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## Electro-optic polymers for THz applications

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# Electro-optic polymers for THz applications

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## ABSTRACT

Electro-optic (EO) polymers are promising materials to be used as THz emitters and sensors due to their high nonlinear coefficients and good phase-matching conditions. We demonstrate efficient THz generation from an 80  $\mu\text{m}$  thick EO polymer emitter which is equivalent to that of a 1000  $\mu\text{m}$  thick ZnTe standard. Also, this kind of EO polymer allows a generation up to 20 THz with ultra-short laser pulses. We have observed resonance-enhanced THz generation in another kind of EO polymer composite near its absorption maximum. Due to a sharp resonance of the EO coefficient near the absorption maximum of the material, the amplitude of THz field generated from a 3.1  $\mu\text{m}$  thick film of this composite is 15% larger than that from a 1000  $\mu\text{m}$  thick ZnTe standard. The estimated EO coefficient of this composite at 800 nm is over 1200 pm/V.

**Keywords :** Optical nonlinearities in organic materials, Ultrafast nonlinear optics.

## 1. INTRODUCTION

During the last 15 years THz radiation has found many applications in industry and science. Due to their long wavelength (100-300  $\mu\text{m}$ ), THz waves propagate through many non-metallic materials, therefore they can be used for package inspection<sup>1</sup> and industrial quality control.<sup>2</sup> In contrast to X-rays, THz radiation is non-ionizing. This makes it a potentially useful diagnostics tool in medicine and biology.<sup>3-5</sup> Another important application, THz time-domain spectroscopy, provides an easy and quick way to obtain information about optical properties of a material, such as the refractive index and absorption coefficient.<sup>6-8</sup>

THz emitters and detectors determine sensitivity, signal to noise ratio, and frequency response for all the THz applications above. Compared to other materials used for coherent THz generation and detection, such as photoconductive dipole antennae<sup>6</sup> and electro-optic (EO) crystals,<sup>9</sup> EO polymers are very attractive for THz systems due to their high nonlinear coefficients and good phase matching conditions.

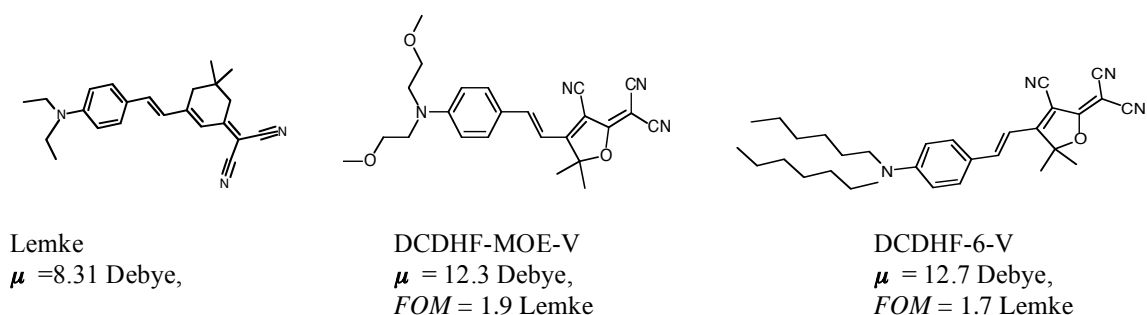
In this paper we present our experimental study of several kinds of EO polymers and their THz performance.

## 2. MATERIALS

We are studying EO polymer composites consisting of two organic molecular compounds : an active guest EO nonlinear optical chromophore and a passive polymer host. The chromophores possess large dipole moments, allowing them to be oriented in external electric field. This poling process, described below, leads to polar order, which is required for nonzero 2<sup>nd</sup> order nonlinear susceptibility necessary for both THz generation and detection.

Initially, we started working with a commercially available chromophore.<sup>10</sup> Then several chromophores (Fig.1) were carefully selected<sup>11</sup> from a wide variety of known organic molecular systems to achieve a more efficient EO polymer composite.

The bulk EO coefficient is directly proportional to the number density of the chromophores in the polymer composite (see Eq.1 in the next section). Therefore the chromophore and polymer host must be physically compatible allowing a reasonable amount of the chromophore (20-40 wt %) to be mixed with the polymer. Chromophores with large static dipole moments tend to dimerize forming aggregates of two chromophores with oppositely oriented dipole moments. This aggregation causes two negative results: decrease of the bulk nonlinearity due to the centrosymmetric arrangement of individual chromophores and crystallization of the layer. Therefore, chromophores with structural features that do not allow them to come close to each other and dimerize are desirable.



**Figure 1.** Chromophores and corresponding dipole moments  $\mu$  and figures of merit ( $FOM = \mu\beta/M$ , where  $\beta$  is the hyperpolarizability of the chromophore and  $M$  is the molecular mass).

The glass transition temperature ( $T_g$ ) of the EO polymer composite determines the thermal stability of its nonlinear properties. The higher the  $T_g$  of the composite, the more stable the pole order of of chromophores at room temperature. Since the added chromophores act to plasticize the polymer host, decreasing its  $T_g$ , the initial  $T_g$  of the host must be high enough that the resulting glass transition temperature of the whole composite will fall in a useful range for poling and stability. The poly(bisphenol A carbonate-co-4,4'-(3,3,5-trimethylcyclohexylidene)diphenol carbonate (APC) that we use as the polymer host has an intrinsic  $T_g = 205^\circ\text{C}$  allowing adding of 30-40% of various chromophores to form EO polymer composites with  $T_g \sim 90$ - $100^\circ\text{C}$ . Poled layers of these EO polymers can be used as THz emitters and sensors for at least a couple of weeks without significant degradation of their performance.

Other issues like the thermal stability of chromophores, rheological properties of the polymer host governing formation of an amorphous film are also important to obtain high performance EO polymer composite. The resulting EO polymer composite needs to demonstrate the following important properties :

- high EO coefficient,
- good optical quality of the layer (low absorption losses and low scattering),
- stable nonlinearity,
- easily processed to form both thin (several microns) and thick (up to several hundred microns) films.

## 1. EXPERIMENTAL RESULTS

### 3.1. DAPC composite and its THz performance

The preparation of our materials has been described earlier.<sup>12</sup> Briefly, films are cast from solution (chromophore and APC mixed together) onto an indium tin oxide (ITO) coated glass substrate. After solvent evaporation the solid polymer film is pressed in vacuum at  $60^\circ\text{C}$  above  $T_g$  for 10-15 minutes and then cooled down to room temperature. This technique allows us to obtain samples as amorphous polymer layers of a size 1 cm x 1 cm between ITO glass slides with thickness in the range of 50-350  $\mu\text{m}$  controlled by appropriate polyimide spacers.

Initially, the chromophores inside the polymer layer are oriented randomly. The medium is centrosymmetric, so the 2<sup>nd</sup>-order nonlinear optical susceptibility  $\chi^{(2)}$  is zero. In order to achieve a nonzero  $\chi^{(2)}$  in the polymer layer, which is required for all nonlinear interactions, it is necessary to align the dipole moments of chromophores. At this step, high voltage is applied to the ITO electrodes and the sample is heated up to the  $T_g$  of the composite allowing the chromophores to orient in the applied electric field. The sample is then cooled down to room temperature with the external electric field still applied, freezing the orientation of the chromophores, resulting in a nonzero  $\chi^{(2)}$  at room temperature without an external field.

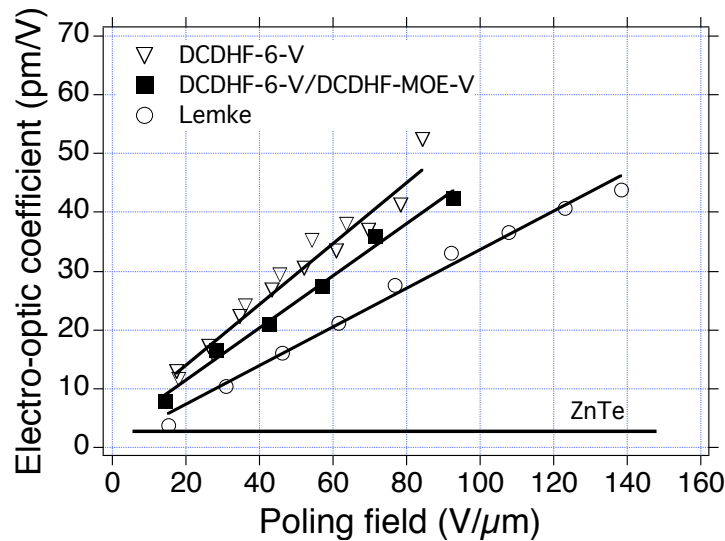
Thermal vibrations tend to randomize chromophore order decreasing the bulk nonlinear properties of EO polymer over time. The higher the  $T_g$  of a composite, the more stable the alignment of the chromophores at room temperature and the more stable the nonlinear properties of EO polymer composite.

After poling of the EO polymer films the resultant EO coefficient is measured using the ellipsometric technique.<sup>13</sup> In the weak field approximation<sup>14</sup> the electro-optic coefficient can be expressed as,

$$r_{33} = \frac{2N}{5} \left( \frac{\epsilon(n^2 + 2)^2}{3n^2(n^2 + 2\epsilon)} \right)^2 \beta_{zzz} \frac{\mu E_p}{kT}, \quad (1)$$

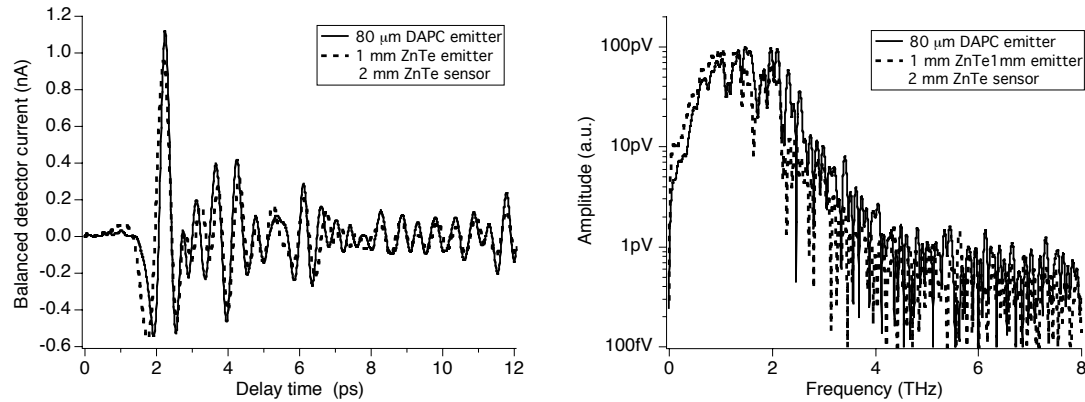
where  $\epsilon$  is the static dielectric constant,  $n$  is the material refractive index,  $k$  is Boltzman's constant, and  $T$  is the absolute temperature. The EO coefficient of the poled polymer is directly proportional to the number density of chromophores  $N$  as well as the second order polarizability  $\beta_{zzz}$ , the molecular dipole moment  $\mu$ , and the poling field  $E_p$ . Our experimental results (Fig.2) demonstrate this linear dependence of  $r_{33}$  with the poling field.

In Fig. 2, the EO coefficient as a function of poling field for EO polymer composites with three different chromophores is presented. All these composites contain APC as the polymer host. For the same poling field, the composite of 40%DCDHF-6-V/60%APC (referred to as DAPC) has the largest EO coefficient compared to the other composites based on DCDHF-MOE-V and Lemke because DCDHF-6-V has the largest dipole moment and 2<sup>nd</sup> order polarizability among these three chromophores. At 785 nm, for our typical poling field of 80-90 V/ $\mu$ m, the DAPC EO coefficient is about one order of magnitude larger than that of ZnTe. Using a DAPC composite we obtained our best THz experimental results, and some of these results are presented in this paper. The absorption maximum of the DAPC is approximately 610 nm, therefore we do not observe significant absorption for the pump beam at 800 nm.



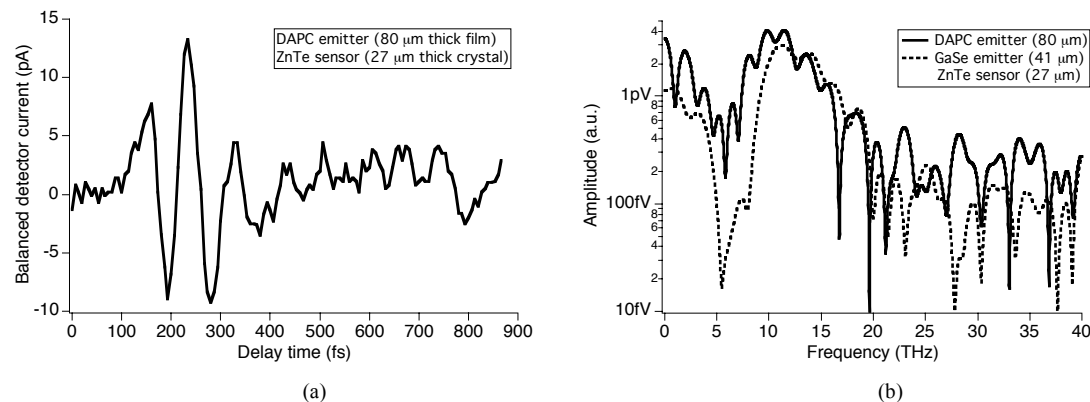
**Fig.2.** Electro-optic coefficient as a function of the poling field at 785 nm for composites with 40%Lemke, 40%DCDHF-6-V and 20%DCDHF-6-V/20%DCDHF-MOE-V mixed with 60% APC. Solid lines are the fit to the linear function. For comparison, the EO coefficient of ZnTe (4 pm/V at 800 nm) is also shown.

With a standard THz experimental set-up<sup>12</sup> based on an amplified femtosecond laser system (45 fs, 30  $\mu$ J/pulse, 800 nm, 1 kHz) we found that the amplitude of the THz field generated from an 80  $\mu$ m thick DAPC polymer film exceeded the corresponding amplitude generated from a 1 mm ZnTe reference (Fig.3). This efficient THz generation from DAPC composite is expected taking into consideration the EO coefficient ( $47 \pm 2$  pm/V at 785 nm), the slanted geometry of the polymer emitter and the thickness of the sample used in this experiment.



**Figure 3.** Comparison of the THz field emitted from a 1 mm (110) ZnTe crystal and an 80  $\mu\text{m}$  DAPC polymer layer. The EO coefficient of the polymer is  $47 \pm 2$  pm/V. A 2 mm thick ZnTe sensor is used in both cases. Temporal traces (left), and corresponding Fourier transforms (right). Experiment is performed in an open air.

With shorter laser pulses, we observe THz generation from a DAPC polymer layer up to 20 THz (Fig.4). In this experiment we compared the THz emission from an 80  $\mu\text{m}$  film of DAPC with that from a 41  $\mu\text{m}$  thick crystal of GaSe. A 27  $\mu\text{m}$  thick crystal of ZnTe was used as the THz sensor. Although in the Fig.4b the GaSe-ZnTe and DAPC-ZnTe systems (dotted and solid lines respectively) demonstrate similar spectra, determined by the pulse width, the phonon band near 5-8 THz causes strong absorption in the pure crystal system. Due to a ZnTe sensor, absorption at 5-6 THz is still present in the DAPC-ZnTe system. However, since EO polymer is amorphous material, phonon absorption is not expected in a system with EO polymers as THz emitters and sensors. Also, it is necessary to note that this experiment was performed in an open air.

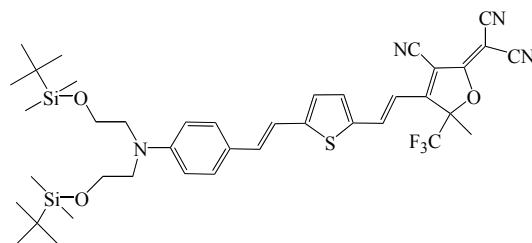


**Fig. 4.** (a) Time domain THz signals generated via optical rectification in a 80  $\mu\text{m}$  thick polymer film of DAPC and detected by a 27  $\mu\text{m}$  thick crystal of (110) ZnTe. (b) Corresponding frequency domain signal (solid line). For comparison, a THz signal generated from a 41  $\mu\text{m}$  thick crystal of GaSe (dotted line) is also shown. Experiment was performed in an open air.

### 3.2 Resonance enhanced THz generation near the absorption maximum of an EO polymer composite

We have observed another interesting experimental result<sup>15</sup> with an EO polymer composite of 20%CF<sub>3</sub>FTC/80%APC (referred to as CFAPC). The CF<sub>3</sub>FTC chromophore is shown in Fig.5. The CF<sub>3</sub> group does not change the dipole moment of chromophore but increases the 2<sup>nd</sup> order polarizability  $\beta$  resulting in an improvement of

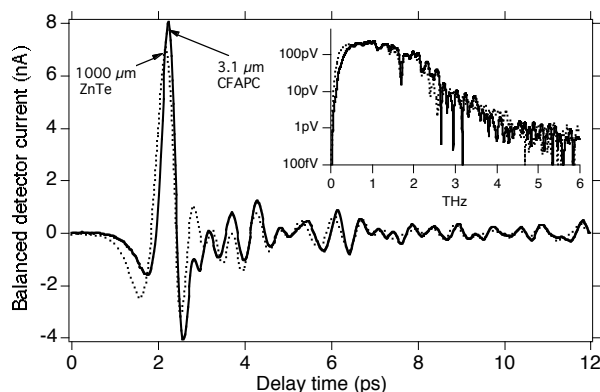
the figure of merit (FOM). An additional three double bonds shift the absorption maximum of CFAPC composite to 710 nm. The  $T_g$  of this composite is  $\sim 145^\circ\text{C}$ .



**Fig.5.** CF<sub>3</sub>FTC chromophore.

The CFAPC solution was spin coated on the glass substrate with an ITO electrode resulting in 1.5-3  $\mu\text{m}$  thick films. A gold electrode was sputtered on the film surface after baking of the polymer layer. The polymer samples were then contact poled in a nitrogen atmosphere and their EO coefficients were measured in reflection geometry.<sup>16</sup>

In Fig.6, THz generation with CFAPC is presented. The amplitude of THz field generated from a 3.1  $\mu\text{m}$  thick CFAPC film is 15% larger than that of a 1000  $\mu\text{m}$  ZnTe reference. In order to understand this result, it is necessary to investigate both the dispersion of the EO coefficient and the absorption of EO polymer composites.



**Fig.6.** Time domain THz signals generated via optical rectification in a 1000  $\mu\text{m}$  thick (110) ZnTe crystal (dotted line) and 3.1  $\mu\text{m}$  thick polymer film of CFAPC (solid line). Inset : the corresponding spectra. The experiment has been performed in an open air.

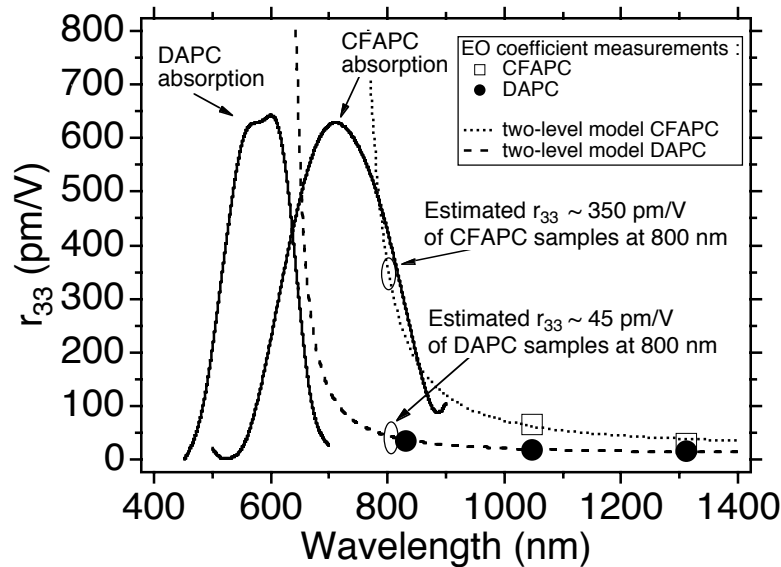
By applying time dependent perturbation theory in the two-level model (TLM) approximation,<sup>17</sup> the dispersion of the second order susceptibility of molecular nonlinear materials can be expressed as :

$$\chi_{333}^{(2)}(\lambda) \propto \frac{\lambda^2(3\lambda^2 - \lambda_{ag}^2)}{3(\lambda^2 - \lambda_{ag}^2)^2}, \quad (2)$$

where  $\lambda_g$  is the wavelength of the transition from the ground state  $g$  to the 1<sup>st</sup> excited state  $a$ . A sharp resonance in the material nonlinear properties is expected at the transition wavelength  $\lambda_{ag}$ .

Fig.7 shows the dispersion of the EO coefficient of both EO polymer composites together with their absorption spectra. The CFAPC material has an absorption maximum near 710 nm, therefore, in the THz experiment, with the pump beam at 800 nm, we are working near the absorption maximum, causing a resonant enhancement of its EO

coefficient and THz generation. In contrast, since the DAPC composite has an absorption maximum near 610 nm, we do not observe an enhancement of its EO coefficient at 800 nm as for the CFAPC composite. Therefore in order to generate a THz amplitude similar to that of 1 mm ZnTe crystal, a much thicker DAPC layer needs to be used, as it was demonstrated before. However if we were to use a pump wavelength closer to 610 nm, we expect to observe a resonance enhancement of the DAPC EO coefficient, and therefore, a corresponding increase in the generated THz amplitude, similar to CFAPC.



**Fig. 7.** Absorption spectra (arbitrary units) and the TLM prediction of the dispersion in the EO coefficient of the CFAPC and DAPC composites. Eq.2 is fitted to the measured  $r_{33}$  for CFAPC sample (open squares) and DAPC sample (solid circles).

The strong absorption of the CFAPC composite at 800 nm causes bleaching of the polymer layer and damage of the chromophores. For this reason, the CFAPC trace in Fig.6 was obtained by averaging of 15 fast scans (with a 30 ms time constant) where each scan was taken on a different spot of the polymer film. For a consistent comparison the ZnTe trace was obtained in the same manner.

#### 4. DISCUSSION

Since during the poling of our EO polymer the high voltage is applied normal to the film, the resultant bulk nonlinearity of polymer is acquired in the direction perpendicular to the layer. Therefore for THz generation via optical rectification, the polymer emitter must be tilted for the polarization of the pump electrical field to have a component parallel to the dipole moment of chromophores. Due to this slanted geometry of polymer emitters the effective value of the nonlinear coefficient  $r_{eff}$  is involved,

$$r_{eff} = r_{51} \cos \gamma \sin 2\theta + \sin \gamma (r_{13} \cos^2 \theta + r_{33} \sin^2 \theta), \quad (3)$$

where  $\theta$  and  $\gamma$  are the propagation angles for the optical and THz beams respectively inside the polymer layer, and  $r_{13} \sim r_{51}$  for our polymers. The film propagation angles are related to the incident angle  $\alpha$  in the air by Snell's law :  $\sin \alpha = n_{opt} \sin \theta = n_{THz} \sin \gamma$  where  $n_{opt}$  and  $n_{THz}$  are the refractive indices of polymer for the optical pump beam and THz beam respectively. In all our experiments the tilt angle for EO polymer emitters was  $\alpha \approx 55^\circ$ , which corresponds to the Brewster angle of our polymers.



Assuming linear dependence of the generated THz amplitude with the emitter thickness and its effective EO coefficient, we can calculate the ratio  $R$  of the expected THz amplitudes generated from 1000  $\mu\text{m}$  ZnTe in reference to that from our 80  $\mu\text{m}$  EO polymer layer,

$$R = \frac{L_{\text{ZnTe}} \cdot r_{41} \cdot t_{\text{air\_crystal\_air}}}{(L_{\text{polymer}} / \cos \alpha) \cdot r_{\text{eff}} \cdot t_{\text{air\_pol\_air}}} \quad (4)$$

where  $L_{\text{ZnTe}}$  and  $L_{\text{polymer}}$  are the thicknesses of ZnTe and EO polymer emitters respectively,  $r_{41}$  and  $r_{\text{eff}}$  are their EO coefficients,  $t_{\text{air\_crystal\_air}}$  and  $t_{\text{air\_pol\_air}}$  are the cumulative Fresnel coefficients at the boundary “air-nonlinear material” for the pump beam and “nonlinear material-air” for the THz beam for ZnTe and DAPC layer respectively. The slanted geometry of the EO polymer emitter is already involved in this formula. For DAPC,  $r_{\text{eff}} = 0.46r_{33}$  and due to the Brewster angle, the Fresnel coefficient  $t_{\text{air\_pol\_air}} = 0.99$ . However, we have significant losses in ZnTe at normal incidence,  $t_{\text{air\_crystal\_air}} = 0.65$ . With these numbers, the calculated ratio of the THz amplitudes of the ZnTe and EO polymer emitters is  $R = 0.91$ , which is in good agreement with the experimental result (Fig.3). This means that the amplitude of generated THz field scales linearly with thickness and nonlinear properties of THz emitters. Previously,<sup>18</sup> we reported linear dependence of THz performance with sample thickness for EO polymer composite of 30%Lemke/70%PMMA when this material is used for both THz emission and detection.

Due to the strong absorption we could not measure  $r_{33}$  of the CFAPC samples at 800 nm, but only at 1047 nm and 1310 nm. The TLM (Eq.2) fit to the experimental data estimates the  $r_{33}$  of CFAPC to be about 350 pm/V at 800 nm (Fig.7). However comparing the THz amplitudes (Fig.6) generated from a 3.1  $\mu\text{m}$  thick CFAPC layer and 1 mm ZnTe crystal and calculating the corresponding amplitude ratio,  $R$ , using eq.4, the EO coefficient of the CFAPC layer at 800 nm is above 1200 pm/V. The TLM is appropriate for the DAPC composite since there is much less resonance enhancement in that system. However, the TLM is too simple an approach to model the EO coefficient close to the absorption resonance. Incorporation of an inhomogeneously broadened dispersion model<sup>19,20</sup> is not expected to alter these results significantly.

The issue of optical damage caused by absorption is certainly an impediment to application development for the CFAPC material at 800 nm. However, we believe that widely available and affordable THz systems for commercial applications may need to operate at 1.06 – 1.55  $\mu\text{m}$ , where more compact and potentially cheaper, ultra-fast fiber lasers operate.<sup>21</sup> In this wavelength range, these materials show great promise as their EO coefficients are still large but the chromophores experience virtually no linear absorption.

In comparison to crystals, EO polymers have two distinct advantages, higher EO coefficients and larger coherence lengths at high frequencies. Both these factors are important for THz applications, especially wideband applications, because the thickness of emitters and detectors should be large to provide a high sensitivity and signal to noise ratio without limiting the frequency response. Additionally, polymers are amorphous materials and therefore they do not have phonon absorption bands which are typical for crystals.

However, EO polymers have some disadvantages. First, the stability of nonlinear properties of EO polymer is limited and depends on the material  $T_g$ , as was discussed above. The  $T_g$  of the DAPC composite is  $\sim 95^\circ\text{C}$ . Stored at room temperature, it can be used for several weeks without significant degradation of its EO properties. The nonlinear properties of CFAPC after poling are more stable due to the higher  $T_g$  of this composite. Higher  $T_g$  EO polymers with larger EO coefficients are being developed.<sup>22</sup> These materials exhibit no appreciable degradation of their EO coefficient over thousands of hours when stored at  $85^\circ\text{C}$ . The second disadvantage is that EO polymers have a low damage threshold compared to crystals. This limits pump power density and eventually SNR. Finally, the thickness of a highly poled polymer layer is limited to a few hundred micrometers, because an extremely high voltage needs to be applied to a thick layer in order to achieve a high poling field. However, the wide frequency response requires thin and efficient emitters and sensors, so this limitation may not be significant for wideband applications.

## 5. CONCLUSION

We fabricated and tested an efficient EO polymer composite, DAPC, which can be poled to have an EO coefficient over 50 pm/V at 785 nm. This EO polymer can be used as an efficient THz emitter and sensor. Direct comparison shows that the THz field emitted from an 80  $\mu\text{m}$  thick DAPC sample is equivalent to that emitted from a 1 mm thick ZnTe crystal.

Another EO polymer composite, CFAPC, demonstrates resonant THz generation when the pump wavelength is near the absorption maximum of the material. This phenomenon is caused by the resonance enhancement of the nonlinear properties near the absorption maximum and allows the generation of a THz field from a 3.1  $\mu\text{m}$  thick layer to be greater than that from a 1 mm thick ZnTe crystal.

EO polymers are versatile, permitting various chromophores and polymer matrices to be employed to fit specific requirements such as peak absorption and material refractive index. In addition, EO polymer composites are easy to prepare and inexpensive compared to crystals. Developing efficient THz emitters and sensors suitable for pump and probe beams at 1.0-1.3  $\mu\text{m}$  is an important step towards creating a compact and cheap THz system based on fiber lasers.

## ACKNOWLEDGEMENT

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