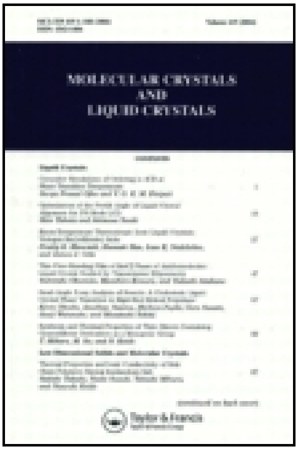

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Poling Behavior of Anisotropic Refractive Index in a Two-Dimensional Charge-Transfer Carbazole

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Poling Behavior of Anisotropic Refractive Index in a Two-Dimensional Charge-Transfer Carbazole

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Poling behavior of anisotropy in refractive index of a two-dimensional (2-D) charge-transfer (CT) molecular system was investigated by means of m-line method. It was found that a dinitro-substituted carbazole with 2-D CT character shows smaller anisotropy and smaller change in refractive index due to orientation relaxation compared with its 1-D CT counterpart, consistent with theoretical prediction.

Keywords: poling behavior; anisotropic refractive index; disubstituted carbazole; two-dimensional intramolecular charge-transfer

INTRODUCTION

In order to design a molecule with a desired function, it is essential to understand the structure-to-property relation. One of the most distinct examples is the relation between anisotropic properties and dimensionality of the molecular structure: anisotropy in linear and nonlinear optical properties is governed by the symmetry of the molecule through the dimensionality of its electronic structure.

It has been theoretically shown that a disubstituted carbazole, which has two-dimensional (2-D) intramolecular charge-transfer (CT) transitions [1,2]

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as shown in Fig. 1, presents much smaller anisotropy in refractive index and thus more tolerant to orientation relaxation compared with its 1-D CT counterpart [3]. This feature is very important in photonic applications, since the performance of photonic devices is generally sensitive to refractive index of the material. For example, in an optical second harmonic generation (SHG) device, the phase matching condition is extremely sensitive to the refractive index. Orientation relaxation in a poled polymer affects refractive index through anisotropy of molecular polarizability, resulting in a fatal degradation of device performance. Therefore the feature of the 2-D CT system mentioned above is extremely advantageous in various photonic applications.

In this paper we report an experimental demonstration of this feature of the 2-D CT system, i.e. smaller anisotropy in refractive index induced by poling, using 3,6-dinitro-N-ethylcarbazole as a 2-D intramolecular CT molecule and 3-nitro-N-heptylcarbazole as a 1-D CT one.

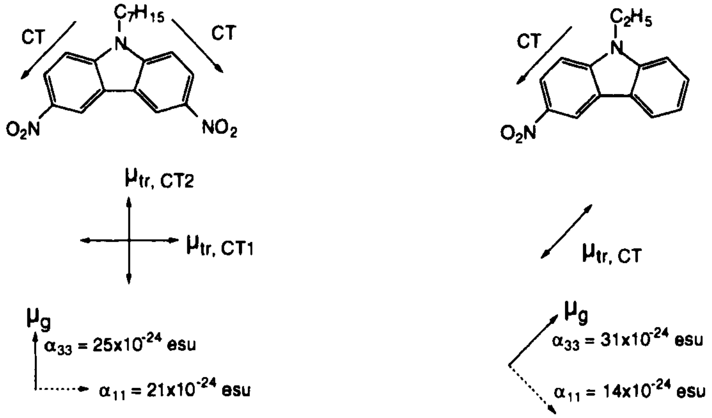

FIGURE 1 Top: molecular structure of 3,6-dinitro-N-heptylcarbazole (left) and 3-nitro-N-heptylcarbazole (right). Charge transfer axes are shown by arrows marked "CT". Middle: direction of CT transition dipole moments $\mu_{tr,\ CTi}$. Bottom: molecular polarizability components in the μ_g-coordinates for perfect uniaxial orientation. Direction of the ground-state dipole moment μ_g is also shown [1-3].

EXPERIMENTAL

Carbazole derivative was doped in PMMA with a concentration of 4.7 wt%, and spin-coated on a Pyrex glass substrate. The sample was dried in vacuum at 100 °C for several hours, and was divided into two. After measurement of absorption spectrum, these samples were simultaneously corona-poled at 15kV for one minute at 105 °C. Anisotropic refractive indices were measured by m-line (mode line) method at 632.8nm with one sample, and the absorption spectrum was measured at the same time with the other sample. After certain period of measurement (about 100 hours), the samples were heated at 105 °C for complete orientation relaxation, and the refractive index and absorption were measured to confirm that there was no sample degradation.

RESULTS AND DISCUSSION

Figure 2 shows order parameter evaluated from the absorption change. Order parameter θ and relative absorption change $\Delta = A / A_0 - 1$ (where A and A_0 are absorbance at λ_{max} after and before poling, respectively) are related as:

$$\theta = -\Delta, \quad \text{(in 1-D CT material)} \tag{1}$$

$$\theta = 2\Delta. \quad \text{(in 2-D CT material)} \tag{2}$$

In derivation of Eq.(2) it is assumed that the CT transition dipole moment responsible to λ_{max} peak ($\mu_{tr,\ CT}$ in Fig.1) is perpendicular to the ground-state dipole moment (μ_g in Fig.1) [2]. As shown in Fig.2, the order parameter just after poling was about 0.1 in both the 1-D and 2-D CT carbazoles. This is consistent with the fact that the ground-state dipole moments of the 1-D and 2-D CT carbazoles are almost equal. After initial relaxation for *ca.* 24 hours, the order parameter reduced to 0.07 in

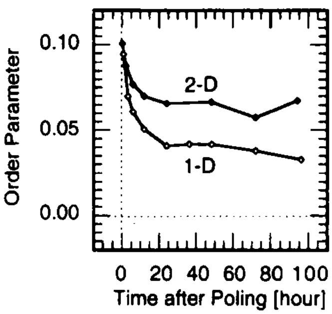

FIGURE 2 Order parameters and their relaxation estimated from absorption change.

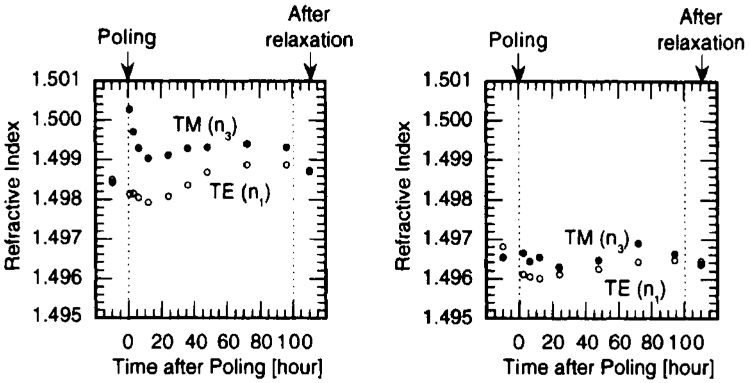

FIGURE 3 Anisotropic refractive indices measured by the m-line method. Left: 1-D CT carbazole. Right: 2-D CT carbazole. Refractive indices measured before poling and after complete orientation relaxation are also shown.

the 2-D CT sample and 0.04 in the 1-D CT one, followed by slow relaxation.

Figure 3 shows the poling behavior of refractive indices. The 2-D CT carbazole presented only a small birefringence of 0.0006 at maximum, which did not change significantly during the whole measurement period of 96 hours. On the contrary, the 1-D CT carbazole presented a significant initial birefringence as large as 0.0022 which steeply reduced to 0.0011 after 24 hours and to 0.0005 after 96 hours, which was still larger than the value of 2-D CT carbazole even though the order parameter was smaller. Refractive indices before poling and after complete relaxation were coincide within measurement error (estimated as 0.0003). This experimental result is consistent with the theoretical prediction [3], demonstrating the advantage of a 2-D CT material in photonic device applications that it is more tolerant to orientational relaxation.

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