

# Pronounced photorefractive effect at wavelength over 1000 nm in monolithic organic materials

Wei You, Zhanjia Hou, and Luping Yu<sup>a)</sup>

Department of Chemistry and The James Franck Institute, The University of Chicago, 5735 South Ellis Avenue, Chicago, Illinois 60637

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Two monolithic organic materials exhibiting high photorefractive (PR) performances at a wavelength of 1064 nm were prepared and characterized. It was found that thiophene-based molecule **T6** demonstrated better PR properties than benzene based molecule **B6**. A net optical gain of  $139.1 \text{ cm}^{-1}$  at a low applied field of  $43.7 \text{ V}/\mu\text{m}$  and a diffraction efficiency of 45.6% at  $35.3 \text{ V}/\mu\text{m}$  were observed for materials made from **T6**. Net optical gain at 1300 nm was also observed for **T6**. The differences in PR behavior between two materials with similar structures were explained based on dipole moment and photoconductivity differences. © 2005 American Institute of Physics. [DOI: 10.1063/1.1900926]

Organic photorefractive materials have been studied extensively in the past decade and various types of materials with high performances have been discovered.<sup>1,2</sup> However, most of these organic materials only function at wavelengths below 800 nm. Considering the potential applications, such as real-time optical data processing at a wavelength ranging from 1.3 to  $1.5 \mu\text{m}$  commonly used in optical communication,<sup>3</sup> photorefractive materials with high performance at these wavelengths are of great interest. Currently, there are only a limited number of hybrid materials found to be sensitive at wavelength over 1000 nm, either by new polymer composites<sup>4</sup> or by using the nanocrystals as the sensitizers.<sup>5</sup>

Recently, our group and others have discovered that chromophores bearing tricyano-dihydrofuran moieties as the electron-withdrawing groups exhibit a pronounced photorefractive effect in the form of monolithic materials.<sup>6,7</sup> For example, a net optical gain of  $280 \text{ cm}^{-1}$  at a low external field of  $38.3 \text{ V}/\mu\text{m}$  was obtained for monolithic materials without any dopant.<sup>6</sup> However, those materials are only sensitive at a wavelength below 800 nm. In this letter we report that extension of the conjugation length of the chromophores caused the bathochromic shift of the absorption and rendered the new materials pronounced photorefractive effects at a wavelength of 1064 nm.

The structures of the molecules are shown in Fig. 1 and their synthetic procedures are similar to the reported procedure.<sup>8,9</sup> The two hexyl groups were introduced to the electron-withdrawing parts so that low glass transition ( $T_g$ ) temperatures of both materials made from **T6** and **B6** can be obtained. Indeed, DSC experimental results indicated  $T_g$  values of  $22.5 \text{ }^\circ\text{C}$  for **T6** and  $19 \text{ }^\circ\text{C}$  for **B6**, respectively. The films for our experiments were fabricated by heating the materials near the melting points and then sandwiching them between two glass substrates coated with indium tin oxide (ITO). The thickness of the sample was predetermined with the polymer film spacer.

The UV-Vis spectra of the two molecules are shown in the inset of Fig. 2. The major absorption bands for **T6** and **B6** appear around 689 and 613 nm, respectively. The photo-

sensitivity at wavelength over 1000 nm (e.g., 1064 nm) was observed due to the tailing into longer wavelength of the absorption spectra. Cyclic voltammetry (CV) studies revealed three oxidation potentials for **T6** due to the presence of electron-rich nitrogen and thiophene moieties while only one oxidation process can be observed for **B6**. Both compounds showed only one reduction process. Based on the measured redox potentials, the HOMO and LUMO energy levels were estimated.<sup>10</sup> The HOMO energy level of **T6** is around  $-4.94 \text{ eV}$ , which is slightly higher than that of **B6** ( $-4.96 \text{ eV}$ ); the LUMO energy level of **T6** ( $-3.74 \text{ eV}$ ) is slightly lower than that of **B6** ( $-3.72 \text{ eV}$ ).

Two-beam coupling (2BC) experiments were performed at  $25 \text{ }^\circ\text{C}$  by intersecting two split *p*-polarized laser beams (Intellite diode laser, 1064 nm) with equal intensity ( $2 \times 230 \text{ mW}/\text{cm}^2$ ) in the film with an external cross angle of  $20^\circ$  to generate the refractive index grating. The film normal was tilted an angle of  $53^\circ$  with respect to the symmetric axis of the two writing beams to provide a nonzero projection of the grating wave vector along the poling axis. The transmitted intensities of the two beams were monitored by two calibrated diode detectors. A pronounced PR effect for both materials at 1064 nm was observed as evidenced by a clear asymmetric energy transfer between the two beams. As indicated in Fig. 2, the gain coefficients ( $\Gamma$ ) for both materials

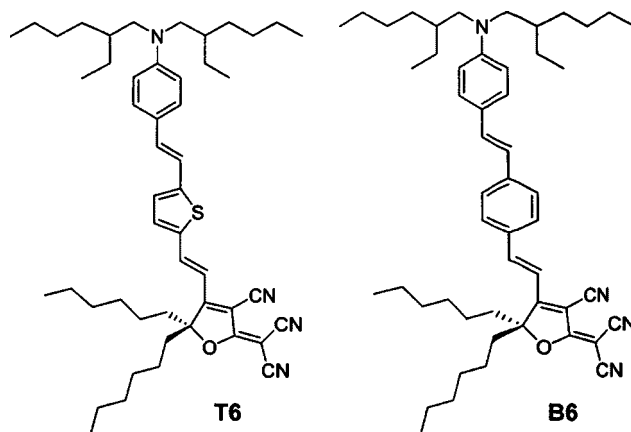


FIG. 1. Structures of PR molecules **T6** and **B6**.

<sup>a)</sup>Electronic mail: lupingyu@midway.uchicago.edu

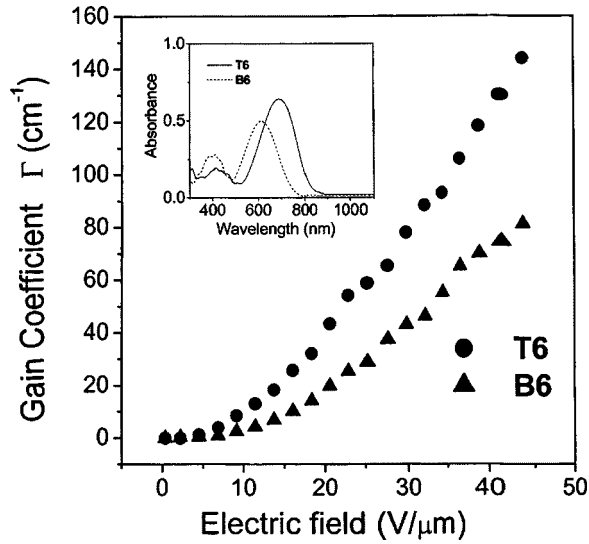


FIG. 2. Dependence of the gain coefficients  $\Gamma$  from 2BC on the applied field, Inset: UV-Vis absorption spectra of **T6** and **B6** measured in chloroform solution ( $1 \times 10^{-5}$  M) at 25 °C.

increase as the external field increases, but the material based on molecule **T6** consistently shows larger optical gain than the benzene-based molecule **B6**. For example, a high gain coefficient of  $144.1 \text{ cm}^{-1}$  at a relatively low applied field of  $43.7 \text{ V}/\mu\text{m}$  can be obtained for **T6**, but only  $81.3 \text{ cm}^{-1}$  for **B6** at the same field. Considering the absorption coefficients ( $\alpha$ ) for **T6** and **B6** are  $5.00$  and  $2.13 \text{ cm}^{-1}$ , respectively, both molecules exhibit net optical gain of  $139.1$  and  $79.1 \text{ cm}^{-1}$  at the field of  $43.7 \text{ V}/\mu\text{m}$ , respectively.

Degenerated four wave mixing (DFWM) experiments were also carried out at 25 °C to gain more insightful information about the amplitude of the refractive index grating. Two *s*-polarized laser beams ( $1064 \text{ nm}$ ) of equal intensity ( $2 \times 230 \text{ mW}/\text{cm}^2$ ) intersected in the film to write the index grating, and a weak *p*-polarized beam (probe beam,  $7.5 \text{ mW}/\text{cm}^2$ ) counterpropagating to one of the writing beams was used to read the index grating formed in the material. The diffracted light intensity of the probe beam was detected by a photodiode and subsequently amplified with a lock-in amplifier. The diffraction efficiency  $\eta$  was calculated as the ratio of the intensity of the diffracted beam to the transmitted beam intensity in the absence of the two writing beams. The maximum diffraction efficiencies were determined to be  $45.6\%$  at  $35.3 \text{ V}/\mu\text{m}$ ,  $18.4\%$  at  $40 \text{ V}/\mu\text{m}$  for **T6** and **B6**, respectively (Fig. 3). Once again, **T6** shows superior properties over **B6** in terms of diffraction efficiency.

Since both materials form amorphous solid with low glass transition temperatures, it can be assumed that the intermolecular interaction in both materials is similar. The CV studies indicated a very similar electrochemical behavior. There are two factors that are responsible for the difference in their PR performances, namely, absorption coefficients and dipole moments. According to the figure of merit (FOM) for low  $T_g$  organic PR materials<sup>11</sup>

$$F = \frac{1}{M} \left( 9 \mu \beta + \frac{2\mu^2 \Delta\alpha}{k_b T} \right), \quad (1)$$

(where  $\mu$  is the dipole moment,  $\Delta\alpha$  the anisotropy of the linear polarizability,  $\beta$  the second-order polarizability,  $k_b$  the Boltzmann constant,  $T$  the temperature, and  $M$  the molar

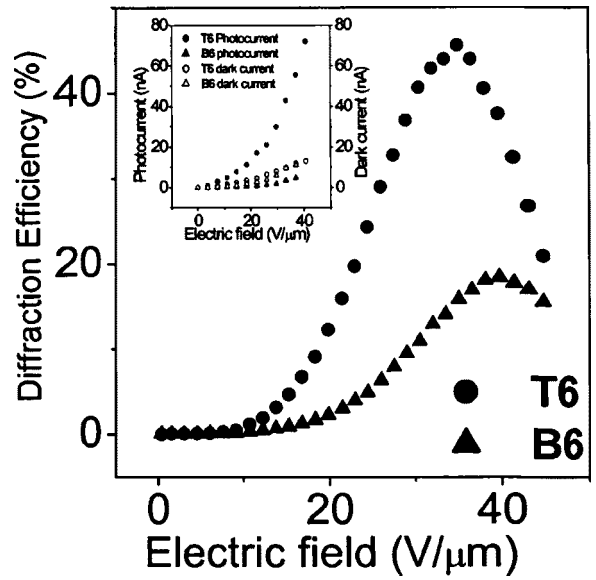


FIG. 3. Applied field dependence of the diffraction efficiency from DFWM experiment. Inset: Dependence of the photocurrent and dark current on the applied field at  $1064 \text{ nm}$ .

mass), maximizing the dipole moment would improve the PR performance. Theoretical calculation by using the optimized geometries at the HF/6-31 G\* level indicated dipole moments of  $18.024$  Debye for **T6** and  $17.064$  Debye for **B6**. Thus, **T6** should possess higher optical gain than **B6**.

However, the small difference in dipole moments alone cannot explain the magnitude of differences in optical gain. As mentioned above, the absorption coefficients ( $\alpha$ ) for **T6** are  $5.00 \text{ cm}^{-1}$ , more than double that of **B6** ( $2.13 \text{ cm}^{-1}$ ). Larger absorption coefficient helps **T6** generate more charge carriers. This is confirmed from photoconductivity measurements. The photoconductivity was measured using a dc technique at the wavelength of  $1064 \text{ nm}$  with an intensity of  $16 \text{ mW}/\text{cm}^2$ . The sample thickness was  $27 \mu\text{m}$ . The data were recorded at the steady state and the net photocurrent was calculated as the difference between the total current in the presence of light and the dark current. It was shown that **T6** has a higher photoconductivity than **B6** upon illumination by the  $1064 \text{ nm}$  laser while their dark currents between **T6** and **B6** have only a slight difference (inset of Fig. 3). At an external field of  $33.3 \text{ V}/\mu\text{m}$ , the observed net photocurrent for **T6** is  $42.9 \text{ nA}$ , but only  $3.4 \text{ nA}$  for **B6**. This difference must also be reflected in PR response times. The higher efficiency in photocharge generation leads to faster internal field buildup and stronger internal charge field where the chromophores can reorient more quickly and easily in response to the integrated fields. From four wave-mixing experiments, it was observed that at an electric field of  $31 \text{ V}/\mu\text{m}$ , space charge field buildup time constant  $\tau_1$  is  $1 \text{ s}$  and dipole reorientation time constant  $\tau_2$  is  $15.6 \text{ s}$  for **T6**. At the same electric field,  $\tau_1$  is  $1.5 \text{ s}$  and  $\tau_2$  is  $95.6 \text{ s}$  for **B6**.

It was also found that **T6** is photosensitive at  $1300 \text{ nm}$  and a photocurrent of  $0.8 \text{ nA}$  was observed at  $33.3 \text{ V}/\mu\text{m}$ . A gain coefficient of  $8.5 \text{ cm}^{-1}$  (absorption coefficient is  $1.86$  at  $1300 \text{ nm}$ ) was obtained for pristine sample at  $43.7 \text{ V}/\mu\text{m}$ .

In summary, monolithic materials exhibiting high PR performances at wavelengths over  $1000 \text{ nm}$  were synthesized and investigated. The materials made from **T6** exhibit larger net optical gain and higher diffraction efficiency than **B6** due

to their difference in dipole moments and absorption coefficients. Further synthetic efforts are needed to push the photosensitivity of organic PR materials to wavelength regions truly useful for telecommunications.

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