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NOVEL MOLECULES FOR PHOTOREFRACTIVE APPLICATION

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Abstract: *Monolithic* multifunctional chromophores have been developed as a new class of organic photorefractive materials. Oligomeric carbazole molecular systems in the form of starburst dendrimers and conjugated trimers were studied. Molecular solids of acceptor-substituted carbazole oligomers and dendrimers exhibit glass transition. The second-order nonlinear optical coefficients d_{ij} were determined to be 50 pm/V by second-harmonic generation measurements. We also examined the photoconductive properties by the xerographic discharge method. Two beam coupling and four-wave mixing experiments were performed to characterize photorefractivities. The photorefractive phase shift measurement indicated that the induced index grating is shifted by 90 ° with respect to the absorption grating. Unlike usual photorefractive polymers containing multi-component systems these multifunctional chromophores can be applied to monolithic photorefractive materials.

INTRODUCTION

In the future optical information processing technologies, the physics of photorefractive effect gives attractive clues to the development of self-diffraction, phase conjugation optics, dynamic holography, holographic memory storage, optical image amplification, adaptive optical processors and so forth. The photorefractive effect consists of an optically induced spatial modulation of refractive index in a host optical crystal, *i.e.*, the thick volume refractive index gratings. This effect was firstly observed in a ferroelectric single crystal of $LiNbO_3$[1] in 1966, since then various inorganic crystals such as $BaTiO_3$ and $Bi_{12}SiO_{20}$ have been studied extensively. For organic materials, on the other hand, the first report should wait until 1990: Günter and his coworkers observed the photorefractive effect in a charge-transfer complex crystal of 2-cyclooctylamino-5-nitropyridine (COANP) slightly doped with TCNQ (as an electron acceptor)[2]. Molecularly doped polymer systems have been developed in the following years as an entirely new and different class of photorefractive material which possesses a lot of advantages compared

to inorganic crystals, *e.g.*, structural flexibility and ease of processing[3-6]. Among them Peyghambarian and his coworkers have recently reported a polymer system with nearly 100 % diffraction efficiency: poly(N-vinylcarbazole) (PVK) as a host matrix, 2,4,7-trinitro-9-fluorenon (TNF) as an acceptor to PVK, 2,5-dimethyl-4-(*p*-nitrophenylazo) anisole (DMNPA), 2,5-dimethyl-4-(*p*-nitrophenylazo)aniline and/or disperse red 1 as the EO chromophore, and N-ethylcarbazole (ECZ) as a plasticizer (reducing the glass transition temperature)[6].

The basic nature of photorefractive effect is simply described by an interaction between optical interference patterns and photoexcited charge carriers generated in the material (bulk crystal or thick film) which exhibits the second-order optical nonlinearity (Pockels effect). Therefore the requirement for materials which show the photorefractive effect is to have both photoconductive properties and Pockels effect at the same time. Most organic photorefractive materials developed in the past are the multi-component system with different functions such as photoconductivity, photosensitizer, and electro-optic response separately. Although these multi-component systems have good film-forming properties, they have multi-step carrier hopping processes which reduce the carrier mobility due to various traps. In order to create effective space charge modulation, efficient photocarrier generation and large drift mobilities are two of key factors which should be addressed. The overlapping wavefunctions in photoconductive chromophores affect photoconductive processes and this overlapping essentially depends on the chromophore concentration and their orientational arrangement. In molecular crystals such as N-isopropylcarbazole, a high drift mobility has been reported in the order of 1.0 cm^2/V sec, while that of amorphous polymers is typically in the order of 10^{-6} cm^2/V sec[7]. Moreover there is a limitation of the maximum concentration of chromophores due to the phase separation in multi-component systems, which leads to the reduction of optical quality. Therefore the multifunctional chromophores with both photoconductive and electro-optic properties, so called '*monolithic*' photorefractive molecules as shown in Figure 1, should be developed. In this paper, we will describe our approach to design and synthesize these molecular systems for photorefractive application.

MULTIFUNCTIONAL CHROMOPHORES

Carbazole molecule has an isoelectronic structure with diphenylamine as shown in Figure 2. In the case of diphenylamine each phenyl ring (ϕ) can rotate easily around the N-ϕ bond and also wag between the ϕ-N-ϕ angle. However the ring structure of carbazole can be stabilized to keep the planarity, and easily substituted chemically at the positions of 3, 6 and 9. This means that the molecular geometry of acceptor substituted carbazoles is

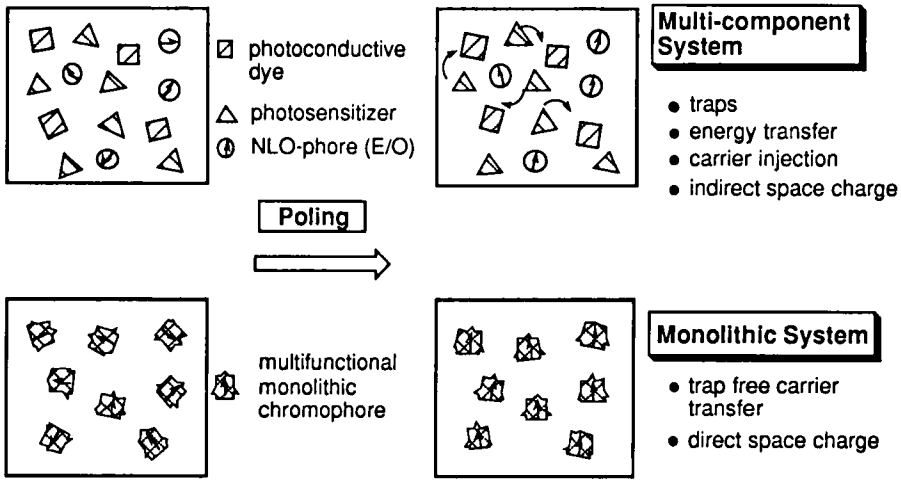


FIGURE 1. Multi-component and monolithic photorefractive materials.

optimized to show the dipolar and molecular axes in parallel and/or in perpendicular each other depending upon the size, electron affinity, and number of substituents. Carbazole compounds are well-known to exhibit good hole transporting properties and their photocarrier generation efficiency can be sensitized by formation of charge transfer complexes. By introducing acceptor groups at the 3- and/or 6-position of the carbazole ring, the intramolecular charge transfer and mesomeric dipole moment can be tuned for optical absorption spectra and molecular polarizability[8]. Besides these positions, N-substitution (9-position) offers various function to chemical modifications: solubilization of substituted carbazole by long alkyl chain, control of noncentrosymmetric packing in the crystalline state through hydrogen bonding[8] and stable electric-field induced alignment with 3,9-linkage of main chain polymers[9].

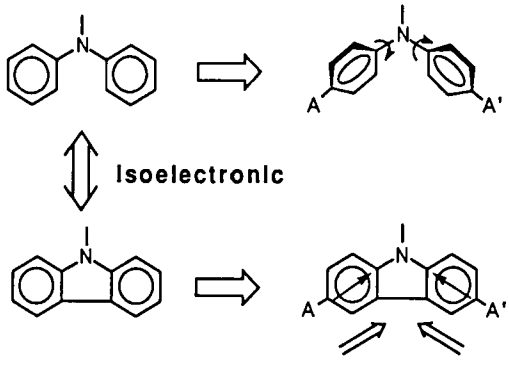


FIGURE 2. Molecular structure of diphenylamine and carbazole.

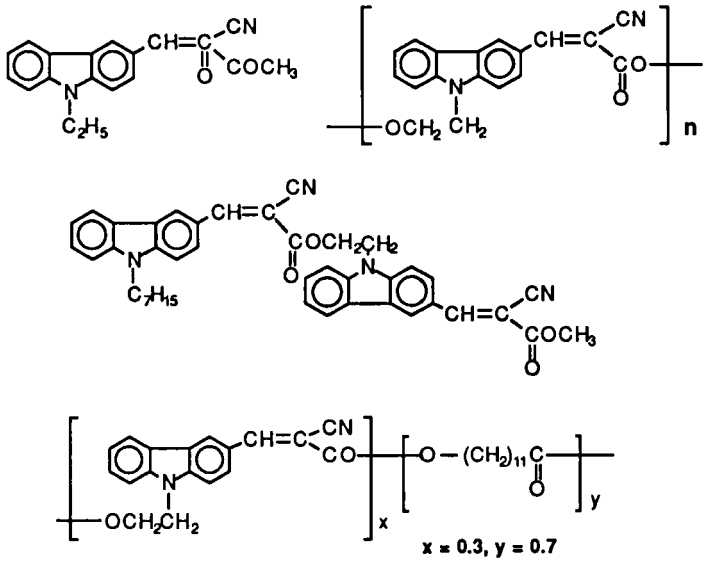


FIGURE 3. Carbazole head-to-tail polymer, copolymer, dimer and monomer structure.

The acceptor-substituted carbazoles were selected as a framework for oligomeric systems, which exhibit the multifunctional properties as reported previously[10]. Starting from point-like carbazole molecules, head-to-tail oligomers can be synthesized through 3,9-linkage and cyclic-oligomer through 3,6-linkage. Carbazole moiety was incorporated into the main chain through the cyanocinnamate linkage as shown in Figure 3. In order to elucidate second-order nonlinear optical properties of this head-to-tail polymer, we separately synthesized monomer and dimer as a model compound. Moreover, a class of supramolecules such as starburst carbazole oligomer was developed by combination of various chemical modification. These carbazole supramolecular systems can be expected to show different optoelectronic responses reflecting their unique chemical structures unlike the point-like carbazole molecules.

DIPOLE MOMENT CALCULATION

According to Willand and Williams[11], macroscopic dipole moment (**M**) and macroscopic polarizability (**B**) for head-to-tail polymer chain with n repeating units can be described by associated vector (**r**) in the chain direction and average directional cosine over the polymer chain:

$$\mathbf{M} = \sum_{i=1}^{n} \boldsymbol{\mu}^{i} = n\mu\langle\cos\phi\rangle\cos\varphi_{\mu} \qquad (1)$$

$$\mathbf{B} = \sum_{i=1}^{n} \boldsymbol{\beta}^{i} = n\beta\langle\cos\phi\rangle\cos\varphi_{\beta} \qquad (2)$$

where the relationship between dipole moment vector ($\boldsymbol{\mu}$), hyperpolarizability vector ($\boldsymbol{\beta}$) in a repeating unit, and end-to-end distance vector (**R**) are shown in Figure 4. In general $\boldsymbol{\mu}$ and $\boldsymbol{\beta}$ vectors are not parallel to **r** vector because of a flexible spacer in the polymer chain. The angles φ_{μ} and φ_{β} are defined with vector pairs ($\boldsymbol{\mu}$, **r**) and ($\boldsymbol{\beta}$, **r**).

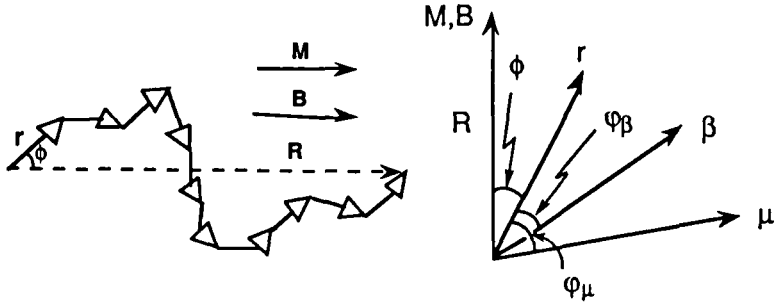


FIGURE 4. Head-to-tail polymer with associated vector (**r**) in the chain direction and the relationship between dipole moment vector ($\boldsymbol{\mu}$) and hyperpolarizability vector ($\boldsymbol{\beta}$).

Two geometric isomers with similar minimized energy were obtained by AM1. Both geometric isomers have similar values of φ_{μ} and φ_{β}. We took E geometric isomer which was usually obtained in cyanocinnamate derivatives[12]. In this case the ester group will be trans to the carbazole group. The azimuthal angles φ_{μ} and φ_{β} were estimated to be 19° and 16°, respectively, by MOPAC calculation on optimized E geometric isomer.

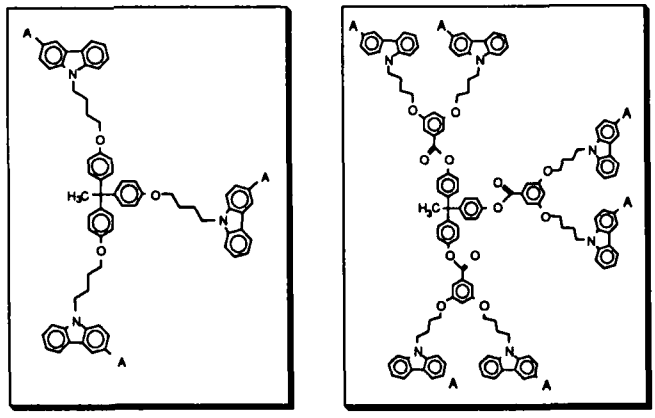
The structure of dimer is assumed to be simply composed of two optimized monomer units connected with a flexible spacer such as CH_2-CH_2 linkage neighboring an ester group. Although there is no significant minimum or maximum in the heat of formation calculated by MOPAC as a function of dihedral angle, the structures at dihedral angles of 0° and 90° have maximum and minimum energies. One key feature in these two structures is that the carbazole ring is perpendicular with each other. The net dipole moment of carbazole dimer is sensitive to their conformation. The net dipole moment calculated by vector summation increased with an increase of a dihedral angle. Judging from the minimized energy and net dipole moment, the structure at a dihedral angle of around 90° was selected for further consideration. From the concentration dependence of dielectric constants of dioxane solution, the values of dipole moment (μ) for monomer and dimer were experimentally determined to be 4.6 D and 6.7 D, respectively. Taking these μ and φ_{μ} values the angle (ϕ) between **r** and end-to-end vector (**R**) for dimer was calculated to

be 40°, which is in good agreement with the theoretical value obtained from the optimized dimer structure.

The enhancement factor of susceptibility per repeating unit can be defined as Equation (3), and expressed using Equations (1) and (2):

$$\frac{\chi^{(2)}_{zzz}(\text{polymer})}{\chi^{(2)}_{zzz}(\text{monomer})} = \frac{\left(\frac{MB}{n}\right)}{\mu\beta} = n\left(\langle\cos\phi\rangle\right)^2 \cos\varphi_\mu \cos\varphi_\beta \qquad (3)$$

Taking ϕ, μ, φ_μ and φ_β values, the enhancement factor was calculated to be 0.53 *n*. Namely, $\chi^{(2)}$ for head-to-tail polymer was enhanced with the degree of polymerization. Although carbazole head-to-tail polymers were obtained by conventional high-temperature polyesterification procedure, these homopolymers did not dissolve in usual organic solvents. In order to improve polymer solubility, copolymers were obtained with 12-hydroxydodecanoate. The mean square dipole moments of processable (3:7) copolyesters increased with an increase of molecular weight.



Nonlinear Optical Susceptibility

A	d_{33} (pm/V)	d_{31} (pm/V)
—CHO	6.9	5.0
—NO_2	30.8	12.5
—CH=C$(CN)_2$	49.6	41.4

FIGURE 5. Carbazole dendrimers and nonlinear optical susceptibilities in their films.

SECOND-ORDER NONLINEAR OPTICAL PROPERTIES

We also synthesized carbazole dendrimers and conjugated trimers as a multifunctional chromophore. In this supramolecular system we can expect molecular level control of size, shape, surface chemistry, topology and flexibility better than point-like molecule. The carbazole starburst oligomers have a film-forming property and show a glass-transition behavior. The values of glass transition temperature (Tg) were controlled by the length of spacer, the number of carbazole rings and acceptor groups. Amorphous molecular solid films could be prepared without supporting matrix by spin-coating from the solution. These thin films were poled above Tg to achieve the noncentrosymmetric alignment of molecular dipoles required for an electro-optic response.

Second-order nonlinear optical responses were examined on these thin films by spectroscopic method and second-harmonic generation (SHG). The values of the second-order nonlinear optical coefficients (d_{ij}) changed depending on the acceptor groups. The chemical structures and d_{ij} values of dendrimers were summarized in Figure 5. Although the optimal poling was not achieved, large d_{ij} values were obtained due to the high density of nonlinear optical chromophores.

OPTICAL IMAGE PROCESSING

Photoconductive properties of these dendrimer systems were examined by means of a xerographic discharge technique. It is clearly confirmed that these molecular systems

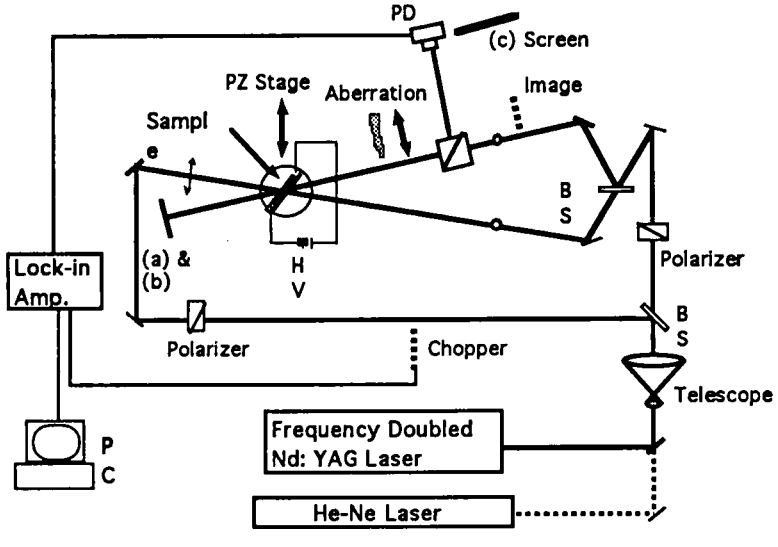


FIGURE 6. Schematic diagram of phase conjugation via four-wave mixing for the correction of distorted images.

have multifunctional properties, *i.e.*, both photoconductivity and second-order nonlinear optical responses. The photorefractive phase shift measurement indicated that the induced index grating is shifted by 90 ° with respect to the absorption grating. Two beam coupling and four-wave mixing measurements were performed to determine their performance as a photorefractive material. Figure 6 shows the phase conjugation setup used in our experiments. We could demonstrate an optical image reconstruction of distorted images using phase conjugation.

CONCLUSION

We have successfully developed novel oligomeric and polymeric systems for photorefractive application. Carbazole dendrimers and trimers were confirmed to be multifunctional and displayed both photoconductivity and second-order nonlinear optical responses. Unlike usual photorefractive polymers containing multi-component systems, these multifunctional chromophores are considered to be monolithic photorefractive materials. These functionalized supramolecules with well-defined structures are one of the promising molecular building blocks which exhibit high performance required for optoelectronic application.

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