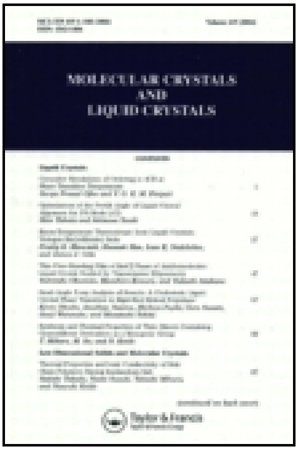

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Version of record first published: 31 Aug 2012.

To cite this article: M. Rutkis , A. Jurgis , V. Kampars , A. Vembris , A. Tokmakovs & V. Kokars (2008): New Figure of Merit for Tailoring Optimal Structure of the Second Order NLO Chromophore for Guest-Host Polymers, Molecular Crystals and Liquid Crystals, 485:1, 903-914

To link to this article: http://dx.doi.org/10.1080/15421400801924847

Mol. Cryst. Liq. Cryst., Vol. 485, pp. 155/[903]–166/[914], 2008
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400801924847

New Figure of Merit for Tailoring Optimal Structure of the Second Order NLO Chromophore for Guest-Host Polymers

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Reliability to forecast SHG efficiency using two sets of non linear optical (NLO) chromophore figures of merit (FOM) was tested. One of them predicts that SHG efficiency d_{33} of the poled guest-host polymer is proportional to ground state dipole $\sim\mu_g$, another to $\sim 1/\mu_g$. Correlation of maximal achieved second order NLO efficiency of the PMMA based systems containing eight dimethylaminobenzylidene-1, 3-indandione (DMABI) related chromophores with proposed FOM have been analyzed. The best correlations were obtained with second set of FOM, especially if high dipole moment ($\mu_g > 7D$) chromophores are included in analysis.

Keywords: figure of merit; guest-host polymers; NLO chromophores; SHG efficiency

INTRODUCTION

Over last two decades there is a constant interest to make use of organic molecular systems in the (NLO) devices [1]. The progress in this field is 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 to use poled polymer guest-host systems, where NLO active

This research was granted by Latvian National Research Program in Materials Science, Project No. 3 "Materials for photonics and nanoelectronics based on novel functional low molecular organic compounds and polymers" and Latvian Council of Science Project 05.1467 "Investigation of Physical Properties of Polar and Photoactive Supramolecular Systems for Photonics".

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chromophores are dispersed in polymer matrix. A controlled modification of the chromophore structure to achieve optimal molecular properties is one of the keystones for the design of NLO material. Along with the first molecular hyperpolarizability (β_0), ground state dipole moment (μ_g), size and shape, CT band wavelength, alignment of β_0 and μ_g are important NLO chromophore properties. Initial modeling of proposed molecular structures can be done by quantum chemical (QC) calculations and allows us to skip time-consuming steps of synthesis and experimental evaluation.

Tailoring the structure of a chromophore to achieve best value for the particular molecular property usually results in some kind of trade-off in other properties. To compare the chromophores and to numerically evaluate their applicability it is very useful to have some kind of the figure of merit (*FOM*) combining all important (see above) molecular properties. Since 90's, when the active search for best chromophores has begun, the product of the ground state dipole moment (μ_g) and first molecular hyperpolarizability (β_0) is widely used as $FOM = \mu_g\beta_0$ (for example see [2,3]). That approach comes from the text books based [4] expressions for macroscopic second harmonic coefficients d_{33} of the poled polymer film:

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

where N is the number density of the chromophores, F is the product of all local field factors; $\langle\cos^3\theta\rangle$ is electric field induced acentric order parameter, E-poling electric field and T-poling temperature. As one can notice from expression (1) number density has high impact on NLO efficiency, so chromophores should be small to achieve high values of N. It is obvious to define second order NLO chromophore $FOM = (\mu_g \times \beta_0)/M_W$ [4], which takes into account the size of a molecule. Sometimes this *FOM* is called "molecular nonlinearity" [6]. During the last decade of previous century best chromophore search paradigm was "small highly polar molecule with high β_0 value", or so called "high $\mu\beta$" chromophore. A typical value of a ground state dipole moment of such chromophore usually was larger than 10 D. In our attempts to search for new highly NLO active molecules within the class of indandion derivatives [7–13], we have also looked for such "high $\mu\beta$" chromophores.

Unfortunately, for "high $\mu\beta$" chromophores as a rule, macroscopic nonlinearity (d_{33})–chromophore number density (or load in Wt%) relation is not linear, as predicted by Eq. (1). 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 chromophores at high load. One of the processes taking place at these conditions is centrosymmetrical aggregation [14] of highly polar molecules, decreasing number density of NLO active chromophores in polymer. A different scenario, assuming a loop-like organization of dipoles, was discussed in [15]. Another phenomena causing reduction of macroscopic nonlinearity is electrostatic repulsion of aligned chromophores. In the last decade Dalton and co-workers have developed an electric field poling model, where electrostatic interactions of chromophores were taken into account [5]. According to this model electric field induced acentric order parameter and therefore nonlinearity is attenuated due to electrostatic repulsion of cromophores during electrical field poling procedure. According to model [1] the chromophore load at what maximal bulk nonlinearity can be achieved reads:

$$N^{\max} = 1.38\frac{kT}{\mu_g^2} \tag{2}$$

Combining Eqs. (1) and (2) one calculates a maximal nonlinearity:

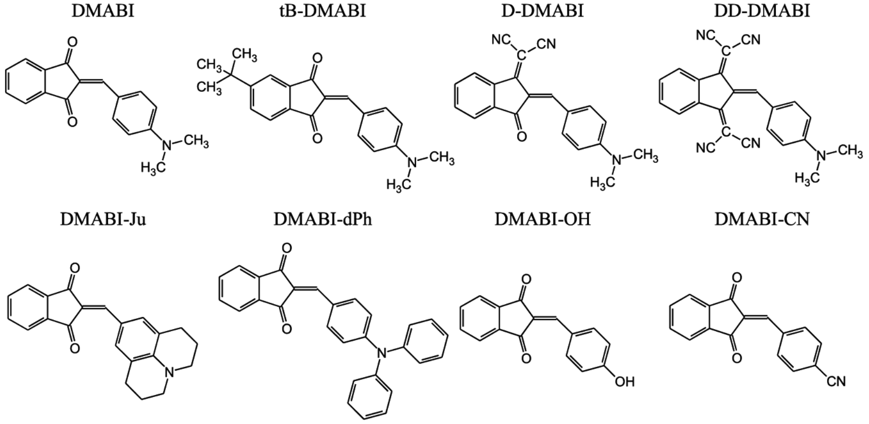
$$d_{33}^{\max} = \frac{1}{2}N^{\max}\beta_0 F\frac{\mu_g E}{5kT} = \frac{1}{2}1.38\mu_g\beta_0\frac{kT}{\mu_g^2}\frac{FE}{5kT} = 0.138\frac{\beta_0}{\mu_g}FE. \tag{3}$$

This equation give us surprising result: maximal value of d_{33} for guest – host film of particular chromophore is proportional to β_0/μ_g instead of the proportionality to $\beta_0\mu_g$ predicted by Eq. (1). Dalton and co-workers [1] have made some conclusions about a shape of chromophore, too: it should be as close as possible to a sphere. To summarize, new century came with a new best chromophore paradigm: small spherical molecule with low μ_g and high β_0. Of course there is some drawback–low μ_g results in smaller orientation energy $\mu_g E$ and reduces induced acentric order parameter value in comparison with high μ_g chromophores. From our point of view in the case of low μ_g one can increase an external poling field. At the same time for high μ_g chromophores at high loads we cannot avoid electrostatic de-poling interaction [5] and aggregation [14,15] of chromophores inside the polymer.

For future progress there is high need for a new *FOM* representing this new paradigm. In this contribution we propose some new equations for *FOM* and test them on our previously reported data [16] for eight dimethylaminobenzylidene-1, 3-indandione (DMABI) related chromophores.

RESULTS AND DISCUSSION

In Scheme 1 we have shown structures of eight indandione derivatives included in our analysis of the proposed *FOM*. Molecular characteristics used for *FOM* calculation are presented in Table 1. They are obtained by HF *ab initio* calculations with standard basis set 6–31G** by HyperChem package. Computation details, experimental conditions and more detailed results were published elsewhere [16]. Our target parameter – maximal achieved nonlinearity for chromophore/PMMA guest-host films was obtained from d_{33} with chromophore load relations (1–25 wt%). Typical example for such chromophore load optimization for DMABI in PMMA is presented in Figure 1. According to two level model [17] frequency corrected value $d_{33}(0)$ was used in correlation analysis to exclude resonant effects on nonlinear efficiency. It is useful to explain for the used molecular parameters a motivation for including them in *FOM* and give their definitions. First of all, normalization to M_w is obvious if we would like to have *FOM* expression applicable to wide range of chromophore sizes. Good μ_g and β_0 alignment is essential in electric field poled polymer films, because projection of β_0 over μ_g is a source of bulk nonlinearity and should be considered in our treatment of the chromophores. In previous investigations, for rod-like chromophores, an alignment supposed to be good and was 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 where probability of misalignment is much higher. The hyperpolarizability β_0 and angle



SCHEME 1 Molecular structures of investigated NLO chromophores.

TABLE 1 Calculated Molecular Parameters of Investigated Chromophores and Maximal Obtained NLO Efficiency in PMMA Host – Guest Films

Compound	M_w	μ_g D	β_0 esu $\times 10^{30}$	$\cos(\mu_\beta)$	Ψ	SP	w %	$d_{33}(0)$ pm/V
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	1.0	0.014
DMABI-CN	259.3	−5.90	1.2	−0.50	0.865	0.035	0.1	0.02

between β_0 and μ_g vectors (μ_β) are calculated by applying so-called finite field (FF) method [18]. In our FOM we would like also to include numerical parameter characterizing how close to sphere a chromophore is. Particle sphericity Ψ ($0 < \Psi < 1$) was an obvious starting point in our attempts to take into account the shape of a chromophore. A standard method to calculate sphericity is using equation $\Psi = \pi^{1/3}(6V)^{2/3}/A$, where is V the volume and A the surface area of particle (molecule). These two characteristics (V and A) of the molecule could

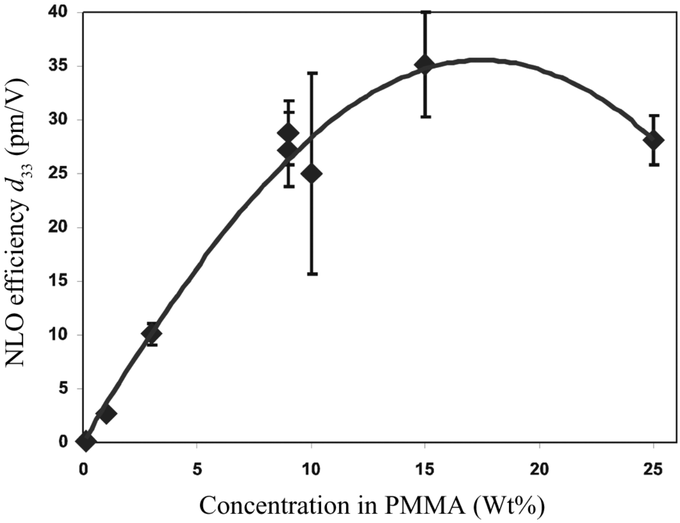


FIGURE 1 Influence of the *DMABI* concentration in *PMMA* matrix on the film d_{33}. Poling temperature 95°C, poling time 10 minutes, poling current 1 μA/cm^2, corona voltage of 4–6 kV, film thickness 1–2 μm.

be easily calculated by HyperChem software package. We have achieved some improvement in our correlations by including Ψ in *FOM*. Unfortunately, values of Ψ obtained by this method are not too sensitive to a molecular overall shape (see Table 1). The source of such insensitivity is the fact that atoms are represented by van der Waals spheres and the sphericity of an isolated atom is $\Psi = 1$. The same result ($\Psi = 1$) one gets for thousands of atoms arranged in a line and just touching each other at one point. Finally, we came up with shape parameter $SP = X^2/(Y{*}Z)$, where X is thickness, Y is width and Z is length of the molecule. These parameters we estimated from the sizes of a smallest rectangular box, where molecule could be fitted in within van der Waals surface. To visualize our definition, in Figure 2 we display the drawings of the C60 ($SP = 1.0$) and our chromophore-DMABI ($SP = 0.12$) in their cages.

For the evaluation of the *FOM* one could state the null hypothesis: linear correlation coefficient between *FOM* and maximal achieved NLO efficiency $d_{33}(0)$ is zero. An alternate to this is hypothesis that statistically significant linear correlation takes place. To reject null hypothesis we could use test statistics:

$$t = \frac{r}{\sqrt{1-r^2}}\sqrt{n-2} \tag{4}$$

where n stands for the number of data in the probe, and r-for the linear correlation coefficient between *FOM* and $d_{33}(0)$. If $|t|$ is larger then critical value t_{α},s, where α denotes the significance level (our choice is 0,05) and $s = n$-2 is degrees of freedom, the null hypothesis is rejected. The r and $t_{0.05,s}$ values are obtained by standard *Excel* functions (*CORREL* and *TINV*). Numerical values of six different *FOMs* for eight chromophores are presented in Table 2. In same table one

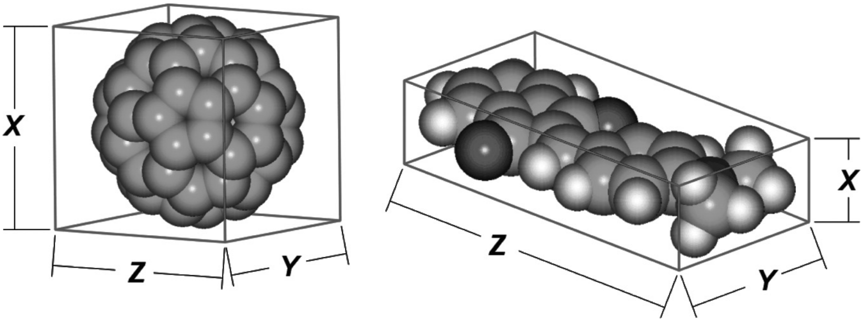


FIGURE 2 Illustration of the metrics used to calculate shape parameter *SP*.

TABLE 2 Calculated figures of merit (*FOM*) for investigated chromophores and their linear correlation statistics with maximal obtained NLO efficiency in PMMA host–guest films

	FOM_1	FOM_2	FOM_3	FOM_4	$FOM_5 \times 10^3$	$FOM_6 \times 10^4$	$d_{33}(0)$ (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
$r(8)$	−0.170	0.547	0.081	0.913	0.197	0.920	$t_{0.05,\ 8-2}$
$t(8)$	−0.424	1.602	0.200	5.503	0.493	5.754	2.447
$r(6)$	0.503	0.539	0.739	0.916	0.699	0.919	$t_{0.05,\ 6-2}$
$t(6)$	1.164	1.280	2.196	4.568	1.954	4.667	2.776

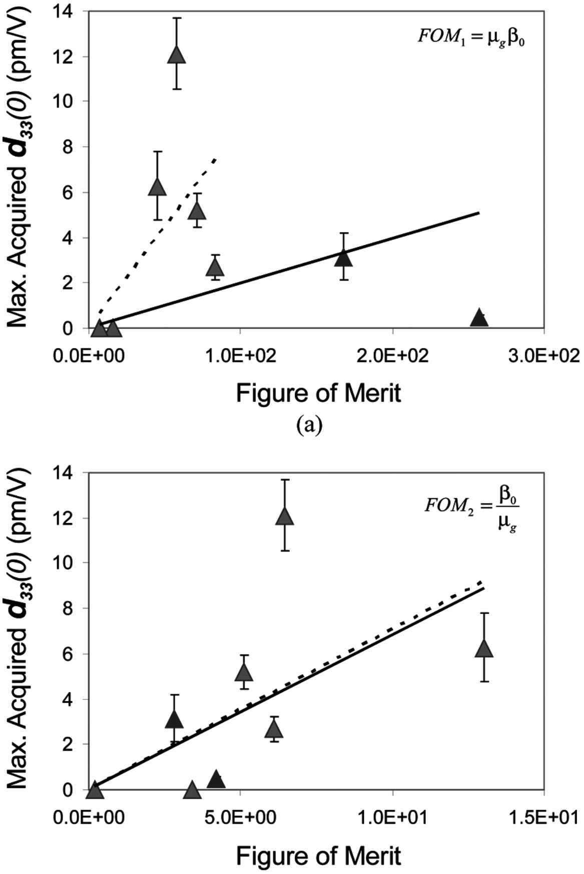
could found r and t values for two cases: calculated taking in to account all eight chromophores, or just six (two chromophores with highest μ are excluded) and critical values for both cases ($t_{005,8-2}$ and $t_{005,6-2}$).

First two *FOM* values in Table 2 are calculated from Eq. (5), (6) and represent two contradicting best NLO chromophore paradigms–an old one “high μ, high β” and new approach of “low μ, high β”.

$$FOM_1 = \mu_g \beta_0, \tag{5}$$

$$FOM_2 = \frac{\beta_0}{\mu_g} \tag{6}$$

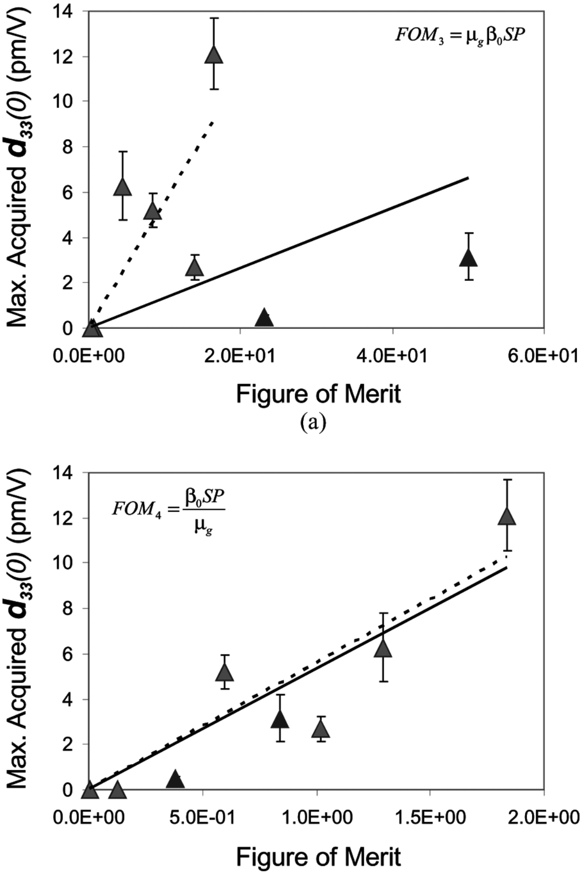
In Figure 3 we have plotted maximal values of nonlinear efficiency d_{33} against FOM_1 and FOM_2. It is clearly evident from the plots, correlation coefficients, and t-test results–there is no significant relationship between efficiency d_{33} and FOM_1 ($r(8) = -0.170$, $|t(8)| = 0.424 < 2.447$). As one could see from Figure 3a two compounds with highest FOM_1 values are mostly responsible for breaking a correlation. These compounds are D-DMABI and DD-DMABI and both of them have $\mu_g > 7$ D (see Table 1). If we exclude these two compounds from analysis, correlation coefficient between d_{33} and FOM_1 increases ($r(6) = 0.503$), but still is not statistically significant ($t(6) = 1.164 < 2.776$). Note (Figure 3a) that slope for linear relation is quite different if we take into account just six low μ_g chromophores,



(b)

FIGURE 3 Relation of the maximal acquired nonlinearity with NLO figures of merit based on ground state dipole moment and molecular hyperpolarizability. Case *a*–"high μ, high β"; *b*–"low μ, high β" best chromophore paradigm. Solid line is linear fit for eight, dashed for six chromophores.

or all eight. In the case of "low μ, high β" paradigm based *FOM*–linear correlation coefficients are higher and similar for both cases taking into account six or eight molecules ($r(6) = 0.539$, $r(8) = 0.547$). The slope of d_{33} relation to FOM_2 is not significantly affected by excluding the two high μ_g chromophores. At the same time we could not reject the null hypothesis, because t values ($t(6) = 1.280$, $t(8) = 1.602$) are below the critical values.



(b)

FIGURE 4 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 μ, high β"; *b*–"low μ, high β" best chromophore paradigm. Solid line is linear fit for eight, dashed for six chromophores.

We have tried to increase the statistical significance of our correlations by including more parameters, characterizing chromophore size (M_w), alignment factor $\cos(\mu_\beta)$ and shape parameter *SP* in our *FOM* expressions. First of all, these parameters are tested one by one. In Table 2 and Figure 4 we have presented results of correlations based on Eqs. (7), (8).

$$FOM_3 = \mu_g \beta_0 SP, \tag{7}$$

$$FOM_4 = \frac{\beta_0 SP}{\mu_g} \tag{8}$$

We have observed that in both cases the most significant increase of the correlations was achieved by correcting *FOM* by *SP*. Replacing β with projection of it over μ is less important, but still improves the reliability of the 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_1 it becomes even worse. This can be due to the fact that the sizes of all chromophores are approximately the same (M_w is within $\pm$ 25%) and concentration is not so high (see Table 1). In case of the "old" paradigm type FOM_3 we have the same situation–high μ compounds are responsible for breaking the correlation. Removing them allows us to obtaining higher values of correlation coefficient ($r(6) = 0.739$ compare to $r(8) = 0.081$) and $t(6) = 2.196$ get closer to critical value 2.766. In the case of correlation with "new" paradigm based FOM_4, there are almost no changes in relation if we take into account six or eight chromophores ($r(6) = 0.913$, $r(8) = 0.916$). For this *FOM* we could reject a null hypothesis ($t(6) = 4.568 > 2.776$, $t(8) = 5.503 > 2.447$) and claim our linear correlation as statistically significant.

Finally we would like to test *FOM* based on both paradigms and combining all important, from our point of view, molecular characteristics:

$$FOM_5 = \frac{\mu_g \beta_0 SP \cos(\mu^\beta)}{M_w}, \tag{9}$$

$$FOM_6 = \frac{\beta_0 SP \cos(\mu^\beta)}{\mu_g M_w}. \tag{10}$$

Results of correlation of the maximal acquired nonlinearity with these *FOM* are shown in Table 2 and Figure 5. In the case of FOM_5 we have a new effect – $r(8)$and $t(8)$ increases, but $r(6)$ and $t(6)$ decreases after more parameters were included into relation. Note that slope values get closer for six and eight chromophore cases. For FOM_6, our correlations get slightly better when we include alignment factor ($r(6) = 0.923$, $t(6) = 4.784$ and $r(8) = 0.925$, $t(8) = 5.946$). Further normalization *FOM* by M_w slightly decreases correlation statistics (see Table 2). Anyhow, it looks like reasonable to include M_w in *FOM* for evaluation of wide range (by size) NLO chromophores.

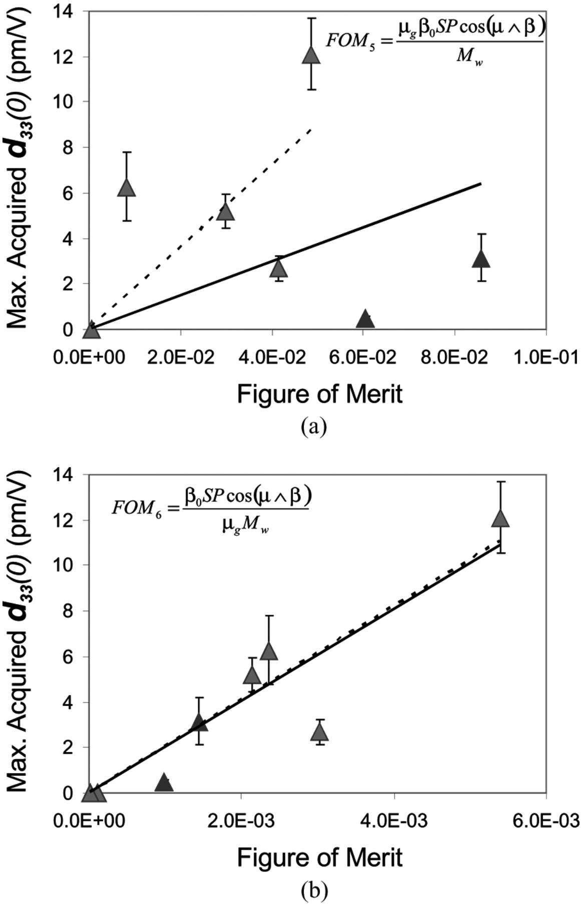


FIGURE 5 Relation of the maximal acquired nonlinearity with NLO figures of merit based on ground state dipole moment, molecular hyperpolarizability, their alignment, shape parameter and molecular weight. Case *a*–"high μ, high β"; *b*–"low μ, high β" best chromophore paradigm. Solid line is linear fit for eight, dashed for six chromophores.

CONCLUSIONS

Our analysis, based on theoretical calculations within a frame of HF *ab initio* method 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 conclusion that maximal achieved NLO efficiency is rather proportional to β/μ then to $\beta\mu$.

Chromophore shape and electrostatic interactions, even for low and moderate ground state dipole moment molecules, are playing a significant role in NLO efficiency and should not to be neglected when tailoring new chromophore structures. New type Eqs. (6, 8 and 10) proposed for NLO chromophore figures of merit allow us, on the basis HF *ab initio* calculations, to predict NLO performance of chromophores in poled host-guest polymer films.

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