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Improved performance of photorefractive polymers based on merocyanine dyes in a polar matrix

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Recently, chromophores with a large figure-of-merit for incorporation into photorefractive polymers with low glass-transition temperature have become available. However, their rather polar nature so far limited their use in typical nonpolar photoconducting matrices due to dye aggregation. By incorporation of an additional polar compound we were able to influence this situation favorably. The material we report here has a factor 4 to 5 (2) improved index modulation amplitude (gain coefficient) compared to the best previously known materials. The material is sufficiently resistant against phase separation and operates in the near infrared at typical wavelengths of commercially available high-power laser diodes. © 1998 American Institute of Physics.

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The photorefractive (PR) effect is currently considered one of the most promising mechanisms for applications such as real-time optical processing and holographic data storage. The hologram is recorded as a spatial modulation of the refractive index induced by an internal electric field which develops as a result of charge carrier separation. Besides inorganic PR crystals such as LiNbO₃ organic PR materials with excellent performance have recently attracted increasing attention.¹ They offer advantages such as simple adjustment of the physical and chemical properties, low cost, and good processing capabilities with excellent reproducibility.

Photorefractivity in organic materials is achieved by combining the appropriate functional molecules or moieties providing photosensitivity, photoconductivity, and electro-optical (EO) response. PR composites with glass-transition temperatures T_g close to room temperature have so far shown the best performance.¹⁻⁵ The low T_g allows *in-situ* orientation of the EO chromophores by an externally applied electric field, necessary to obtain a macroscopic EO effect in the material. By the same token chromophores are also aligned by the internal PR space-charge field, giving rise to a birefringence contribution to the index modulation in addition to the one through the EO (*Pockels*) effect,⁶ unlike in conventional PR crystals. It was shown that this local response of the low T_g PR materials to the superposition of the external and internal electric field can be consistently interpreted in terms of their *Kerr* susceptibility.^{7(a)} The suitable figure-of-merit (FOM) F for chromophores used in such materials is

$$F = [9\mu\beta + 2\mu^2\Delta\alpha/(kT)]/M, \quad (1)$$

where μ is the dipole moment, $\Delta\alpha = \alpha_{\parallel} - \alpha_{\perp}$ the difference of the first-order polarizability α parallel and perpendicular

to the molecular axis (anisotropy), β the second-order polarizability along the dipole moment, and M the molar mass.⁷

Recently, we reported a new class of merocyanine dyes in the cyanine limit with the main structural feature aminothiényl-dioxypyridine (ATOP).⁴ These dyes possess highly improved FOMs and excellent compatibility with the commonly used photoconducting polymer poly(N-vinylcarbazole) (PVK). Surprisingly, the holographic experiments revealed best performance at dye contents of only $x \approx 20$ –25% wt, while higher loading led to a cancellation of the PR response.⁴ We ascribe this undesired effect to interactions between the highly polar dye molecules, leading to aggregates which cannot be oriented and, thus, do not contribute to the PR effect. In this letter, we sought to reduce the electrostatic interaction between the dipoles by increasing the polarity of the matrix in order to overcome aggregation. We did so by adding a second dipolar EO chromophore, which can by itself contribute to the PR effect, leading to a composite with unprecedented PR properties.

For our investigations we chose 1-butyl-5-[2-(5-dibutylamino-thienyl)methylene]-4-methyl-2,6-dioxo-1,2,5,6-tetrahydro-pyridine-3-carbonitrile (ATOP-1, **3g** in Ref. 4). By electro-optical absorption measurements (EOAM)⁸ we determined μ , $\Delta\alpha$, and β for ATOP-1 and also for the reference chromophore 2,5-dimethyl-4-(p-nitrophenylazo)anisole (DMNPAA), which was used in the first high-performance PVK-based organic PR material.² From these data the dispersion-free FOM at infinite wavelength was calculated for ATOP-1 (DMNPAA, respectively) according to Eq. (1)^{4,7} to be $F_{\infty} = 1.40 (0.20) \times 10^{-74} \text{ C}^2 \text{ V}^{-2} \text{ m}^4 \text{ kg}^{-1} \text{ mole}$. By applying known two-level dispersion formulas for α and β [explicitly given for example in Ref. 7(a)] and considering the wavelengths of maximum absorption of the chromophores (536 and 391 nm, respectively, in dioxane) we estimated the FOM at $\lambda = 790 \text{ nm}$, the wave-

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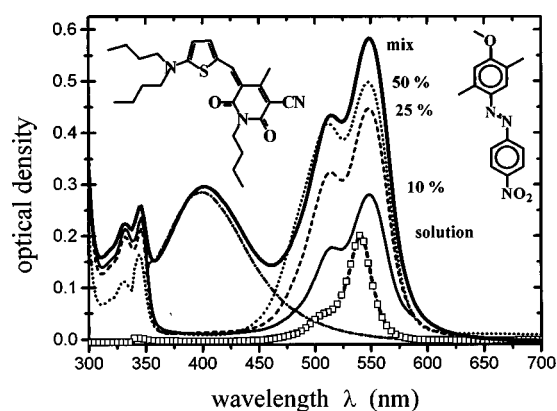


FIG. 1. Absorption spectra of thin films of various PR composites ATOP-1:DMNPAA:PVK:ECZ:TNFM normalized to 100 nm: 10% wt ATOP-1 (thin solid line); 25% wt ATOP-1 (thin dashed line); 50% wt ATOP-1 (thin dotted line); 25% wt DMNPAA (thin dash-dot line); 25% wt ATOP-1 and 25% wt DMNPAA (fat solid line). For reasons of comparison, we also plotted the spectrum of ATOP-1 in chloroform solution (line & symbols, arbitrary units, $c < 10^{-5}$ mole/l). Inset: chemical structures of ATOP-1 (left) and DMNPAA (right).

length used for the holographic experiments below: $F_{790} = 2.63(0.28) \times 10^{-74} \text{ C}^{-2} \text{ V}^{-2} \text{ m}^4 \text{ kg}^{-1} \text{ mole}$. Thus, at $\lambda = 790 \text{ nm}$ the FOM of ATOP-1 is almost an order of magnitude larger than for DMNPAA. The dispersive enhancement is much stronger for ATOP-1 than for DMNPAA due to the longer absorption wavelength of ATOP-1. It is important to note that this does not create marked absorption losses at 790 nm (see below) because of the sharp absorption band of ATOP-1. The possibility of utilizing such dispersive enhancement effects without paying the price of an increased absorption is another distinct advantage of the recently introduced merocyanine chromophores.⁴

Composites containing various amounts of ATOP-1 and/or DMNPAA, PVK, the plasticizer N-ethylcarbazole (ECZ), and the sensitizer (2,4,7-trinitro-9-fluorenylidene) malononitrile (TNFM) for use in the near infrared were prepared. In each case, T_g was adjusted close to room temperature by adding the appropriate amount of ECZ. First, we checked for the existence of aggregates of ATOP-1 at higher concentrations by optical absorption measurements on 100–200 nm thin films. The latter were spin-coated from toluene:cyclohexanone 4:1 solutions, and their exact thickness was determined with a profilometer. The spectra (Fig. 1) show that (i) the dependence of the optical density on the ATOP-1 content x is strongly sublinear, (ii) the main absorption band is red shifted to 548 nm for $x > 10\%$ wt compared to 545 nm for $x = 1\%$ wt and 540 nm in chloroform solution, (iii) the peak at $\lambda \approx 515 \text{ nm}$ increases relative to the main absorption band, and finally (iv), an additional shoulder appears at about 480–490 nm for the highest chromophore content. Qualitatively, we take these observations as an indication of dye aggregation. A more quantitative interpretation of this effect will be published elsewhere.⁹

As the second chromophore to increase the polarity of the matrix we chose DMNPAA due to its excellent compatibility with PVK. After addition of DMNPAA, the absorption spectrum reveals a strong increase of the absorption bands related to ATOP-1 and the ratio of the two main bands is increased (Fig. 1). This clearly indicates that the formation

of aggregates from ATOP-1 is reduced in the presence of DMNPAA, promising better PR performance of the mixtures. The fact that the absorption spectrum does not exhibit additional features shows that the improvement was not caused by complex formation between the two dyes or similar effects.

The PR properties of the different composites were investigated by degenerate four-wave mixing (4WM) and two-beam coupling (2BC) holographic experiments. The devices consisted of 105- μm -thick films of the respective composite sandwiched between two glass slides covered with transparent indium-tin oxide electrodes, to which the electric field could be applied. We define $E > 0$, when the cathode faced the pump beams. Two equally polarized writing beams ($\lambda = 790 \text{ nm}$, $\Phi \approx 2 \text{ mm}$) were overlapped inside the device with an angle of $2\theta_{\text{ex}} = 20^\circ$ in the commonly used tilted geometry (tilt angle $\psi_{\text{ex}} = 60^\circ$).^{1–7} In the 2BC experiments the power density of the amplified beam was $I = 0.25 \text{ mW/cm}^2$, the pump beam was 100 times stronger. The PR gain coefficient Γ was calculated according to Ref. 2. In 4WM experiments the index grating recorded in the PR material by two equally strong s -polarized writing beams ($I = 25 \text{ mW/cm}^2$) was read by diffracting a weak p -polarized probe beam ($I \approx 0.05 \text{ mW/cm}^2$) counterpropagating one of the pump beams. The field polarity was $E < 0$. The diffraction efficiency is given by $\eta = C_1 \sin^2(C_2 \Delta n)$, where Δn is the index modulation amplitude of the recorded hologram and C_1 and C_2 are constants.¹⁰ Thus, Δn is constant at the field of maximum diffraction efficiency $E(\eta_{\text{max}})$. Provided constant experimental conditions, $E(\eta_{\text{max}})$ can be regarded as a direct measure for the PR performance of a material. Assuming a linear dependence of the space-charge field on the externally applied field E ,⁶ a square dependence of Δn on E is expected. Thus, a factor X change in $E(\eta_{\text{max}})$ corresponds to a X^2 -fold change in Δn . This formalism is justified considering that the internal dc field in our experiment (the dielectric constant is $\epsilon > 6$) is much smaller than the saturation field $E_q \approx 60 \text{ V}/\mu\text{m}$ obtained for a similar PVK-based material.³

The field necessary to achieve complete internal diffraction for ATOP-1:PVK:ECZ:TNFM 20:45:33:2 was determined to be $E(\eta_{\text{max}}) = 65 \text{ V}/\mu\text{m}$,⁴ which is almost identical to the result obtained under similar experimental conditions with the recently published composite DHADC-MPN:PVK:ECZ:TNFM 25:49:25:1 [$E(\eta_{\text{max}}) = 59 \text{ V}/\mu\text{m}$ @ 830 nm].⁵ Note the higher chromophore content necessary in the latter case, which is probably related to the smaller FOM $F_\infty \approx 0.6 \times 10^{-74} \text{ C}^2 \text{ V}^{-2} \text{ m}^4 \text{ kg}^{-1} \text{ mole}$ for this chromophore.

For the reference composite DMNPAA:PVK:ECZ:TNFM 50:39:10:1 we obtained $E(\eta_{\text{max}}) = 71 \text{ V}/\mu\text{m}$. A tremendous improvement in PR performance was observed for the mixtures. Within a series of composites containing ATOP-1 and DMNPAA with varying ratio, but constant total content of 50% wt the best performance was achieved for the composition ATOP-1:DMNPAA:PVK:ECZ:TNFM 25:25:34:15:1% wt. $E(\eta_{\text{max}})$ occurred at only 33 V/ μm (Fig. 2, solid triangles). The grating buildup time was about 2 s at $E(\eta_{\text{max}})$. The absorption coefficient of the composite was $\alpha(790 \text{ nm}) = 15 \text{ cm}^{-1}$, limiting the external diffraction efficiency to about 85%. Thus, there is a factor of $(71/33)^2 \approx 4.6$ in Δn between the new and the reference composite

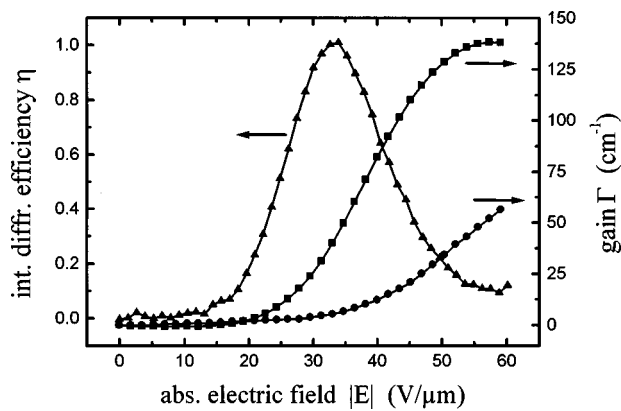


FIG. 2. PR Performance of ATOP-1:DMNPAA:PVK:ECZ:TNFM 25:25:34:15:1% wt: Dependence of the normalized internal diffraction efficiency η_p for p -polarized readout of a grating written by two s -polarized write beams (triangles) and the two-beam coupling gain coefficients Γ_p for p -polarized ($E < 0$, squares) and Γ_s for s -polarized ($E > 0$, circles) write beams on the absolute value of the applied electric field $|E|$.

(50% DMNPAA). From the FOMs one would expect $[25 \times (0.28 + 2.63)] / [50 \times 0.28] = 5.2$, assuming an ideal orientational behavior of the chromophores (no aggregates) and that the parameters determining the PR performance, such as T_g , magnitude of the space-charge field, etc. are identical. In any case, one can conclude that in the presence of DMNPAA most of the ATOP-1 chromophores contribute to the PR effect in agreement with the UV/VIS investigations. The new material by far outperforms previous materials.²⁻⁵

The apparent gain coefficient Γ depended strongly on the field polarity. It was recently demonstrated that this is a result of beam fanning, leading to the loss of transmitted light due to wave-guiding effects.^{11,12} For the field polarity, where no wave guiding occurs, the gain is only slightly affected by the fanning. Therefore, we present only this data ($E > 0$ for s polarization, $E < 0$ for p polarization). The apparent gain was as large as $\Gamma_p = 140 \text{ cm}^{-1}$ at $E = -60 \text{ V}/\mu\text{m}$ for p polarized (Fig. 2, solid squares) and $\Gamma_s = 60 \text{ cm}^{-1}$ at $E = +60 \text{ V}/\mu\text{m}$ (solid circles) for s -polarized light, thus clearly exceeding the absorption losses (15 cm^{-1}) in both cases. This is by a factor of about 2 larger than the gain reported in the Refs. 2-4 at $E = 60 \text{ V}/\mu\text{m}$.

Devices made from the optimized composite and stored under regular laboratory conditions did not show phase separation within the period of our investigation so far (approx. 2 to 3 months). However, due to the high content of low-molecular-weight components, the composite is thermodynamically metastable. At an elevated temperature of $T = 60^\circ\text{C}$ the devices showed after about one hour first indication of reduced transmission due to the formation of crystallites. This is to be compared to only about 60 s for the reference composite containing 40% wt DMNPAA under the same conditions.¹³ The shelf lifetime of the devices at room

temperature is expected to be about 4 to 5 orders of magnitude larger, since the diffusional mobility of the low-molecular weight components is drastically reduced around T_g .

In conclusion, chromophores with extremely large PR figure-of-merit have become available.⁴ However, in typical nonpolar photoconducting matrices (such as the commonly used PVK) aggregation of these rather polar dyes may occur, leading to a cancellation of the PR effect at high dye content. By incorporating an additional polar compound, we were able to influence this situation favorably. As a result, a new PR polymer composite was obtained which exhibits a tremendously enhanced performance compared to previously known materials.²⁻⁵ The material is sufficiently resistant against phase separation and performs in the near infrared, thus lending an excellent material for actual wide-spread applications such as real-time holographic optical processing using commercially available laser diodes. The new concept may also be applied to other highly polar PR dyes using a variety of different additives to increase the polarity.

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