represented by van der Waals spheres and the sphericity of isolated atom is 1. The same result one could get, calculating sphericity this way, when thousands of atoms stands in line and is just touching each other at the one point. Finally, we came up with \( SP = \frac{X^2}{(Y \times Z)} \), where \( X \) is thickness, \( Y \) is width and \( Z \) is length of the molecule.

These metrics we estimated from smallest rectangular box size parameters where molecule could be fitted in within van der Waals surface. To visualize our definition, in Figure 1 one could find drawings of the C60 (\( SP=1.0 \)) and our chromophore - DMABI (\( SP=0.12 \)) in their cages.

Figure 1. Illustration of the metrics used to calculate shape parameter \( SP \)
Numerical values of the six different forms of FOM for eight chromophores are presented in Table 2. For the evaluation of the FOM we are providing correlation coefficients of the relationship between FOM and \(d_{33}(0)\). These coefficients are calculated by standard Excel function.

**Table 2.** Calculated figures of merit FOM for investigated chromophores and their correlation results with maximal obtained NLO efficiency in PMMA host – guest films.

|        | FOM\(_1\) | FOM\(_2\) | FOM\(_3\) | FOM\(_4\) | FOM\(_5\) \(\times 10^2\) | FOM\(_6\) \(\times 10^4\) | \(d_{33}(O)\) (pm/V) |
|--------|-----------|-----------|-----------|-----------|-------------------------|-------------------------|----------------------|
| DD-DMABI | 168.1     | 2.83      | 49.96     | 0.840     | 85.63                   | 14.41                   | 3.14                 |
| D-DMABI  | 257.6     | 4.20      | 23.17     | 0.378     | 60.53                   | 9.87                    | 0.46                 |
| DMABI-Ju | 83.1      | 6.09      | 13.93     | 1.020     | 41.35                   | 30.03                   | 2.68                 |
| DMABI-dPh | 45.0      | 13.01     | 4.48      | 1.295     | 8.15                    | 23.55                   | 6.28                 |
| DMABI    | 71.4      | 5.11      | 8.37      | 0.598     | 29.88                   | 21.36                   | 5.20                 |
| tB-DMABI | 57.9      | 6.43      | 16.52     | 1.835     | 48.55                   | 53.94                   | 12.10                |
| DMABI-OH | 16.0      | 3.42      | 0.60      | 0.128     | 0.50                    | 1.08                    | 0.006                |
| DMABI-CN | 7.3       | 0.21      | 0.25      | 0.007     | 0.49                    | 0.14                    | 0.02                 |
| CORR(8) | 0.170     | 0.547     | 0.081     | 0.913     | 0.197                   | 0.920                   | 1.00                 |
| CORR(6) | 0.503     | 0.539     | 0.739     | 0.916     | 0.699                   | 0.919                   | 1.00                 |

First two FOM values in Table 2 are calculated by equations (6, 7) and representing two contradicting best NLO chromophore paradigms – an old one “high \(\mu\), high \(\beta\)” and new approach of “low \(\mu\), high \(\beta\)”.

\[
FOM_1 = \mu_g \times \beta_g
\]  

(6)

\[
FOM_2 = \frac{\beta_g}{\mu_g}
\]  

(7)

In Figure 2 we have plotted NLO maximal obtained nonlinear efficiency \(d_{33}\) with FOM\(_1\) and FOM\(_2\). It is clearly evident from the plots and correlation coefficients – there is no relationship between efficiency \(d_{33}\) and FOM\(_1\). As one could see from Figure 2a two compounds with a highest FOM\(_1\) values are responsible for breaking a correlation. These compounds are D-DMABI and DD-DMABI and both of them have \(\mu_g > 7\) D (see tab.1). If we exclude these two compounds from analysis, relation between \(d_{33}\) and FOM\(_1\) became evident (for six chromophore case CORR\(_1(6)\) = 0.503). That observation is in agreement with conclusion by L. Dalton [1]: “intermolecular electrostatic interactions will not make an important contribution for concentrations of normal interest (<45 wt/wt%) for chromophores with dipole moments of 7 D or less”. Note at Figure 2a that slope for linear relation is quite different if we take into account just six low \(\mu_g\) chromophores, or all eight. By that reason looks like application of that kind of FOM over a wide range of chromophores is inappropriate.

Completely different situation we have in a case of “low \(\mu\), high \(\beta\)” paradigm based FOM correlation became evident, never the less we take into account six or all eight molecules. The slope of \(d_{33}\) relation to FOM\(_2\) and correlation coefficient is not significantly affected by excluding of the two high \(\mu_g\) chromophores.
Figure 2. Relation of the maximal acquired nonlinearity with NLO figures of merit based on ground state dipole moment and molecular hyperpolarizability. Case a – “high $\mu$, high $\beta$”; b - “low $\mu$, high $\beta$” best chromophore paradigm. Solid line is linear fit for eight, dashed for six chromophores.

Further we would like to find out if could save correlation in case of $FOM_1$ and increase reliability of $FOM_2$ by including parameters characterizing chromophore size ($M_w$), alignment factor $\cos<\mu^\beta>$ and shape parameter $SP$ in our expressions. In Table 2 and Figure 3a and Figure 3b we have presented results of correlations based on equations (8, 9).

Figure 3. Relation of the maximal acquired nonlinearity with NLO figures of merit based on ground state dipole moment and molecular hyperpolarizability and shape parameter. Case a – “high $\mu$, high $\beta$”; b - “low $\mu$, high $\beta$” best chromophore paradigm. Solid line is linear fit for eight, dashed for six chromophores.

$$FOM_3 = \mu_g \times \beta_{ef} \times SP$$  \hspace{1cm} (8) \\
$$FOM_4 = \frac{\beta_{ef} \times SP}{\mu_g}$$  \hspace{1cm} (9)

We would like to highlight these expressions because of observation, that in both cases most important improvement of the correlations was achieved by correcting $FOM$ by $SP$. Replacing $\beta$ with projection of it over $\mu$ is less significant, but still improving reliability of relation. Normalization of $FOM$ by molecular weight $M_w$ gives us almost no gain for correlation of $d_{33}$ with $FOM_2$ and in case of
**FOM** it becoming even worse. This can be due to fact that size of chromophores is approximately the same ($M_w$ is within ±25%) and concentration is not so high (see Table 1).

In case of the “old” paradigm type **FOM** we have the same situation when high $\mu$ compounds are responsible for bad correlation. Excluding of them allows obtaining high value of correlation coefficient. If we take correlation with “new” paradigm based **FOM**, there are almost no changes in relation never the less we take into account six or eight chromophores.

To take into account alignment is quite important if we would like to use calculated molecular $\beta$ values in **FOM** instead of values from EFISH experiment, that really measures $\mu \times \beta \times \cos(\mu \cdot \beta)$ product. Of course, in the majority previous investigated cases of rod like chromophore an alignment of $\mu$ and $\beta$ supposed to be good and is not a source of concerns. The situation has changed since best chromophore shape was defined [1] and our search is focused on bulky (“spherical”) molecules. Probability of misalignment for such molecules is much higher and should be considered in our judgment of the chromophores. Finally, if we would like to come up with **FOM** expression that could be applicable to wide range of chromophore sizes over a wide range of concentrations, normalization to $M_w$ looks like reasonable. We have included these both parameters in our two final **FOM** defined by equations (10, 11):

\[
FOM_5 = \frac{\mu_g \times \beta_g \times SP \times \cos(\mu \cdot \beta)}{M_w} \tag{10}
\]

\[
FOM_6 = \frac{\beta_g \times SP \times \cos(\mu \cdot \beta)}{\mu_g \times M_w} \tag{11}
\]

Results of correlation of the maximal acquired nonlinearity with these **FOM** one could find in Table 2 and Figure 4a and Figure 4b.

![Figure 4a](image1.png) ![Figure 4b](image2.png)

**Figure 4.** Relation of the maximal acquired nonlinearity with NLO figures of merit based on ground state dipole moment, molecular hyperpolarizability, their alignment, shape parameter and molecular weight. Case a – “high $\mu$, high $\beta$”; b - “low $\mu$, high $\beta$” best chromophore paradigm. Solid line is linear fit for eight, dashed for six chromophores.

In the case of **FOM** we have dual situation – **CORR(8)** increases but **CORR(6)** decreases when we include more parameters relation. Note that slope values get closer for six and eight chromophore cases. For **FOM**, our correlations get slightly better at every step when we include alignment and normalization to $M_w$. Finally if we take a look on plot, just two chromophores are not in a straight line. Both of them have closest absorption to resonant 532 nm (DMABI-Ju - 512 nm, D-DMABI – 555 nm) and could be that correction to zero frequency according to two level model is not so accurate.
3. Conclusions

Our analysis, based on theoretical calculations within a frame of HF \textit{ab initio} calculations and experimental investigations of the second order NLO efficiency of the poled host – guest films of DMABI related chromophores in PMMA, allows us to draw following conclusions:

- Maximal achieved NLO efficiency is rather proportional to $\beta/\mu$ than to $\beta \times \mu$;
- Chromophore shape play a significant role in NLO efficiency;
- Even for low and moderate ground state dipole moment NLO chromophores electrostatic interactions should not to be neglected;
- We have developed new type equation (11) for NLO chromophore figure of merit, what allows us on the basis HF \textit{ab initio} calculations to predict NLO performance of molecule in poled host – guest polymer films.

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