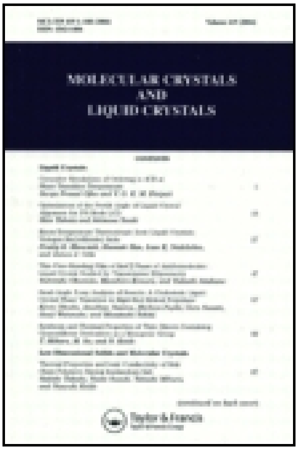

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Molecular Engineering of Push-Pull Molecules: Towards Photorefractive Materials

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Molecular Engineering of Push-Pull Molecules: Towards Photorefractive Materials.

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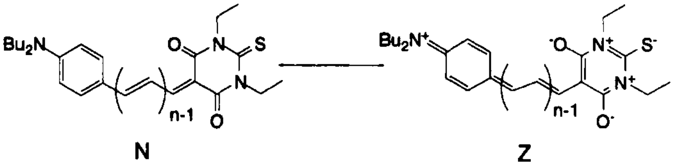
In low glass-transition temperature photorefractive materials, push-pull chromophores induce photorefractivity essentially via two mechanisms: optical birefringence and Pockels electrooptic effect. A 2-state 2-form description of these molecules indicates how the molecular structure can be optimized to maximize the photorefractive effect. At the optimum structure the two contributions have opposite signs. For the molecular sizes used currently the optical birefringence should dominate photorefractivity. Lengthening the conjugation path leads to a steeper increase of the Pockels electrooptic effect. Yet for the molecular sizes examined in this work, this contribution remains smaller than the optical birefringence at the optimum structure. Huge photorefractive responses could by attained if the molecular structure can be tuned towards the cyanine limit while increasing the molecular size.

Keywords: push-pull chromophores, limiting-resonance forms, optical birefringence, Pockels electrooptic and photorefractive effects

INTRODUCTION

Organic photorefractive (PR) materials doped have attracted considerable attention these last years in photonic technologies [1, 2]. PR polymer films with almost 100% diffraction efficiencies have been reported [3]. The push-pull chromophores, incorporated in these materials, have been extensively investigated for their quadratic nonlinear optical properties [4]. These compounds, consisting of donor and acceptor end-substituents interacting through a conjugation path, possess a 1-dimensional quadratic polarizability tensor, and the dominant (i. e. along the charge-transfer axis) static component $\beta(0)$ can be approximated by a 2-state expression [5].

Recently, we have developed a 2-state 2-form model based on the description of push-pull molecules as a combination of two limiting-resonance forms (see Scheme 1) [6]. A coordinate MIX, defined as the weight in the ground state of the zwitterionic (Z) form less that of the neutral (N) form, characterizes the mixing between these forms. This approach allows to express *analytically* the ground-state dipole μ_g, the linear and the nonlinear polarizabilities as functions of MIX. The four parameters of this model -the energy gap V, the coupling element t between N and Z and their dipole (μ_N and μ_Z)- can be determined experimentally [7].



SCHEME 1 Neutral and zwitterionic resonance forms of Series 1.

FIGURE OF MERIT OF PUSH-PULL CHROMOPHORES FOR PHOTOREFRACTIVITY : TWO-STATE TWO-FORM ANALYSIS

Static figures of merit are essential to assess the chromophores effectiveness. In low glass-transition (T_g) temperature materials, PR effect arises both from the optical birefringence (0B) -generated by poling of the chromophores by the light-induced space-charge modulated electric field- and from the Pockels electrooptic (EO) effect -caused by the quadratic polarizability of poled chromophores. The PR figure of merit can be defined by Equation 1 [8, 9]:

$$\mathrm{FOM} = \left| \frac{2\,\mu_g^2\,\Delta\alpha(0)}{9\,k\,T} + \mu_g\,\beta(0) \right| \qquad (1)$$

where the anisotropy $\Delta\alpha(0)$ of the linear polarizability is defined as the difference between the linear polarizabilities along and perpendicularly to μ_g. For high-T_g PR materials, the appropriate figure of merit can be derived from Equation 1 by omitting the first term leaving only the Pockels EO effect to generate photorefractivity.

Experimental studies indicate that $\Delta\alpha(0)$ can be approximated by the 2-state expression of the linear polarizability $\alpha(0)$ coefficient lying along the charge-transfer axis [8]. By using the 2-state 2-form expressions of μ_g, $\alpha(0)$ and $\beta(0)$ as functions of MIX, it is straightforward to derive the PR figure of merit [6]. In this section we have made the reasonable assumption that μ_N is negligible in comparison to μ_Z, a reduced expression of FOM is then given by Equation 2:

$$\mathrm{FOM} = \frac{81\,\mu_Z^4}{1024\,t^2} \left| 0.26\,\frac{t}{kT}\,\mathrm{OB(MIX)} + \mathrm{EO(MIX)} \right| \qquad (2)$$

The normalized functions EO(MIX) and OB(MIX) are discussed below.

Optimization of the Pockels Electrooptic Contribution

The Pockels EO contribution to the PR effect depends on the chromophore via ratio μ_Z^4 / t^2 and on the system-independent function EO(MIX):

$$\mathrm{EO(MIX)} = 64\,(-\mathrm{MIX})\,(1+\mathrm{MIX})^3\,(1-\mathrm{MIX})^2 / 27 \qquad (3)$$

In Figure 1, we have plotted the variation of EO versus MIX. The negative peak, with a magnitude equal to 1, is reached when MIX = +1/2. This implies that the optimized ground-state structure -yielding a maximized Pockels EO response- is dominated by the Z form. The positive peak, reached when MIX = -1/3, amounts roughly to 1/2 of the maximum value. This indicates that a substantial Pockels EO effect can be obtained for a "quasi"-optimized ground-state structure exhibiting dominant neutral character. Near the cyanine limit (i.e. MIX=0), the EO contribution vanishes.

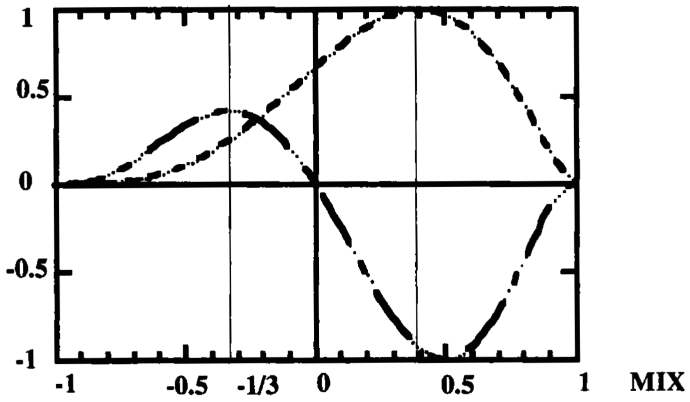


FIGURE 1 EO (—— -) and BO (- -·- -) functions versus MIX.

Optimization of the Optical Birefringence Contribution

The OB contribution to photorefractivity depends on the molecular system via ratio μ_Z^4 / t and is proportional to the system-independent function OB(MIX):

$$\mathrm{OB} = (1+\mathrm{MIX})^{7/2}\,(1-\mathrm{MIX})^{3/2} / 1.51 \qquad (4)$$

We have also plotted in Figure 1 the variation of OB versus MIX. The positive peak is reached when the value of MIX equals + 2/5. So that optimization of the molecular structure yielding maximum OB response requires the elaboration of molecules beyond the cyanine limit (i.e. MIX>0). The OB retains 2/3 of its peak value at the cyanine limit.

Comparison between the OB and the Pockels EO Contributions

If the value of MIX is fixed, the respective weight of the OB and of the Pockels EO contributions depends both on ratio EO(MIX) / OB(MIX) and on scaling factor t / kT. Before the cyanine limit (i.e. MIX<0), functions OB and EO have the same sign so that the two mechanisms add up yielding the PR effect. This is the case for most push-pull chromophores that have been incorporated in low-T_g PR polymers. At the cyanine limit, only the OB gives rise to the PR effect. Beyond this limit, the functions have opposite signs and photorefractivity origins from the difference between the two contributions.

The factor *t / kT* depends on the chromophore and on the operating temperature. Assuming $T \approx 300$ K, Equation 2 can be transformed into:

$$\mathrm{FOM} = \frac{81\,\mu_Z^4}{1024\,t^2}\left|\frac{t\,(\mathrm{kJ/mol})}{10}\,\mathrm{OB(MIX)} + \mathrm{EO(MIX)}\right| \qquad (5)$$

For example for a compound having a "quasi"-optimized MIX = -1/3 structure, the EO contribution to the PR figure of merit should be 6 times less than that of the OB if $t \approx$ 100 kJ/mol. In previous studies performed on push-pull polyenes having similar sizes than the chromophores currently incorporated in low-T_g polymers, we have found that the value of coupling element t ranges from 80 kJ/mol to 120 kJ/mol [7, 11]. This could explain why up to now the OB has been found to dominate photorefractivity. If low-T_g PR polymers were doped with molecules having smaller *t* values, the weight of the EO contribution could be enhanced. For instance, for a molecule having MIX = -1/3 both contributions would become comparable if $t \approx$ 20 kJ/mol. This would also result in a significant global enhancement of FOM.

LENGTH DEPENDANCE OF THE PR FIGURE OF MERIT

As noted from Equation 1, enhancement of FOM could be accomplished by both increasing μ_Z and decreasing t. This can be obtained for a given donor / acceptor pair by lengthening the conjugation path [7, 11]. To analyse the effect of the molecular size on the PR figure of merit we have chosen to discuss the results obtained on Series **1** (see Scheme 1). The total number n of double bonds in the conjugation path equals 1, 2, 3, 4 and 5 units. The 2-state 2-form parameters can be determined from absorption and electrooptic absorption data [10] as reported in Reference 11. We have then been able to derive the contributions of the OB at T=300 K and of the EO effect to the PR figure of merit. For these calculations we have not neglected μ_N as in Equation 2. The variations of FOM versus MIX are shown in Figure 2. The magnitudes of the OB peak FOM_{OB}^{peak} and of the main EO peak $\left|FOM_{EO}^{peak}\right|$, of the optimum MIX^{opt} values maximizing the PR figure of merit and of the resulting peak FOM^{peak} magnitudes, and the FOM values obtained at the cyanine limit are collected in Table I. For comparison, semi-empirical calculations performed on $(Me)_2N(CH{=}CH)_4CHO$ chromophore yield the following peak magnitudes: $FOM_{OB}^{peak} \approx 10000\ 10^{-46}$ e s u and $\left|FOM_{EO}^{peak}\right| \approx 200\ 10^{-46}$ e s u [9].

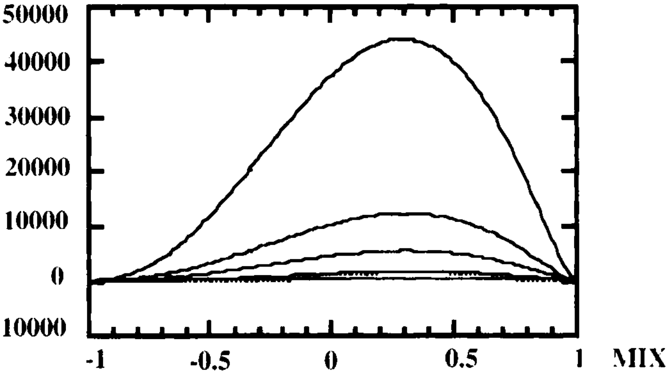


FIGURE 2 PR figures of merit (in 10^{-46} e s u) versus MIX for Series **1**.

TABLE I 2-state 2-form data calculated for Series **1**.

n	*t* kJ/mol	FOM^{peak}_{OB}	$\lvert FOM^{peak}_{EO}\rvert$	FOM^{peak} (MIX^{opt})	FOM (MIX=0)
		10^{-46} e s u			
1	109	520	45	480 (0.36)	360
2	86	1750	180	1600 (0.34)	1200
3	67	6000	720	5400 (0.32)	4400
4	60	13800	1900	12200 (0.31)	10100
5	50	51000	8400	43800 (0.30)	37000

The peaks magnitudes of both contributions rise steeply with increasing n as can be seen from Table I. As expected, the rise is more marked for $\lvert FOM^{peak}_{EO}\rvert$ than for FOM^{peak}_{OB}. However even for the longest compound of Series **1**, the magnitude of the negative EO peak remains small compared to that of the OB. This is illustrated by Figure 2 where the shape of all the curves is dominated by the OB. Note that this difference in trends induces a slight shift towards the cyanine limit of the optimum MIX value with increasing *n*. For the lengths investigated in this work, the resulting FOM^{peak} peak magnitude rises steeply with n. Actually even for the cyanine structure the longer compounds of this series would lead to huge values of the figure of merit (see Table I). For comparison the static FOM value, estimated from data reported in Reference 12, of the DMNPAA chromophore equals 470 10^{-46} e s u.

CONCLUSION

It is useful to characterize the effectiveness of push-pull chromophores by using a figure of merit. In low-T_g PR polymers, FOM contains mainly the OB and the Pockels EO contributions. A 2-state 2-form model, describing the ground state of push-pull molecules as a mixture of the N and the Z forms, helps understand how these contributions relate to the molecular structure. An optimum MIX value -half way between the cyanine limit and the Z form-maximizes these two contributions but then they have opposite signs.

Results obtained on a series of push-pull polyenes indicate that the magnitudes of the OB and the Pockels EO peaks increase steeply when lengthening the conjugation path. For the sizes investigated in this work the PR figure of merit remains dominated by the OB. The peak FOM value increases markedly with *n* leading to huge potential values of the PR figure of merit. Simultaneously the peak position shifts towards the cyanine limit. At this limit, the PR figure of merit retains more than 80% of its maximum value.

In conclusion for visible and near-infrared PR applications, molecular engineering of the compounds and tuning of the polarity of the host medium -aimed at obtaining structures close to the cyanine limit- could lead to unequalled PR performances.

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