論 文
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새로운 광굴절재료의 제작 및 특성

Synthesis and Properties of the New Photorefractive Material

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Abstract - Considerable progress has been made in organic photorefractive materials, since the first observation of photorefractive phenomena from organic materials. Within recent years, a large number of organic photorefractive materials, especially amorphous materials, have been developed based on polymeric composites, fully functional polymers and the multi-functional chromophore approach. Among these organic photorefractive materials, some of them containing carbazole components as a charge transporting function have been demonstrated to exhibit high performance photorefractive effects. The carbazole building blocks with charge transporting function or multifunctions play a very important role in photorefraction. In this paper, it confirmed that acceptor-substituted carbazoles show the multifunctionality both of photoconductivity and electro-optic(EO) activity and photorefractive materials newly can be developed with acceptor-substituted carbazoles.

Key Words : Photorefractive material, Carbazole, Amorphous, Second-order nonlinear optical material, Two-beam coupling

1. INTRODUCTION

Photorefractive(PR) nonlinear optics has drawn a great deal of attention during the last two decades due to its ability to exhibit a high refractive-index modulation amplitude, high sensitivity, and real-time operation. Devices based on photorefractive nonlinear optics have a potential role in dynamic interferometry and other optical information processing. Polymer materials for these applications have many positive attributes regarding their potential including high figures of merit, easy processing, and material flexibility. A change in refractive index(photorefraction) of a material may have many origins. Most of the mechanisms generally lead to irreversible photorefraction processes. However, some are reversible which is very important for potential applications.[1,2] Reversible photorefraction process can be due to several microscopic mechanisms, such as the space charge field induced photorefractive effect, photodimerization, photoisomerization, thermo-optic effects and photoinduced inter- or intra-molecular structural changes.[3,4] The photorefractive effect has now been observed in a large number of inorganic materials[1,2] such as $KNbO_3$, $BaTiO_3$, $Bi_{12}SiO_{20}$(BSO), $B_{12}GeO_2$,(BGO), GaAs, and InP:Fe. Many different devices have been developed for numerous applications, including high density optical data storage, optical image processing, dynamic holography, optical computing and phase conjugated mirrors.[5,6] In 1990, the first observation of the photorefractive effect in an organic doped crystal was reported.[7, 8]

Amorphous organic photorefractive material can offer many advantages over photorefractive crystals, such as large optical nonlinearities, low cost, low relative permittivity(ε), structural modification flexibility and ease of fabrication. Compared with inorganic photorefractive crystals, the low relative permittivity of organic materials is an important reason for pursuing the development of organic photorefractive materials. For organic materials, the nonlinear optical(NLO) response is molercular property arising from the asymmetric distribution of the electronic charges in the molecular ground and excited state.[9] For this reason, in organic materials large electro optical(EO) coefficients are not accompanied by large dc ε values thus a potential improvement in the performance of the photorefractive effects of organic materials can be achieved by a suitable and reasonable molecular design. It is well known that the growth and preparation of single crystals is generally a time-consuming and difficult processes. This is an even more important factor when attempting to engineer the properties of a single crystal by the modification of the crystal to include desired

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functions for the materials. On the other hand, the photorefractive properties of amorphous organic materials may be improved by both chemical and physical modifications. Amorphous organic materials are generally more amenable to processing into device structures with large areas and useful geometries by coating and other methods. In this paper, recent progress in organic photorefractive materials with carbazole moieties is described. An introduction to the necessary functional components for molecular design approaches to organic photorefractive materials, characterization of organic photorefractive materials and identifying the nature of nonlocal photorefractive effects are also described. Using two beam coupling experiment, photorefractive effect newly is observed in the film of dicyanovinyl-substituted carbazole trimer doped with different TNF(2,4,7-trinitro-9-fluorerone) concentration.

2. Characterization of organic photorefractive effect

2.1 Absorption coefficient for the charge generation

In order to observe a photorefractive effect, a material should have a suitable optical absorption coefficient at the operating laser wavelength for the generation of the photocharges. In the optimal case, this absorption coefficient should come from the contribution of the charge generation molecules, such as C_{60} and charge-transfer complex. The absorption coefficient for charge generation from any of the other components, such as second-order NLO chromophores, will increase other competing processes. When we design molecules for photorefractive materials, the absorption coefficient at the operating wavelength from the charge generation molecules should first be confirmed by a spectroscopic measurement. Any absorption due to other functional components should be avoided from the operating laser wavelength for photorefraction.

2.2 Photoconductivity for the establishment of the space charge field

Photoconductivity in amorphous organic materials consists of photocharge generation and charge transport processes. The charge generation molecules absorbing photons produce electron-hole pairs which, under the influence of a driven electric field, dissociate to produce electrons and holes. These free carriers then migrate through the material via a hopping mechanism by the charge transport components. Measurement of these properties is an important first step for the characterization of a potential organic photorefractive material. The photocharge generation quantum yield and the photoconductivity can be measured using a simple photocurrent technique or a xerographic discharge technique. Charge mobility can be measured by the time-of-flight technique.

2.3 Linear EO effect for formation of a refractive index grating

A number of different methods have been developed to measure the EO coefficient in polymer films. The most widely used methods for thick polymer films are the reflection technique. This method is also widely used for measuring the EO coefficients of amorphous organic photorefractive materials. It should be pointed out that the EO coefficients obtained at low frequencies contain the contribution from the field induced birefringence. More accurate measurements of the EO coefficients should be performed at high modulation ac frequencies at which the birefringence effect is insignificant and only the EO effect of chromophores can respond to these ac frequencies.

2.4 Two-beam coupling measurements

In order to unambiguously distinguish between the photorefractive effect and other types of gratings, two-beam coupling measurements must be performed. The phase shift between the refractive index grating and the light interference pattern can be determined by two-beam coupling techniques. This phase shift, or nonlocal nature of the photorefractive effect, gives rise to an asymmetric energy transfer between the two writing beams which does not occur in any of the other refractive index change processes. Therefore, the nonlocal character of the photorefractive effect can be directly confirmed by an observation of the phase shift or the asymmetric energy transfer in two-beam coupling experiments.

3. Photorefractive design and Experiment

3.1 Functional components to photorefractive design

To be photorefractive, a material must have photoinduced charge generation, charge transporting and charge trapping properties, as well as an EO response. When light is incident on a photorefractive material, if the incident light is not uniform in intensity, photogenerated charges will migrate through the transporting component from the illuminated area to the dark area, where these charges get trapped by trapping centers. Tbe resulting charge redistribution creates the space charge fields in the material. These fields produce measurable changes in the refractive index through the linear EO effect in noncentrosymmetric materials. The formative process of the refractive index grating in organic photorefractive materials is similar to that of the inorganic crystals. According to the requirements and the mechanism of the photorefractive effects, photorefractive materials must have two main functions, Photoconductivity for the establishment of a space charge field and the linear EO effect for the formation of a refractive index grating. Photoconductivity in organic materials consists of photocharge generation and charge transporting processes. In amorphous organic photorefractive materials, photocharges can be induced by addition of appropriate sensitizers, such as organic dyes; generated charges can be transported through the hole transporting component, such as carbazole and triphenylamine; the defects in the materials can play a trapping role for these charges. Second-order NLO chromophores can provide the linear EO effect when the dipole orientation of chromophores is achieved by an applied electric field. Thus the multifunctionality of organic photorefractive materials can be achieved by two molecular design approaches: the guest-host composite approach and the fully functional polymeric material approach. Most of the reported amorphous photorefractive materials were based on guest-host composite systems using second-order NLO polymers, a charge transporting polymer, or an inert polymer as a host doped with the corresponding necessary functional components. Recently, bifunctional chromophores combining both charge transporting function and EO function doped in inert polymers have also been reported. The composite materials approach has the advantage of easy optimization of the multifunctionality by independently varying the nature and concentration of each component.

3.2 Design approaches

Since the first observation of photorefractive effects in amorphous organic polymeric composites, many amorphous organic materials for photorefraction have been developed based on two molecular design approaches: the guest-host composite approach and the fully functional approach. In these two approaches, materials always contain multicomponents to offer multifunction properties. Development of bifunctional chromophores was the approach to try to develop one chromophore with more than one function.[10] High performance of photorefractive effects has been obtained using this design approach. These chromophores provide two main functions, such as EO activity and sufficient charge transport properties for photorefractive behavior; they also provided charge trapping capability which allowed the demonstration of truly long-lived gratings in a photorefractive polymer, quasi-nondestructive readout.[11] These materials also exhibited improved optical quality due to the reduction in the number of dissimilar constituents. Recently, we developed fully amorphous chromophores for photorefractive materials.[12,13] These chromophores were synthesized based on carbazole building blocks. The design approach is shown in Fig. 1. The chromophores combining photoconductive and EO functions are plasticized by introducing a suitable flexible alkyl chain. The use of different plastic chains can provide us with a chance to obtain amorphous compounds with controllable T_g. We believe that our carbazole-based design approach has more flexibility for chemical modification, and different types of materials can be obtained. Amorphous carbazole conjugated oligomers and amorphous carbazole dendrimers have been developed for photorefractive materials in this way. A conjugated carbazole structure was used to produce photorefractive materials because of its excellent charge transporting properties and relatively high carrier mobility of the conjugated carbazole polymers and oligomers. It is well known that photorefractive materials are multifunction. Until now, this multifunction has been limited in molecular design approaches to multicomponent systems for photorefraction. One of our design targets is to develop multifunctional chromophores based on carbazole building blocks by chemical modification. We have tried to find one way of designing photorefractive materials with second-order NLO chromophores. Some successful examples follow.

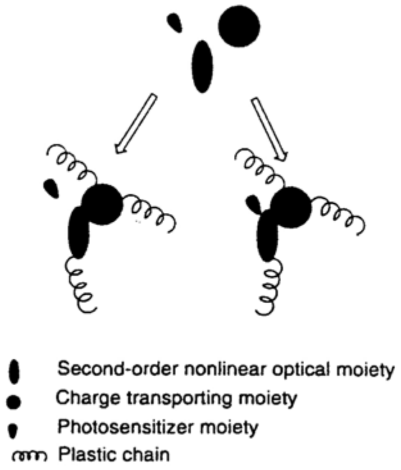

Fig. 1 Molecular design approach to amorphous non-polymer photorefractive materials.

3.3 Amorphous carbazole trimers as multifunctonal chromophores.

In carbazole conjugated trimers(X) with acceptor

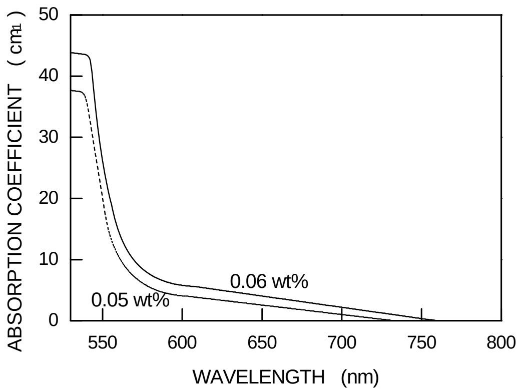

Fig. 2 Absorption spectra of trimer doped with different TNF concentrations.

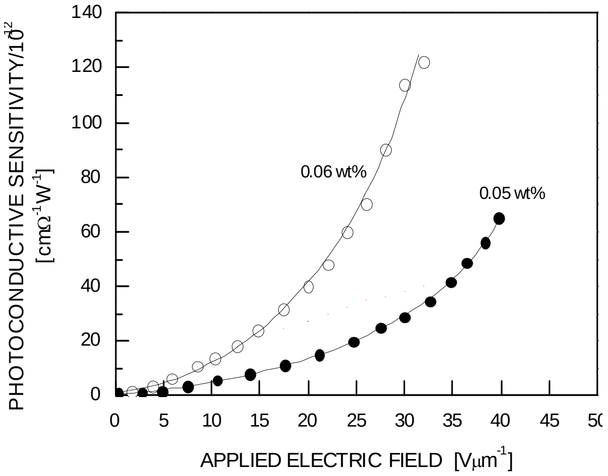

Fig. 3 Photoconductive sensitivity as a function of the applied electric field for dicyanovinyl-substituted carbazole trimer doped with different TNF concentrations.

groups for photorefractive materials, three carbazole rings are linked by ethynyl groups, with the peripheral carbazoles substitutes with electron-withdrawing groups which make the materials EO active. The central carbazole can act as a charge transporting function. In order to obtain amorphous carbazole trimers with a low T_g, the three long aliphatic groups are introduced to the trimers at the 9-position of each of the carbazole moieties. The T_g was strongly dependent on the length of the alkyl spacer between the carbazole chromophores and of the alkyl group at the 9-position of the carbazole ring. The T_g could be controlled in the range from 29-87℃. Among these carbazole main-chain polymers, polymers with a relatively low T_g enable photorefractive measurements to be made at room temperature. These carbazole main-chain polymers have proved to have both photoconductivity and EO activity. Films for NLO and photorefractive measurements were made by spin-coating and casting from chloroform solution, revpectively. The second-harmonic generation(SHG) measurements were performed using a Q-switched ND-YAG laser beam(1064 ㎚) as a fundamental beam. In the two beam coupling experiment, two p-polarized laser beams from ND-YAG laser also were used for writing holographic gratings.

4. Result and Discussion

4.1 Multifunctional carbazole conjugated trimers

A dicyanovinyl substituted trimer with a T_g, of 29℃ has been used as a model example for studies of photorefractive effects. A single carbazole trimer with a dicyanovinyl group does not exhibit any absorption coefficient at a wavelength of 633nm. However, the trimer could be sensitized by addition of a small amount of TNF(2,4,7-trinitro-9-fluorerone). The charge transfer complex formed by the central cabazole moiety of the trimer and TNF shows a controllable absorption coefficient at 633nm. Fig. 2 shows the absorption spectra of the trimer and the trimer doped with different concentrations of TNF. The photoconductive sensitivities were measured on a 10㎛ thick sample sandwiched between Al and indium-tin oxide(ITO) electrodes. It was found that the TNF concentration has a significant influence on photoconductivity and the good photoconductivity sensitivity value was observed in a 0.06wt% TNF doped trimer in Fig. 3. The density of charge transfer complex units which act as the charge generation functions increased with the doping concentration of TNF. Uncomplexed TNF can also act as the hole trap. The density of free carbazole units, which are responsible for hole-transport decreased simultaneously, and sensitively influenced the magnitude of charge drift mobility.[14] Therefore, there is a balance between the charge generation and charge transporting components, which results in the observation of an optimized TNF concentration of 0.06wt% in photoconductivity. Due to the low T_g of the trimer, the chromophores could be effectively aligned at room temperature by applying a dc electric field across the sample. The EO coefficient was measured on the same sample(134㎛) for the photorefractive measurements using a transmission technique.[15]

In order to avoid the birefringence contributed from orientation of second-order NLO chromophores, more accurate measurements of EO coefficients have been performed at high modulation ac frequencies at which the birefringence effect is insignificant and only the EO effect

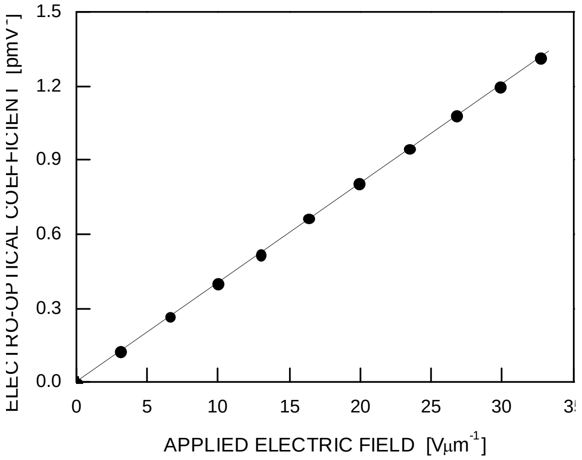

Fig. 4 The electro-optic coefficient of dicyanovinyl-substituted carbazole trimer as a function of the applied electric field at an ac frequency of 6 KHz.

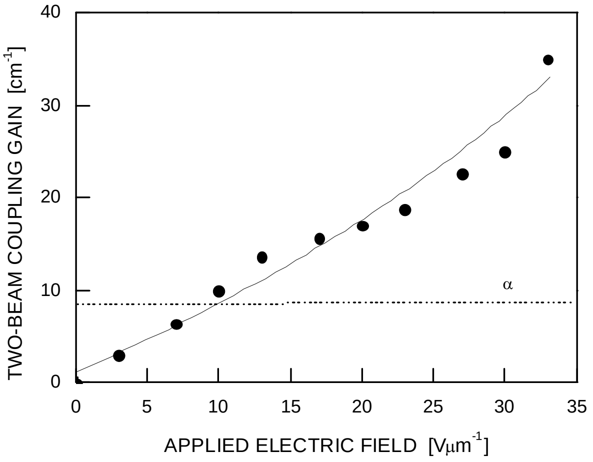

Fig. 5 The photorefractive gain coefficient as a function of the applied electric field for dicyanovinyl-substituted carbazole trimer doped with different TNF concentrations: (●) 0.06 wt%.

of chromophores can respond to the applied ac frequencies.[16] Fig. 4 shows the electric field dependence of the EO coefficient for a trimer(134㎛) doped with 0.06%wt of TNF concentration. These values are comparable with those obtained from other photorefractive materials systems.[17] The photorefractive nature of the trimer was confirmed by a two-beam coupling experiment. Fig. 5 shows the two-beam coupling gain as a function of the applied electric field for the trimer doped with different concentrations of TNF. The diffraction efficiency was measured with a four-wave mixing experiment. The modulation of the photorefration from both measurements is in good agreement within experimental error as shown in Fig. 6. This result indicates that the nonlocal index grating is the dominant mechanism of the holographic gratings.

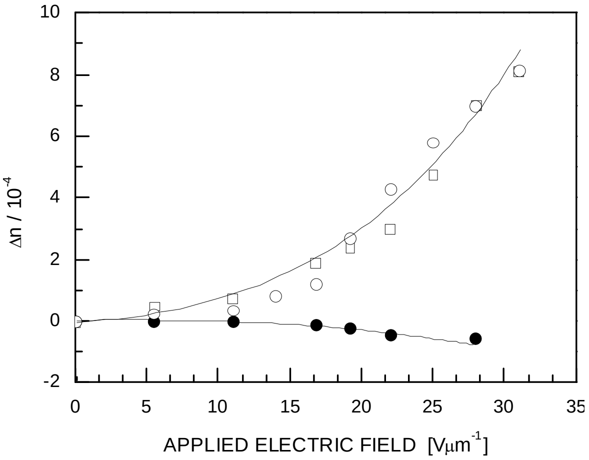

Fig. 6 Magnitude of index modulation of dicyanovinyl-substituted carbazole trimer doped with 0.06 wt% of TNF versus applied electric field: calculated from (○) p-polarized two-beam coupling gain, (●) s-polarized two-beam coupling gain and (□) p-polarized diffractionefficiency

The amorphous trimer as the first multifunctional chromophore has been demonstrated to exhibit good photorefractive effects. This trimer approach has several advantages: (1) high concentration of carrier transporting agent and second-order NLO moieties, (2) large carrier mobility arising from the conjugated structure, (3) good film-forming properties without any amorphous supporting matrix, (4) flexibility in optimizing the photorefractivity by adjusting the concentration of TNF, and (5) phase-separation-free due to very low concentration of the dopant.

4.2 The amorphous carbazole trimer as a monolithic photorefractive chromophore

A novel multifunctional conjugated carbazole trimer X with nitro acceptor groups has been found to be the first monolithic photorefractive material. It was found that this trimer doped with no other functional components showed an efficient photorefractive effect.[18] In this trimer, carbazole rings were also linked by the ethynyl group and peripheral carbazoles were substituted with nitro groups. The nitro-substituted carbazole trimer displays a suitable absorption coefficient of 8.2㎝-1 at a wavelength of 532㎚. This absorption coefficient can allow observation of the photorefractive properties of this trimer at an operating wavelength of 532㎚. This trimer was demonstrated to be both photoconductive and to have second-order NLO activity. The noncentrosymmetric alignment of the chromophores can be achieved by an electric poling field at room temperature due to its low T_g of 20℃ and this can be confirmed by a second harmonic generation(SHG) measurement. The SHG experiment was

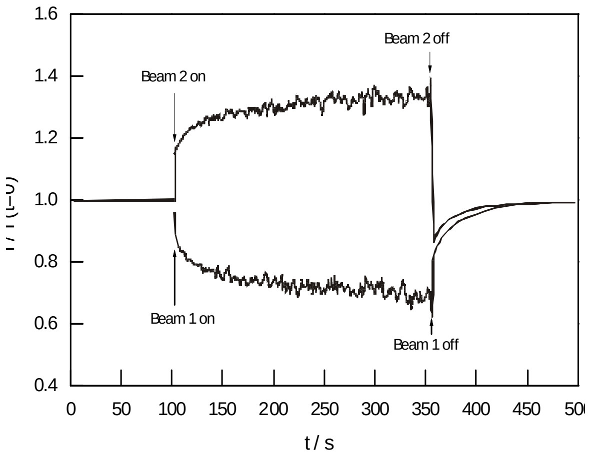

Fig. 7 The intensity of beam I (upper trace) monitored as beam 2 (lower trace) is switched on at time t = 0 s and off at t = 255 s, and the intensity of beam 2 monitored as beam I is turned on and off. The applied electric field was 33V㎛-1.

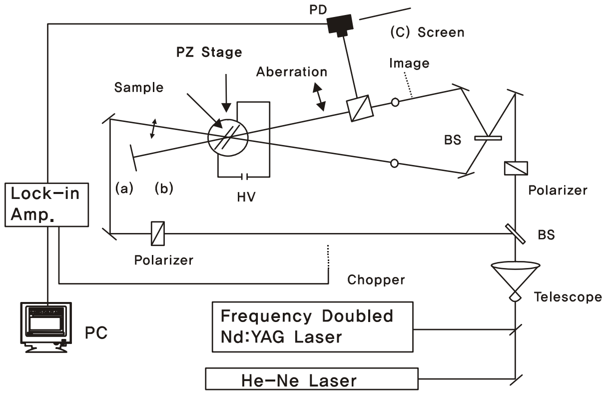

Fig. 8 Experimental geometry for optical image reconstruction.

carried out on the same sample for the photorefractive measurements at a fundamental wavelength of 1064㎚ in transmission mode. With no electric field applied, the SH intensity could not be observed, as a result of the centrosymmetric random arrangement of the chromophores. After switching on the electric field, repeatable orientation of the chromophores was realized, reaching a stable plateau value within a few seconds. This partial orientation of the chromophores at room temperature came as a result of the low T_g of the carbazole trimer. The SH intensity is strongly dependent on the applied electric field.

Fig. 7 shows typical asymmetric behavior for the monolithic carbazole trimer at an applied electric field of 33V㎛-1. The two-beam coupling gain coefficient could be estimated from the asymmetric energy transfer. In Fig. 8, the second-harmonic generation(SHG) measurements were performed using a Q-switched ND-YAG laser beam (1064㎚) as a fundamental beam. In the two beam coupling experiment, two p-polarized laser beams from ND-YAG laser were used for writing holographic gratings such as Fig. 9.

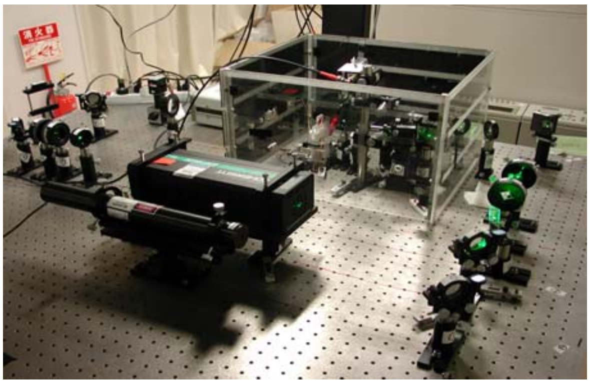

Fig. 9 ND-YAG laser system for the two beam coupling experiment.

5. CONCULSION

Considerable progress has been made in understanding both the photorefractive origins as well as the molecular design of amorphous organic photorefractive materials. However, before amorphous organic photorefractive materials can be considered for practical applications, many important issues have to be addressed. The amorphous trimer as the first multifunctional chromophore has been demonstrated to exhibit good photorefractive effects. This trimer approach has several advantages as fellows: (1) high concentration of carrier transporting agent and second-order NLO moieties, (2) large carrier mobility (3) good film-forming properties (4) flexibility in optimizing the photorefractivity by adjusting the concentration of TNF, and (5) phase-separation-free due to very low concentration of the dopant. Using two beam coupling experiment, photorefractive effect newly is observed in the film of dicyanovinyl-substituted carbazole trimer doped with different TNF concentration.

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