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High-performance photorefractive organic glass with near-infrared sensitivity

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A high-performance organic glass mixture comprised of two dicyanomethylenedihydrofuran derivatives is presented. A pronounced two-beam coupling effect was observed at a wavelength of 830 nm in an unsensitized composition. Sensitization with (2,4,7-trinitro-9-fluorenylidene)malononitrile (TNFM) led to a significant increase in the two-beam coupling gain coefficient, reaching a net value of $\sim 370\ \mathrm{cm}^{-1}$ at an electric field of 45 V/μm at 1% TNFM, and resulted in an improvement in photorefractive speed. © *2003 American Institute of Physics.*
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The photorefractive (PR) effect, in which the refractive index of the medium changes under nonuniform illumination via space-charge field formation and electro-optic nonlinearity,[1] is of interest due to potential applications in dynamic holography, optical image processing, optical communication, and others.[2] During the past decade, PR organic materials have received considerable attention due to their low cost, easy processability, and possibility of manipulation of PR properties by chemical modifications. While most studies of PR polymers and organic glasses were carried out in the red wavelength region,[3–6] the extension to near-infrared (NIR) wavelengths has several advantages, which include the use of low-cost semiconductor diodes available at many NIR wavelengths, and the tissue transparency window at 700–900 nm in biological applications.[7,8]

The PR wavelength sensitivity is embedded in the photogeneration process, and is usually determined by a sensitizer added to the PR polymer composite and its interactions with the other components of the composite. In most NIR studies,[7,9–11] PR sensitization is achieved using (2,4,7-trinitro-9-fluorenylidene)malononitrile (TNFM, also called TNFDM) as a sensitizer, although organic glasses based on methine dyes, exhibiting NIR sensitivity without added charge generator, were reported.[12] To date, the best-performing materials in the NIR exhibit net gain coefficients of $\sim 120\ \mathrm{cm}^{-1}$ at an electric field of 30 V/μm,[10] 100% diffraction efficiencies at electric fields of 50–55 V/μm,[13] and PR response times of ~ 17 ms at an electric field of 84 V/μm and total intensity of $\sim 3\ \mathrm{W/cm}^2$,[12] all at wavelengths of 780–790 nm.

Recently, we reported several high-performance monolithic organic glasses containing dicyanomethylenedihydrofuran (DCDHF) chromophores, sensitized with either C_{60} or TNFM.[11] In this letter, we report on improved NIR (830 nm) performance of a DCDHF mixture, sensitized with TNFM. Much higher gain coefficients and enhanced PR response speed are achieved in this glass compared to previously studied DCDHF/TNFM composites.[11]

Samples were prepared from a 1:1 wt mixture of DCDHF-8 and TH-DCDHF-6V chromophores (inset of Fig. 1), sensitized with TNFM, added at the concentrations of 0, 0.1, or 1 wt %. The detailed synthesis, thermal properties, and sample preparation of DCDHF glasses were reported elsewhere.[11,14] The thickness of the samples (d) was $80 \pm 5\ \mu$m. The DCDHF-8 chromophore itself forms an unstable glass with glass transition temperature $T_g \sim 1\ ^\circ$C,[11] while TH-DCDHF-6V does not form a glassy state. By mixing these two chromophores in 1:1 wt ratio, we obtained a glass-forming compound with $T_g \sim 23\ ^\circ$C, which was stable for several weeks. We assume that addition of 0%–1% TNFM does not influence the T_g. All measurements were done at room temperature ($\sim 21\ ^\circ$C).

The chemical structures of the two chromophores as well as their normalized solution absorption spectra are shown in the inset of Fig. 1. Absorption coefficients (α) obtained in PR

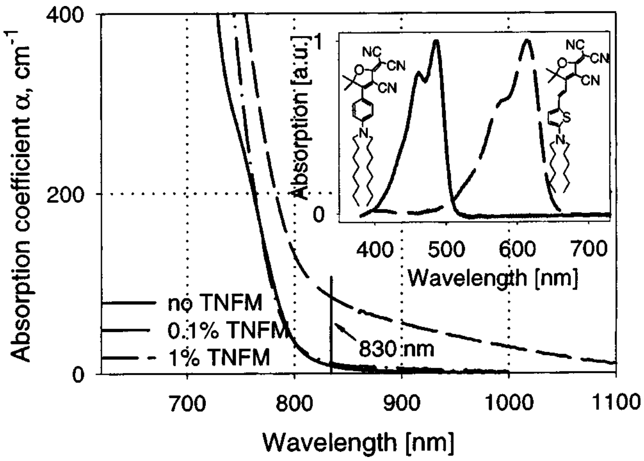

FIG. 1. Wavelength dependence of the absorption coefficient of photorefractive samples made with a 1:1 TH-DCDHF-6V/DCDHF-8 composition sensitized with either 0%, 0.1%, or 1% TNFM. Inset shows normalized absorption spectra of TH-DCDHF-6V (right) and DCDHF-8 (left) molecules in toluene. Chemical structures of the molecules are also shown.

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samples of the TH-DCDHF-6V/DCDHF-8 mixture sensitized with 0%, 0.1%, and 1% TNFM as a function of wavelength are also shown in Fig. 1. In the unsensitized (0% TNFM) samples, an absorption coefficient $\alpha = 9.9\ \mathrm{cm}^{-1}$ is obtained at $\lambda = 830$ nm. Adding 0.1% and 1% TNFM resulted in the absorption coefficient increasing to $\alpha = 12.8$ and $\alpha = 87.8\ \mathrm{cm}^{-1}$, respectively.

The photoconductive properties of our samples at 830 nm were examined using a conventional dc technique.[11] At an electric field of 15 V/μm, all three composites exhibited a similar dark conductivity of ~0.03 pS/cm. At this same electric field and with light intensity of 20 mW/cm^2, the photoconductivity obtained in the 0%, 0.1%, and 1% TNFM samples was 0.37, 0.78, and 1.75 pS/cm, respectively. Similar to DCDHF/C$_{60}$ glasses studied at 676 nm,[11] all three composites exhibited close to linear intensity dependencies of photoconductivities ($\sigma_{\mathrm{ph}} \sim I^a$, with $a = 0.96$–0.98) at 830 nm. The photoconductivity values given above are "apparent" values, calculated from the measured total current (i), dark current (i_d), applied electric field (E), and electrode area (S): $\sigma_{\mathrm{ph}} = (i - i_d)/(ES) = \sigma_{\mathrm{tot}} - \sigma_d$, where σ_{tot} is the total conductivity, and σ_d is dark conductivity. To assign the change in photoconductivity upon sensitization to a certain process, it is necessary: (i) to account for the beam attenuation responsible for a deviation of "apparent" values of photoconductivity from intrinsic values,[15] and (ii) to eliminate the contribution of the increase in absorption to the increase in photoconductivity. (i) In the samples with relatively large absorption coefficients, the beam considerably attenuates as it propagates through the medium. If the absorbing medium is viewed as a sequence of resistors[15] whose resistance increases monotonically as the beam is attenuated, then the intrinsic photoconductivity (σ^i_{ph}) of the sample (assuming uniformly illuminated electrodes) is

$$\sigma^i_{\mathrm{ph}} = \sigma_d \frac{\exp[\alpha d a] - \exp[\alpha d a \sigma_d/\sigma_{\mathrm{tot}}]}{\exp[\alpha d a \sigma_d/\sigma_{\mathrm{tot}}] - 1}, \qquad (1)$$

where a is a power law exponent ($\sigma^i_{\mathrm{ph}} \sim I^a$), d is the sample thickness, and α is the absorption coefficient. At small absorption coefficients ($\alpha d \ll 1$), Eq. (1) transforms into a commonly used form: $\sigma^i_{\mathrm{ph}} = \sigma_{\mathrm{tot}} - \sigma_d$.
(ii) To normalize the intrinsic photoconductivity values at the absorbed light intensity, we introduce the normalized photoconductivity ($\sigma_{\mathrm{ph},n}$) as follows: $\sigma_{\mathrm{ph},n} = \sigma^i_{\mathrm{ph}}/[1 - \exp(-\alpha d)]$ and compare its values for all three TNFM concentrations. In the case of 0%, 0.1%, and 1% TNFM, $\sigma_{\mathrm{ph},n}$ yields values of 5.1, 8.7, and 4.9 pS/cm, respectively. Normalized photoconductivity is directly proportional to photogeneration efficiency, charge carrier mobility, and charge carrier lifetime. Upon sensitization, only photogeneration efficiency is likely to increase, while mobility and charge carrier lifetime should decrease due to increased trap density.[16–18] We attribute the increase in $\sigma_{\mathrm{ph},n}$ in our 0.1% TNFM sensitized DCDHF glass to improved photogeneration efficiency. The decrease upon further sensitization is most likely due to reduced mobility and enhanced trapping and recombination, limiting the carrier lifetime, which counteract increased charge photogeneration, so that overall free charge carrier density is reduced. We observed a several orders of magnitude increase in both dark and photoconductivity in all our samples at the eventual onset of crystallization, possibly due to increase in charge carrier mobility in a crystalline phase. Since the phase heterogeneity significantly affects the experimental results, only fresh samples without crystallization were used for all the measurements reported here.

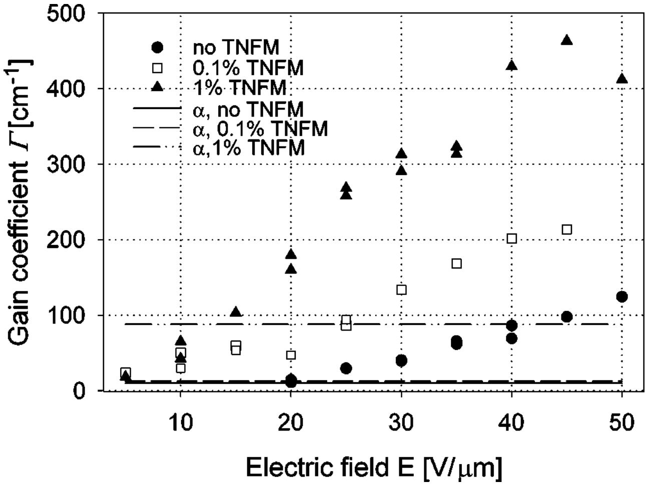

FIG. 2. Gain coefficient as a function of applied electric field in TH-DCDHF-6V/DCDHF-8 glass sensitized with either 0%, 0.1%, or 1% TNFM. Double symbols correspond to different samples. Lines illustrate the absorption coefficients measured in the samples.

The electric-field-induced birefringence (Δn_{BR}) was evaluated in a transmission ellipsometry measurement.[11] As with other DCDHF glasses, high birefringence values of ~0.01 at an electric field of 35 V/μm were achieved in TH-DCDHF-6V/DCDHF-8 mixture. The values of orientational speed $k_{\mathrm{BR}} \sim 0.07\ \mathrm{s}^{-1}$ and dispersion parameter $\beta \sim 0.8$–0.9, obtained from stretched exponential fits to the birefringence rise in response to a step-function electric field $\{\Delta n_{\mathrm{BR}} \sim 1 - \exp[-(k_{\mathrm{BR}} t)^{\beta}]\}$, are typical for DCDHF glasses measured at the same temperatures relative to T_g.[11,19]

The PR experiments were conducted at a wavelength of 830 nm, as previously described.[11,19] The two-beam coupling experiment was performed at total light intensity of 100 mW/cm^2 at various electric fields. Gain coefficients (Γ) obtained in unsensitized and 0.1% and 1% TNFM sensitized composites as a function of electric field are shown in Fig. 2 (double symbols correspond to different samples). Net gain $(\Gamma - \alpha) > 0$ was achieved at electric fields of 5–25 V/μm, depending on the composite. As seen in Fig. 2, even without TNFM, considerable net gain coefficients of $\sim 100\ \mathrm{cm}^{-1}$ at 50 V/μm are obtained in the TH-DCDHF-6V/DCDHF-8 mixture. The importance of a sensitizer for steady-state PR performance has been previously indicated.[16–18,20] In our composites, sensitization with 0.1% TNFM led to a more than two-fold increase in the gain coefficient ($\sim 200\ \mathrm{cm}^{-1}$ at 40 V/μm), in comparison with that of the unsensitized composite ($\sim 80\ \mathrm{cm}^{-1}$ at 40 V/μm). Increases in TNFM concentration up to 1% resulted in an additional twofold increase in gain coefficient ($\sim 415\ \mathrm{cm}^{-1}$ at 40 V/μm). Similar to other DCDHF glasses,[11] even in a geometry minimizing amplified scattering, TH-DCDHF-6V/DCDHF-8 composites exhibited strong beam-fanning effects, which led to saturation and/or decrease in the gain coefficient at electric fields above ~45–50 V/μm. The observed increase in gain coefficient as a function of sensitizer concentration is due to improved

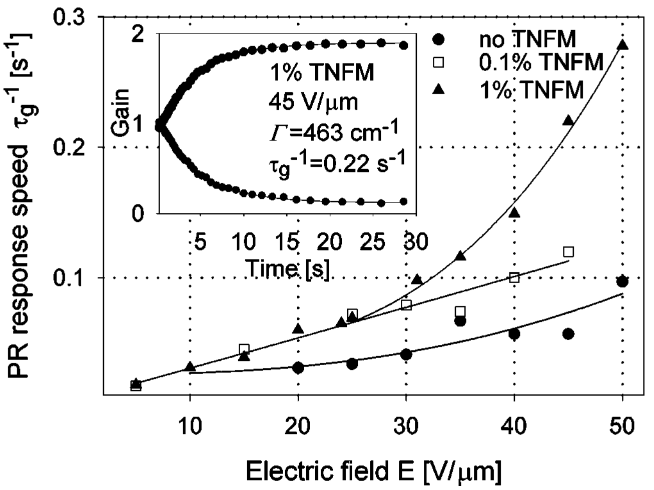

FIG. 3. Photorefractive response speed as a function of electric field in TH-DCDHF-6V/DCDHF-8 glass sensitized with either 0%, 0.1% or 1% TNFM. Lines are guides for eye. Inset shows a single exponential fit (lines) to the gain signal (symbols) measured at an electric field of 45 V/μm and total light intensity of 100 mW/cm^2 in TH-DCDHF-6V/DCDHF-8 glass sensitized with 1% TNFM.

photogeneration efficiency as well as higher effective trap density,[18] a key determinant of the gain coefficient.[16] Similar trends were observed in poly(*N*-vinylcarbazole) (PVK)-based composites as the concentration of TNFM increased from 0% to ~1.5% TNFM.[17] However, the change in gain coefficient is much larger in the present case.

To analyze the dynamics of the two-beam coupling effect, we fit the growth transients obtained in two-beam coupling experiments with a single exponential function [$\gamma \sim 1 - \exp(-\tau_g^{-1} t)$, where γ is a ratio of signal beam intensity with and without pump beam] and determined response speed τ_g^{-1} as a function of electric field. A representative fit of the data obtained at an electric field of 45 V/μm and total writing-beam intensity of 100 mW/cm^2 in the sample containing 1% TNFM is shown in the inset of Fig. 3. At these experimental conditions, the sample yielded a gain coefficient $\Gamma = 463$ cm^{-1} and a response speed τ_g^{-1} of ~0.22 s^{-1}. Figure 3 shows the electric field dependence of τ_g^{-1} obtained in 0%, 0.1% and 1% TNFM sensitized samples. At low electric fields, PR response speed is ~0.02–0.04 s^{-1} in all composites, which indicates a limitation of the chromophore reorientational speed, independent of sensitization, to the PR dynamics. As the electric field increases, the PR response speed increases in all samples due to the increased contribution of photoconductivity to PR dynamics. At electric fields above ~35 V/μm, a significant difference in response speed is obtained in the composite containing 1% TNFM compared to those containing 0.1% or 0% TNFM. We note that as with photoconductivity, the measured ("apparent") PR response speed in the 1% TNFM compound could underestimate the true speed.[15] Therefore, the intrinsic response speed in this compound is likely to be higher than that shown in Fig. 3.

In conclusion, we have presented a high-performance DCDHF-containing PR organic glass, with PR sensitivity in the NIR wavelength region. Unsensitized samples exhibited significant two-beam coupling net gain coefficients, which drastically increased upon sensitization with TNFM, reaching the value of ~370 cm^{-1} at an electric field of 45 V/μm in the sample containing 1% TNFM. Similarly, the PR response speed (τ_g^{-1}) increased upon TNFM sensitization and yielded a value of ~0.28 s^{-1} at an electric field of 50 V/μm and light intensity of 100 mW/cm^2. Finally, it is possible to modify the mixture studied here by mixing the TH-DCDHF-6V chromophore with other DCDHF derivatives[14] and fine-tune its T_g to 17–18 °C. This would lead to an order of magnitude improvement in PR dynamics at room temperature,[19] preserving excellent steady-state performance. More generally, future studies should pursue DCDHF chromophores with both intrinsic longer wavelength absorption and glass-forming properties.

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