Photorefractive Polymers with Non-Destructive Readout**

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Photorefractive polymers are suitable for real-time holographic applications. Since the recording and readout of a hologram is carried out with laser beams with the same wavelength, the readout process partially erases the stored information, a problem common to all current photorefractive materials and referred to as destructive readout. In this paper we describe photorefractive polymers that are sensitized by two-photon absorption. Holographic recording is achieved with high-intensity writing beams and readout using low light intensity, but high power beams. Using this nonlinear recording scheme, non-destructive readout was demonstrated.

1. Introduction

Photorefractive materials are being investigated for their use as phase recording media for holographic applications. Photorefractivity is a reversible process that provides the material with the dynamic response that is needed for real-time holographic applications. Photorefractive materials combine photoconductivity and a field-induced mechanism to change the refractive index. Optical excitation of these materials by interfering laser beams generates a spatially inhomogeneous distribution of carriers. The redistribution and trapping of these carriers over macroscopic distances leads to the build-up of an internal electric field that in turn changes the refractive index of the material. After recording, the holograms can be erased with a spatially uniform light beam. An attractive feature of holographic recording and processing techniques is the serial nature of the recording and retrieval of information, leading to fast data transfer rates. In holographic storage for instance,[1] the reconstruction of an entire page of digital information stored can be performed by sending on a detector array the signal of a spatially homogeneous reading beam that is diffracted by the index modulation of the phase hologram. To achieve high diffraction efficiency during information retrieval, or high angular selectivity for the multiplexing of numerous holograms (such as to obtain high storage densities), the phase holograms are generally written in thick media. To retrieve a particular page of information with a good fidelity, the reading and writing beams must have the same wavelength. Since the material is photosensitive at this wavelength, the readout process partially erases the stored information, a problem referred to as destructive readout.

In inorganic photorefractive crystals several methods have been proposed to achieve non-destructive readout without compromising the overall ability to erase the hologram when desired. The first method proposed by von der Linde was based on two-photon absorption (TPA)[2] and involved the use of high-intensity writing beams for recording and low light intensity for readout. Later it was shown that the peak intensity needed for two-photon recording could be reduced by using two-step resonant excitation,[3] which involves the excitation of an intermediate state. Other methods that avoid large recording intensities are based on the population of photochromic centers.[4]

Recently, photorefractive polymers have emerged[5] as a low cost alternative to photorefractive crystals. Polymer composites with high diffraction efficiency,[6] two-beam coupling gain coefficients,[6] and millisecond response times[7] have been demonstrated. However, except for the observation of quasi-non-destructive readout in a photorefractive polymer under low reading intensity,[8] non-destructive readout has been demonstrated in these new materials only recently.[9] Independently, TPA in organic molecules and polymers has gained increasing attention in recent years for three-dimensional fluorescence imaging,[10] and microfabrication.[11] New strategies[12,13] for the design of molecules with large nonlinearities led recently to the synthesis of new molecules with unprecedented TPA cross sec-

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tion δ. Here, we present a detailed study of the TPA properties of a photorefractive polymer composite based on poly(*N*-vinylcarbazole) (PVK) a standard p-type photoconductor doped with the molecule 4-{[4-(2-ethoxyethoxy)phenyl]ethynyl}-2,6-difluorobenzonitrile (FTCN) that has the dual function of being a two-photon sensitizer and the chromophore leading to refractive index changes due to orientational photorefractivity.[14] The paper is organized as follows: we first discuss the design requirements for a two-photon photorefractive polymer composite. Then, we present a detailed experimental study of the linear and nonlinear absorption properties of our new composites, as well as the results of quantum chemical calculations of the TPA cross section of the sensitizer. Recording of volume holograms with femtosecond pulses using TPA and their nondestructive readout using cw lasers with the same wavelength is demonstrated in the last section.

2. Design of Two-Photon Photorefractive Polymer Composites

As for inorganic materials, polymers must combine several key functionalities to exhibit photorefractive properties: weak absorption, transport of either positive or negative carrier species, trapping, and a field-induced refractive index modulation mechanism. Owing to the rich structural flexibility of organic molecules and polymers these functionalities can be incorporated into a given material in many different ways. The organic materials can be amorphous as is the case for polymer composites,[5–8] or exhibit liquid crystalline phases,[15,16] or can consist of nanocomposite phases such as polymer dispersed liquid crystals,[17,18] or hybrid materials such as sol–gels.[19] In each of these materials, the following functions must be incorporated: photogeneration of charge carriers, their transport, and trapping, and a field-induced refractive index modulation. Any of these functions can be performed by a particular component of the photorefractive polymer composite or some dopants can be multifunctional.[20] Glass forming chromophores, for instance, with charge-transport properties have been proposed as organic photorefractive materials.[21] In most of these materials, the glass-transition temperature of the polymer composite is close to room temperature and allows for the reorientation of the chromophores by the total electric field, which is the sum of the applied field and the photogenerated space-charge field. In such materials, high refractive index modulation amplitudes can be achieved through orientational photorefractivity.

To produce two-photon photorefractive polymers, we designed a polymer composite in which the chromophore was bifunctional and provided for photosensitivity and refractive index changes. Transport was provided by the well-known PVK matrix and plasticizers were added to allow for orientational photorefractivity. The material we studied had the following composition: FTCN/PVK/BBP/ECZ 25:55:10:10 wt.-%. BBP and ECZ stand for benzyl butyl phthalate and *N*-ethylcarbazole, respectively, and were used as plasticizers to lower the glass-transition temperature. The molecular structures of these compounds are shown in Figure 1. Samples for our studies

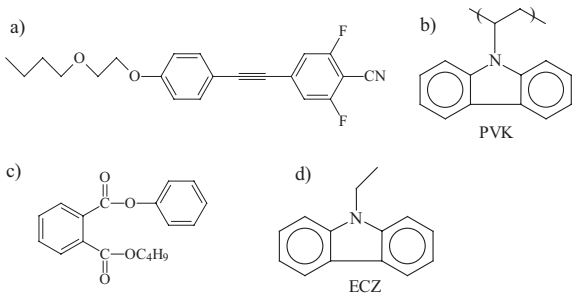

Fig. 1. Structure of the compounds mixed in the photorefractive polymer composite used in our experiments: a) the chromophore and nonlinear absorber FTCN, b) the hole transport polymer PVK, c) and d) the plasticizers BBP and ECZ, respectively.

were obtained by melting the polymer composite between two indium tin oxide (ITO) coated transparent electrodes. By having the chromophore as the TPA sensitizer, large enough nonlinear absorption can be obtained without diluting the compounds that provide for transport and electro-optic activity.

TPA is a third-order nonlinear optical process[22,23] that leads to an intensity dependent absorption coefficient $\alpha = \alpha_2 I$ when the linear part of the absorption is ignored. α_2 is the nonlinear absorption coefficient. Consequently, TPA can be observed in all materials and does not have non-centrosymmetric symmetry requirements as for even-order nonlinear optical effects. Nevertheless, in centrosymmetric molecules and polymers, two-photon absorption is allowed between states that have the same parity according to parity selection rules. In short organic conjugated molecules with a large bond length alternation, the lowest excited state ^1B_u is usually one-photon allowed and two-photon forbidden. Two-photon allowed states are higher in energy. Here, FTCN is a non-centrosymmetric donor–acceptor tolane (diphenylacetylene) derivative that can be approximated by the three-level model shown in Figure 2. The lowest excited state $|1\rangle$ in such compounds is two-photon allowed. Recent studies have shown that higher TPA cross sections can be obtained between the ground state $|0\rangle$ and the higher energy excited state $|2\rangle$. When reaching the level $|2\rangle$ by TPA,[12] the overall TPA cross section is enhanced by a quasi-resonance effect associated with the small detuning between the one-photon transition and the lowest excited state $|1\rangle$ (such an en-

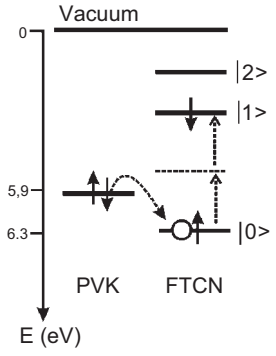

Fig. 2. Schematic of the relative position of the frontier orbitals of the two-photon sensitizer FTCN and the photoconducting matrix PVK. Full arrows denote electrons and their spin, dashed arrows show optical transitions and electron transfer reactions.

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hancement is particularly pronounced when driving the structure towards the cyanine limit). However, in this case it is difficult to maintain nearly zero linear absorption due to one-photon absorption because of the spectral proximity of the one-photon transition and the broad absorption band associated with the $|0\rangle - |1\rangle$ transition. To avoid this problem, we excited by TPA the lowest excited state of the FTCN chromophore.

For the observation of photorefractivity under two-photon excitation, the polymer composite should exhibit an absorption coefficient of a few cm^{-1} at optical intensities that are below the damage threshold of the sample. On a molecular level, the nonlinear response is characterized by the TPA cross section δ for which the unit is GM (for Göppert–Mayer) with $1\ GM = 10^{-50}\ cm^4\ s\ photon^{-1}$. α_2 and δ are related through

$$\alpha_2 = \frac{N\delta}{h\omega} \tag{1}$$

where N is the density of molecules, and $h\omega$ the photon energy. At a 25 wt.-% loading level of the sensitizer with a molecular weight of $M = 355$ g and assuming a density of $\rho = 1\ g\,cm^{-3}$ we obtain a density of sensitizers of $N = 4.2 \times 10^{20}\ cm^{-3}$. With $\delta = 100$ GM, $1\ GW\,cm^{-2}$ of optical intensity with 1.9 eV photon energy leads to an absorption coefficient of $1.4\ cm^{-1}$. Hence, we anticipate that intensities of a few $GW\,cm^{-2}$ will be required to observe two-photon photorefractivity in our polymer composites. These intensity levels are below the damage threshold of these samples for excitation at 650 nm.

After excitation of the sensitizer by TPA, its relative energy levels must be appropriate to enable an electron transfer reaction to PVK, which is the transport material. As illustrated in Figure 2, a hole can be injected efficiently into the PVK matrix if the ionization potential (IP) of the sensitizer is higher than that of PVK (i.e., higher then 5.9 eV). The ionization potential of FTCN was evaluated by cyclic voltammetry experiments performed on the molecule in 0.005 M solutions of acetonitrile using the ferrocene/ferrocenium couple as a reference. An IP value of 6.35 eV could be deduced from the relative oxidation potential. Hence, we believe that photoconduction in PVK is activated by electron transfer from the highest occupied molecular orbital (HOMO) level of neutral PVK into the FTCN HOMO, followed by field-induced dissociation to prevent geminate recombination.

3. Linear and Nonlinear Optical Properties

Here, we present a characterization of the optical properties of 105 μm thick samples of FTCN/PVK/BBP/ECZ. Figure 3a shows the linear absorption spectra of such samples. For comparison, we have included the spectrum of a traditional sample that also contained C_{60} as a one photon sensitizer. These spectra show that with a one-photon sensitizer such as C_{60} the absorption spectrum has a long tail that extends into the near infrared. Absorption is usually provided not only by the sensitizer itself but through formation of charge transfer complexes with transport moieties or the chromophore. In contrast, the

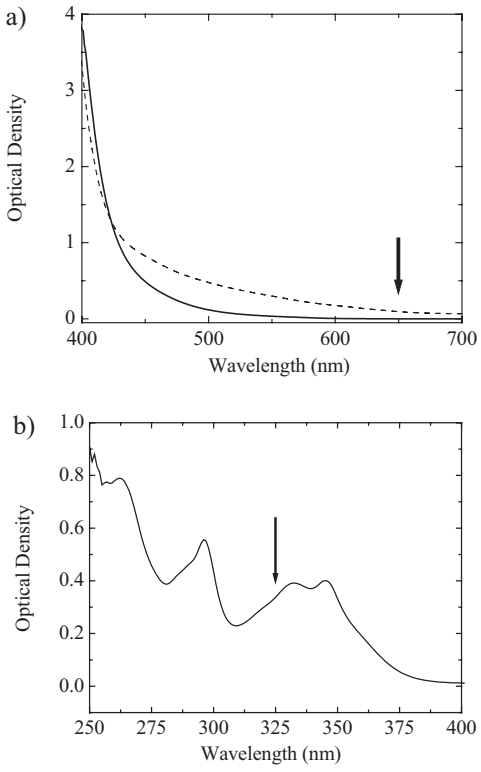

Fig. 3. a) Linear absorption spectra of a two-photon photorefractive polymer with composition FTCN/PVK/BBP/ECZ (full line) and that of a sample with composition FTCN/PVK/BBP/ECZ/C_{60} 49.5:35:5:10:0.5 wt.-% (dashed line). The arrow indicates the spectral location of the laser source. b) Linear absorption spectrum of a thin film of the sample with composition FTCN/PVK/BBP/ECZ, showing the lowest excited state of the FTCN molecule. The arrow indicates the spectral position of the two-photon excitation.

two-photon photorefractive polymer does not show any detectable linear absorption at wavelengths beyond 600 nm in a 105 μm thick sample. Note however, that residual absorption is observed for wavelengths up to 550 nm despite the fact that the chromophore has an absorption maximum of 340 nm as shown in Figure 3b.

To measure the two-photon absorption coefficient of the photorefractive polymer composite, we performed single-beam nonlinear transmission experiments with femtosecond pulses. Ignoring any background linear absorption and any higher-order effects, the transmitted intensity from a sample of thickness d is given by:

$$I(d) = \frac{I_0}{1 + \alpha_2 I_0 d} \tag{2}$$

where I_0 is the incident intensity. Using Equation 2 we calculated the best fit to the experimental data obtained for excitation intensities ranging between 0.5 and 25 $GW\,cm^{-2}$ using α_2 as a fitting parameter. As shown in Figure 4 a good fit was obtained for $\alpha_2 = 1 \times 10^{-9}\ cm\,W^{-1}$. According to Equation 1, this value yields a molecular TPA cross section of $\delta = 75$ GM at 620 nm. To check that at these high intensities we did not induce any permanent damage to the sample, we also recorded the fluorescence from the FTCN molecules excited by TPA during these experiments. As shown in Figure 5, the spectrally

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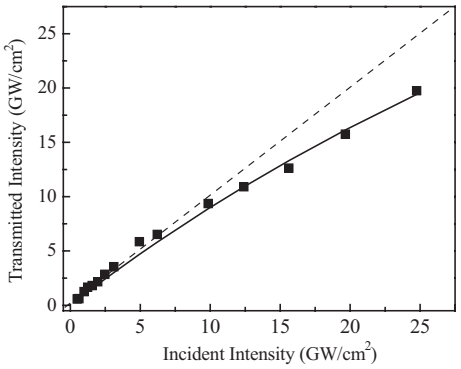

Fig. 4. Nonlinear transmission data measured in 105 μm thick samples of FTCN/PVK/BBP/ECZ. Symbols are experimental data, the solid line is a fit using Equation 2. The dashed line shows a linear fit.

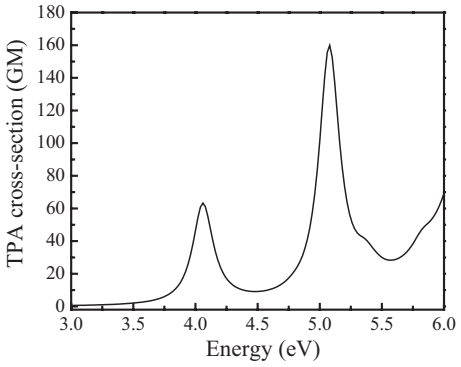

Fig. 6. Calculated two-photon absorption spectra for the chromophore FTCN. Linewidth has been set to 0.1 eV. Note that the energy of the incoming light has been multiplied by two.

integrated luminescence originating from the chromophore has a quadratic dependence on the excitation intensity for values of the excitation up to 25 GW cm^{-2}, as expected for TPA. Note, that the relatively strong fluorescence from the sensitizer indicates that the photogeneration efficiency of free carriers is rather low in these samples and that geminate recombination is strong.

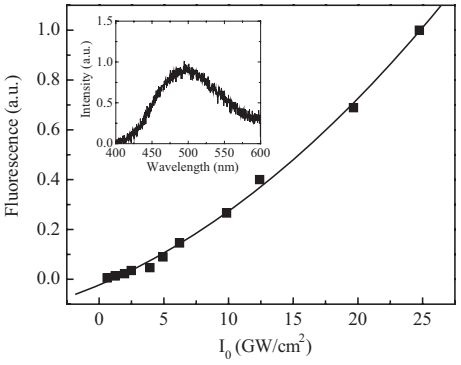

Fig. 5. Spectrally integrated fluorescence intensity detected from the FTCN/PVK/BBP/ECZ sample as a function of excitation intensity when excited at 620 nm. Symbols are experimental data; the solid line is a quadratic fit. Inset: fluorescence spectrum of the FTCN chromophore.

4. Theory of Two-Photon Absorption

To verify that the TPA cross sections measured from nonlinear absorption measurements were sound, we also conducted quantum chemical calculations of δ for the molecule FTCN. The methodology adopted to calculate the TPA cross section has been described in detail elsewhere.[12,24] Briefly, the ground-state geometry of the molecule is first fully optimized at the AM1 level.[25] The equilibrium geometric structure is then used as input for excited-state calculations, performed at the intermediate neglegt of differential overlap/multireference determinant confirmation interaction (INDO/MRD-CI) level.[26] The Ohno–Klopman[27] potential has been adopted to depict electron–electron interactions. Figure 6 shows the simulated two-photon absorption spectra. A TPA cross section on the order of 60 GM is calculated at the first resonance peak (incident photons at ~2 eV). This resonance corresponds to the lowest singlet excited state $|1\rangle$ (related to the ^1B_u state of the unsubstituted molecule) that dominates the linear absorption spectrum. This value is in good agreement with the experimental value deduced from nonlinear transmission experiments.

The mechanism for the TPA response in the molecule investigated can be described on the basis of the energy diagram shown in Figure 2. Calculated values of the transition dipole moments for the transitions $|0\rangle$–$|1\rangle$ and $|1\rangle$–$|2\rangle$ are 7.5 D and 6.7 D, respectively. For two-photon absorption in the lowest energy excited state $|1\rangle$, it turns out that a two-state model (including the ground state and the lowest excited state) usually provides a reliable estimate of δ.[12] Within such a model, the TPA cross section has been shown to be controlled by the amount of charge transfer from the donor to the acceptor through the bridge and the associated difference in state dipole moment[12] (which is calculated to be on the order of 8 D in the present molecule). Note that a second, more intense, TPA resonance is calculated at higher energy (peak at ~2.5 eV) and involves an excited state whose wavefunction is reminiscent of the ^2A_g state in the unsubstituted conjugated bridge. As found previously,[12] part of the enhancement in δ for resonance into this state is due to a favorable detuning energy (difference between half the energy of the target TPA state and the energy of the lowest excited state) that enters the expression of the TPA cross section. Based on these calculations, TPA excitation of the higher energy excited state $|2\rangle$ would require excitation with a laser emitting at around 500 nm. As shown in Figure 3a, the sample has substantial linear absorption at this wavelength, preventing efficient excitation by TPA solely.

5. Four-Wave Mixing Results

To investigate the recording of photorefractive gratings in our polymers, we performed four-wave mixing experiments with a femtosecond laser source emitting at 650 nm. Figure 7 shows

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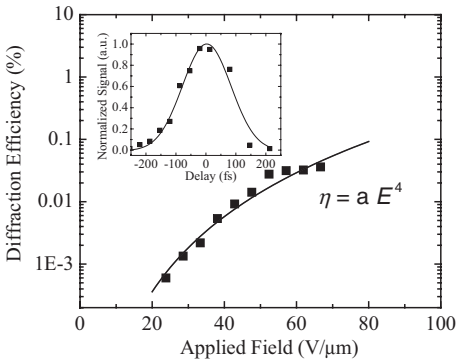

Fig. 7. Diffraction efficiency as a function of applied field. Squares are experimental points. The solid line is the function $\eta = aE^4$ with $a = 2.25 \times 10^{-9}$, where E is the applied field. The sum of the intensities of the two writing pulses was 5 GW cm^{-2}, measured at maximum temporal overlap of the writing beams. Inset: Diffraction efficiency as a function of the delay between the two writing pulses measured at an applied field of 50 V μm^{-1} and with an average power of the writing beams of 0.5 mW (5.3 GW cm^{-2}). The squares are experimental points and the solid line is a fit with a Gaussian function.

the diffraction efficiency η defined as the ratio between the intensities of the diffracted and the incident beams as a function of the applied field. For a nearly lossless media and for small refractive index changes, the diffraction efficiency for a thick phase grating is given by:

$$\eta = \left(\frac{\pi \Delta n L}{\lambda \, (c_i c_d)^{1/2}} \right)^2 \tag{3}$$

where L is the thickness of the grating, λ the wavelength, c_i and c_d are obliquity factors for the incident and diffracted beams, respectively. For our geometry, they are given by: $c_i = \cos\alpha_1$ and $c_d = \cos\alpha_2$ with $\alpha_1 = 11.6°$ and $\alpha_2 = 30.6°$. Note, that due to the finite coherence length of the pulsed laser source used for these experiments and the non-colinear propagation of the two writing beams, the effective thickness of the grating is smaller than the sample thickness. For orientational photorefractivity, using the oriented gas model in the low poling field approximation, the refractive index modulation amplitude is given by:[19,21]

$$\Delta n = \frac{2\pi}{n} A f(N, \Delta\alpha, 1/T, \mu^2) E_{ext} E_{sc} \tag{4}$$

where A is a geometrical factor and f is a number that depends on the density of chromophores, which in our case is also the density of TPA sensitizers, on their polarizability anisotropy $\Delta\alpha$, on the square of their permanent dipole moment μ and the temperature T. E_{ext} is the external field applied between the ITO electrodes and E_{sc} is the amplitude of the photorefractive space-charge field, which, according to the Kukhtarev model, is proportional to the applied field when the photorefractive trap density is high enough. Under such conditions, according to Equations 3 and 4, the diffraction efficiency is expected to vary as the fourth power of the applied field. Such a fit is shown as a solid line in Figure 7 and suggests that the photorefractive space-charge field is saturated for field values up to 65 V μm^{-1} where a maximum diffraction of $\eta = 0.03$ % is measured. The build-up time to reach steady-state conditions was of the order of a few seconds. This slow response time can be attributed to a small photogeneration efficiency as discussed above. This response time also supports the attribution of these gratings to the photorefractive effect and rules out the assignment of these gratings to electronic effects that might occur with high intensity laser pulses, since such electronic effects would have a nearly instantaneous response.

To study the dynamic nature of the gratings, we measured the diffraction efficiency η as a function of the delay between the two writing beams. In this experiment, for each data point, the value of the delay between the writing beams was pre-set and the diffraction efficiency was allowed to reach a steady-state value. This took a few seconds for each new value of the delay. The diffraction efficiency increased as the temporal overlap of the beams was increased and reached a maximum for zero delay when the visibility of the fringes of the two interfering beams was the highest. When the delay was further increased, the visibility of the fringes was reduced and the diffraction efficiency was decreased accordingly as expected for a dynamic grating.

To demonstrate non-destructive readout, we changed the wavelength of the pulsed laser source experiments to 700 nm and replaced the pulsed reading beam with a cw laser diode emitting at the same wavelength. No changes in diffraction efficiency could be detected for a reading power as high as 5 mW, which is an order of magnitude higher than the average power of the pulsed writing beams. However, when one of the pulsed writing beams was blocked, the grating could be erased completely within a few seconds. No evidence of any grating was found when wave-mixing experiments were performed entirely with the cw laser diode. The power stability of our laser source did not provide us with the sensitivity required to perform two-beam coupling experiments in our samples in view of the low index changes.

Finally, we performed cw photoconductivity experiments at a wavelength of 633 nm on two-photon photorefractive polymers and compared the results to those of a reference sample that has been doped with the one photon sensitizer C_{60}. As shown in Figure 8, no one-photon photoconductivity could be detected in the two-photon photorefractive polymers with composition FTCN/PVK/BBP/ECZ within the detection limit of our experiment. In contrast, a sample doped with C_{60} shows the typical increase in photoconductivity as the intensity of the excitation is increased.

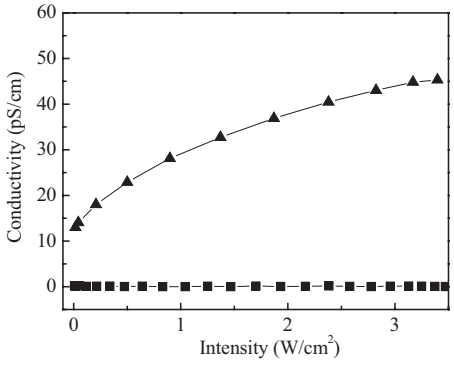

Fig. 8. Photoconductivity as a function of intensity measured with a cw He:Ne laser at 633 nm in samples with compositions PVK/FTCN/BBP/ECZ (■) and PVK/FTCN/BBP/ECZ/C_{60} (▲). The applied field was 38 V μm^{-1}.

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6. Conclusions

In conclusion, we demonstrated the recording of holograms in a photorefractive polymer through TPA and their non-destructive readout with a cw beam. In the studies presented here, photoconductivity was enabled by the initial two-photon excitation of a sensitizer followed by an oxidation of the hole-transport moieties, leading to transport. The field dependence of the diffraction efficiency was strongly supportive of the photorefractive nature of the grating. Note, that our work differs completely from the studies reported by Gu et al. on the use of a photorefractive polymer to write three-dimensional bits of information by use of TPA.[28] In the latter experiments, local index changes are produced in the bulk of the polymer at the focus of the laser beam without a bias electric field. In such a case, charge generation and charge transport are negligible and the build-up of a photorefractive space-charge field very improbable. However, at the excitation wavelength used the two-photon excitation is resonant with the π–π* absorption of the azo-benzene chromophore 2,5-dimethyl-4-(*p*-nitrophenyl-azo)anisole (DMNPAA), which is known to undergo reorientation through multiple trans–cis photoisomerization processes when excited with polarized light.[29] This process does not require any applied field and is the most probable origin of the index changes that were observed.

Our experiments should be considered proof-of-principle experiments as the diffraction efficiency measured in these samples are rather small at this stage, and the response time of the order of a few seconds. However, we believe that the observation of non-destructive readout is an important milestone in the development of photorefractive polymers and that future studies on two-photon photorefractivity will address some of the current limitations by capitalizing on the progress made in developing organic molecules with high TPA cross sections. In future work it will be important to optimize TPA cross sections to allow for the use of longer pulses (picoseconds) to increase the coherence length and effective thickness of the holograms. Nonlinear effects associated with the nonlinear recording scheme will have to be addressed. Two-photon photorefractive polymers can play an important role in providing ways to extend the sensitivity of these materials to the telecommunication wavelengths as demonstrated for instance in inorganic photorefractives,[30] or in improving the sensitivity of imaging through scattering media using holographic time-gating through photon-gated recording using multiphoton absorption.[31]

7. Experimental

Photorefractive polymer samples were prepared by mixing FTCN, PVK, BBP, and ECZ in THF. After solvent removal, the solid material was processed into a thick film through multiple melting and mixing of the raw material before a good sample with high dielectric strength and without air bubbles was obtained. A piece from this preform was then melted between two ITO coated glass slides and the thickness was controlled with calibrated glass spheres. All samples were 105 μm thick. The glass-transition temperature of the composite was measured to be $T_g = 3$ °C by differential scanning calorimetry.

Nonlinear transmission experiments were performed using the amplified output of a colliding pulse mode-locked dye laser (CPM) (pulses of 150 fs, wavelength of 620 nm, repetition rate of 1 kHz). The laser beam was normal to the sample. Each transmission data point was obtained by averaging over 50 000 laser pulses. Fluorescence emitted from the sample during nonlinear transmission experiments was collected by lenses and analyzed using a spectrometer and an optical multi-channel analyzer (OMA).

Holographic recording was achieved through four-wave mixing experiments with 130 fs pulses at a wavelength of 650 nm produced at a repetition rate of 1 kHz by an optical parametric amplifier pumped by the amplified output of a Ti:sapphire laser system. The two writing beams were s-polarized, formed an angle of 40° in air, had an equal average power of 0.25 mW each, and were focused to a spot size of 300 μm. The sample surface normal was rotated by 40° with respect to the bisector of these beams. The grating period in the sample was 1.2 μm given a refractive index of 1.7. Reading was achieved by diffracting a delayed weak p-polarized beam with average power of 0.25 μW.

Photoconductivity experiments were performed using a cw He:Ne laser emitting at 633 nm and a Keithley 6571 A electrometer. The typical noise level for the experiment was below 1 pA.

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