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Synthesis and photorefractivity of 2-{4-[4-(6-carbazol-9-yl-hexyl)-piperazin-1-yl]-benzylidene}-malononitrile

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Abstract

The present article describes the synthesis and characterization of amorphous low molecular weight glasses via flexible covalent bonds with hexyl-group, 2-{4-[4-(6-carbazol-9-yl-hexyl)-piperazin-1-yl]-benzylidene}-malononitrile (Cz-C6-DCST). At room temperature, this molecule forms a stable amorphous glassy material which exhibits a low T_g (40 °C) and no crystallization based on our DSC experiments. The films prepared from CH_2Cl_2 solutions containing 1 wt% TNF and 10 wt% *N*-ethylcarbazole are transparent and of excellent optical quality. The 50 μm thick film showed the maximum diffraction efficiency of 78.5% at 70 V/μm.

Keywords: Photorefractive; Dual-functional chromophore; Diffraction efficiency

1. Introduction

Photorefractivity (PR) in organic systems attract much interest in recent years because of their possible application in optical computing, optical switching and holographic data storage, and was first observed in an organic polymer in 1991[1]. The PR effect observed in that are both electro-optic and photoconducting. Nonuniform illumination of such a material results in the creation of photoexcited charges, which migrate out of the illuminated areas and eventually get trapped in the dark areas, giving rise to a spatially varying electric field (space-charge field, E_{SC}). The E_{SC} alters the index of refraction via the electro-optic effect [1,2].

Since that report [1,3] considerable progress has been made in the research on PR polymers and composite materials because these materials offer many potential advantages over inorganic PR crystals including large optical nonlinearities, low dielectric constants, low cost and ease of fabrication.

Up to now, most polymers that have been studied in the field of PR organics are based on the photoconductor poly(*N*-vinylcarbazole). The guest−host composites based on photoconducting polymer doped with chromophore and charge generator have been extensively studied, due to their remarkable PR properties. However, there are some disadvantages for this type of polymer composites, i.e., the electro-optical chromophore tends to aggregate or crystallize, which limits the durability of PR devices, leading to a smaller PR figure-of-merit. To avoid this and other problems, we are now focusing on yet another approach to the combination of charge transporting and second-order nonlinear optical properties on a single molecule, which further reduced the tendency of phase separation. From this point of view, multifunctional low molecular weight compounds take advantage.

Our design strategy was outgoing from bifunctional molecule to improve upon stability and photorefractivity in the device. Bifunctional molecule, which possesses photoconductive and electro-optic properties in one molecule, was synthesized as a new photorefractive material. Carbazole and aminodicyanostyrene (DCST) were chosen as the photoconductive component and the NLO chromophore, relatively. The long aliphatic chain serves to prevent the materials from

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crystallization and help the resulting compounds remain amorphous at room temperature. In this paper, we report on testing this interesting compound as potential new organic PR molecule and also report on the material's properties and performance in PR device.

2. Experimental

2.1. Materials and instrumentation

All reagents and solvents were of commercial quality and were purified or dried and stored under nitrogen using standard procedures. 2,4,7-Trinitro-9-fluorenone (TNF) photosensitizer was supplied by the Kanto chemical Inc. The chemical structure of the new multifunctional molecule was characterized by ^{1}H NMR spectrometry (Varian, INOVA, 400 MHz) and FT-IR spectrometry (Perkin–Elmer, Paragon 500). The absorption maximum (λ_{max}) of molecule in methylene chloride solution was recorded in Duksan Mechasys, Optizen III. New bifunctional molecule, 2-{4-[4-(6-carbazol-9-yl-hexyl)-piperazin-1-yl]-benzylidene}-malononitrile (hereafter referred to as Cz-C6-DCST) was synthesized using the reaction scheme, as shown in Scheme 1.

2.2. Sample preparation and measurement

The PR material with a low glass transition temperature (T_g) was prepared by doping *N*-ethylcarbazole (ECz) as a plasticizer into composite system. The composition was Cz-C6-DCST:ECz:TNF, in the ratio of 89:10:1 wt%. The mixtures containing Cz-C6-DCST chromophore were sandwiched between the two indium tin oxide (ITO) glasses to form 50 μm thick film with a Teflon spacer. The glass transition temperature (T_g) of this composite was determined by differential scanning calorimetry (DSC, Perkin–Elmer DSC7).

The electro-optic property (EO) and diffraction efficiency of the PR material was determined at the wavelength of 632.8 nm by ellipsometry technique, simple DC method, and degenerate four-wave mixing (DFWM) measurement at 28–29 °C [3,4]. For diffraction efficiency of PR material, two coherent laser beams at the wavelength of 632.8 nm were irradiated on the sample in the tilted geometry with the incident angle of 30° and 60° with respect to sample normal. The writing beams both were *s*-polarized and had the equal intensity of 60 mW/cm^2. The recorded PR grating was read out by a *p*-polarized counter-propagating beam. Attenuated reading beam with the very weak intensity of 0.1 mW/cm^2 was used. The internal diffraction efficiency (η_{int}) of PR material was determined from Eq. (1) [3].

$$\eta_{int} = \frac{I_{R,diffracted}}{I_{R,diffracted} + I_{R,transmitted}} \tag{1}$$

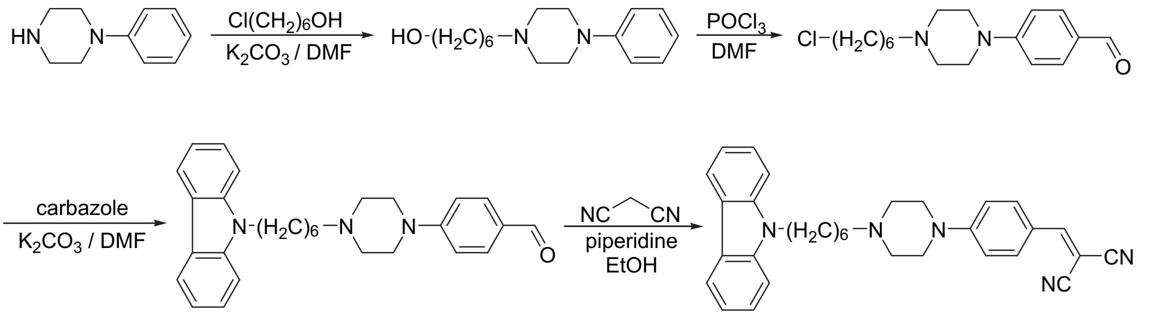
where $I_{R,diffracted}$ and $I_{R,transmitted}$ are the diffracted and transmitted intensities of reading beam, respectively.

2.3. Synthesis of 6-(4-phenyl-piperazin-1-yl)-hexan-1-ol (1)

1-Phenylpiperazine (5.00 g), potassium carbonate (2.3 eq.), and tricaprylymethylammonium chloride (2 drops) were stirred at room temperature in 20 mL *N*,*N*-dimethylformamide (DMF) for 2 h. To this was added dropwise a solution of 6-chloro-1-hexanol (1.2 eq.) in DMF (5 mL) over 30 min. This was refluxed for an additional 12 h. The resulting mixture was poured in water, extracted with 2 × 150 mL of ethylene acetate. The organic layer was dried over $MgSO_4$. After filtration and evaporation, the oil residue was chromatographed on silica gel with 1:1 ethyl acetate/hexane to yield **1** (76%). ^{1}H NMR ($CDCl_3$, ppm): δ 1.25–1.91 (m, 8H), 2.61 (m, 2H), 3.19 (m, 4H), 3.63 (m, 4H), 4.29 (t, 2H), 6.92 (m, 3H), 7.29 (m, 2H). IR (KBr pellet, cm^{-1}): 3447 (–OH).

2.4. Synthesis of 4-[4-(6-chloro-hexyl)-piperazin-1-yl]-benzaldehyde (2)

Phosphorous oxychloride (2.0 eq.) was added dropwise to DMF (5 mL) at 0 °C and for additional 1 h at 25 °C. Compound **1** (4 g) in DMF (20 mL) was then added slowly to the solution, and the mixture was further heated at 90 °C for overnight. After completion of the reaction, the mixture was poured into crushed ice (50 g) and extracted with methylene chloride three times. The organic layer was washed with a saturated sodium bicarbonate solution and water. The organic layer was dried over sodium sulfate and the dichloromethane was removed under reduced pressure. After, the crude product was chromatographed on silica gel with 3:7 ethyl acetate/hexane to yield **2** (43%). ^{1}H NMR ($CDCl_3$, ppm): δ 1.32–1.84 (m, 8H),



Scheme 1. Synthetic route of Cz-C6-PDCST.

3.31–3.71 (m, 10H), 4.15 (m, 2H), 6.88 (d, 2H), 7.78 (d, 2H), 9.89 (s, 1H). (KBr pellet, cm^{-1}): 1666 (−CHO).

*2.5. Synthesis of 4-[4-(6-carbazol-9-yl-hexyl)-piperazin-1-yl]-benzaldehyde (**3**)*

Compound **3** was synthesized as described above for compound **1**. The product was purified via absorption chromatography over silica gel with 1:1 $CHCl_3$/hexane to yield **3** (61%). ^1H NMR ($CDCl_3$, ppm): δ 1.35 (br m, 4H), 1.58 (br m, 2H), 1.83 (br m, 2H), 3.41–3.61 (br m, 8H), 4.03 (t, 2H), 4.43 (t, 2H), 7.10 (d, 2H), 7.23 (t, 2H), 7.48 (t, 2H), 7.62 (d, 2H), 7.89 (d, 2H), 8.19 (d, 2H). IR (KBr pellet, cm^{-1}): 1668 (−CHO).

*2.6. Synthesis of 2-{4-[4-(6-carbazol-9-yl-hexyl)-piperazin-1-yl]-benzylidene}-malononitrile (**4**)*

Compound **3** (2 *g*), malononitrile (1.2 eq.), piperidine (1 drop) as catalyst, and ethanol (20 mL) was refluxed for 24 h. The solution was then cooled to room temperature. The resulting precipitates were washed with sufficient ethanol to get the title compound **4** in 87% yields after drying in vacuum oven. $T_g = 40\ °C$. ^1H NMR (DMSO-d_6, ppm): δ 1.34 (br m, 4H), 1.56 (br m, 2H), 1.83 (br m, 2H), 3.40–3.62 (br m, 8H), 4.01 (t, 2H), 4.40 (t, 2H), 7.10 (d, 2H), 7.24 (t, 2H), 7.48 (t, 2H), 7.61 (d, 2H), 7.71 (s, 1H), 7.90 (d, 2H), 8.12 (d, 2H). IR (KBr pellet, cm^{-1}): 2234 (−CN). λ_{max} (nm) = 420 in methylene chloride.

3. Results and discussion

Cz-C6-DCST was synthesized as described in Scheme 1 in four-step reaction. Carbazole was chosen as the photoconductive component for hole transport. Condensation of aldehyde **3** with electron withdrawing group, malononitrile yielded DCST dye as the NLO chromophore. The molecule synthesized (Cz-C6-DCST, **4**) thus possesses dual functions: photoconductivity and second-order NLO activity. The long aliphatic chain ($-(CH_2)_6-$) was introduced to prevent the materials from crystallization and help the resulting compounds remain amorphous at room temperature. The structure of the compound was confirmed by spectroscopic method such as FT-IR, ^1H NMR, and UV−vis. The UV−vis spectrum of the Cz-C6-DCST in methylene chloride showed an absorption maximum of DCST chromophore at 420 nm.

In order to get better NLO chromophores operating on birefringence enhancement which are linked to the photoconducting carbazole moiety via a flexible hexyl-group, was designed. This chromophore was chosen because of its well-known electro-optic property [3,6]. The relatively long-alkyl chain is attached to facilitate the orientation of NLO chromophore under the poling field and to decrease the glass transition temperature (Fig. 1). Interestingly, the Cz-C6-PDCST chromophore can also form an amorphous organic glass by itself. Although the glassy state of Cz-C6-PDCST is not thermodynamically stable, the crystallization seems to be hindered enough at room temperature to provide samples useful over the time frame of at least several weeks so far. The material studied in this paper contains a carbazole covalently linked to an NLO chromophore, a DCST dye. The long-alkyl chains on the NLO chromophore were introduced to prevent the materials from disordering, crystallizing and to lower the glass transition temperature (T_g) of the compound. The T_g of the material is 40 °C as measured by DSC. It is well known that the refractive index modulation of a low-T_g PR material can be enhanced by the orientation of an NLO chromophore in response to the space-charge [5]. Unfortunately this T_g was not measured it's photorefractivity such as EO and FWM experimental, because our experimental conditions have not heat the air to 40 °C.

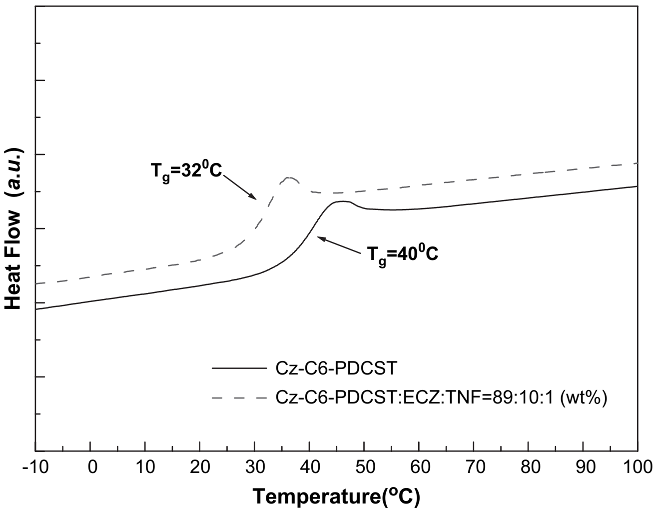


Fig. 1. Glass transitions of Cz-C6-DCST glass and **I**. The T_g is obtained from the second heating by DSC (at the heating rate of 10 °C/min under a nitrogen atmosphere).

Therefore we prepared by doping ECz as a plasticizer into composite system. The films prepared from methylene chloride solutions containing 1 wt% TNF and 10 wt% ECz showed an absorption tail extending beyond 600 nm due to the charge transfer (CT) complex formed by the electron transfer from the highest occupied molecular orbital of the carbazole moiety to the lowest unoccupied molecular orbital of the associated TNF molecule, and are transparent and of excellent optical quality. T_g of a novel PR composite (**I**) was 32 °C, and the stability of the device survived more than two months.

The absorption of this chromophore at the laser wavelength $\lambda = 632.8$ nm is negligible, the samples for the optical measurement was doped with 1 wt% TNF, giving an absorption coefficient $\alpha \sim 15.5\ cm^{-1}$.

We performed both electro-optic and degenerate four-wave mixing (DFWM) measurements. The field-induced birefringence of the photorefractive organic system was characterized using transmission ellipsometry under various applied fields. These data from the transmission ellipsometer experiments can be used to predict both the steady-state holographic contrast of the PR composite and to quantify the rotational freedom of the chromophores within the sample. As shown in

Fig. 2, the birefringence (Δn) of a composite containing the Cz-C6-DCST increased quadratically with increasing applied field. At an applied potential of 70 V/μm ($I = 10$ mW/cm), $\Delta n = 0.0043$ for **I**, which is sufficiently large value for the preparation of efficient *photorefractive* materials. Since the chromophores are rotating within an amorphous medium, they typically exhibit a non-exponential dynamic behavior.

The diffraction efficiency for a 50 μm thick sample obtained by a DFWM experiment is presented in Fig. 3. This field dependence is typical of low-T_g materials since the electro-optic coefficient and the space-charge fields are both electric field dependent. Fig. 3 (top) shows the dependence of an applied electric field on the steady-state diffraction efficiency.

As reported earlier [3] there are two contributions to the PR grating. The first contribution is due to the refractive index change based on the electro-optic effect Δn_{EO}. The second contribution stems from the field-induced orientational birefringence Δn_{BR} which is modulated periodically by the space-charge field. This mechanism of a change of the refractive index occurs since the chromophores can change their orientation quite readily in a material which has a low glass transition temperature.

The index grating recorded in the material was further tested by the DFWM experiment, where a third beam (632 nm, *p*-polarized) counter-propagating to one of the writing beams was Bragg diffracted from the refractive grating. The diffraction efficiency, η, defined as the ratio of the diffracted to incident reading beam power, is recorded. The value of η increased rapidly with the external field E through increase in both the PR space-charge field E_{sc} and the EO response $n^3 r_{eff}$. At an external field of 70 V/μm at $T = T_g$ ($I = 40$ mW/cm^2), the values of the maximum diffraction efficiency (η_{max}) of guest–host systems containing **I** were 78.5%. This composition showed high diffraction efficiencies. In addition, under identical experimental conditions, such as NLO chromophore (Δn), sensitizer, plasticizer, and experimental temperature (T_g), the PR properties of guest–host systems were largely determined by the magnitude of the photoconductivity and mobility of NLO chromophore, etc. Of course, in the case of **I**, the high electro-optic properties may be due to a large orientation induced, as well as to the low viscose medium. The diffraction efficiency of **I** reaches a maximum of 78.5% at $E = 70$ V/μm, which corresponds to the refractive index modulation (Δn) of ca. 0.0043 at 70 V/μm.

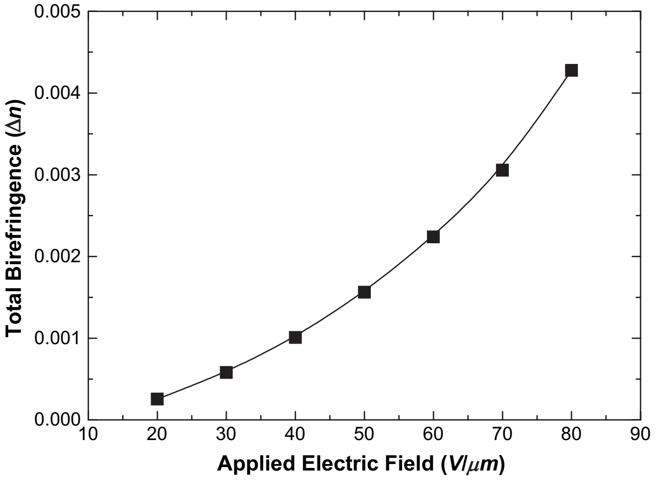


Fig. 2. Electric field-induced birefringence of **I** versus applied electric field.

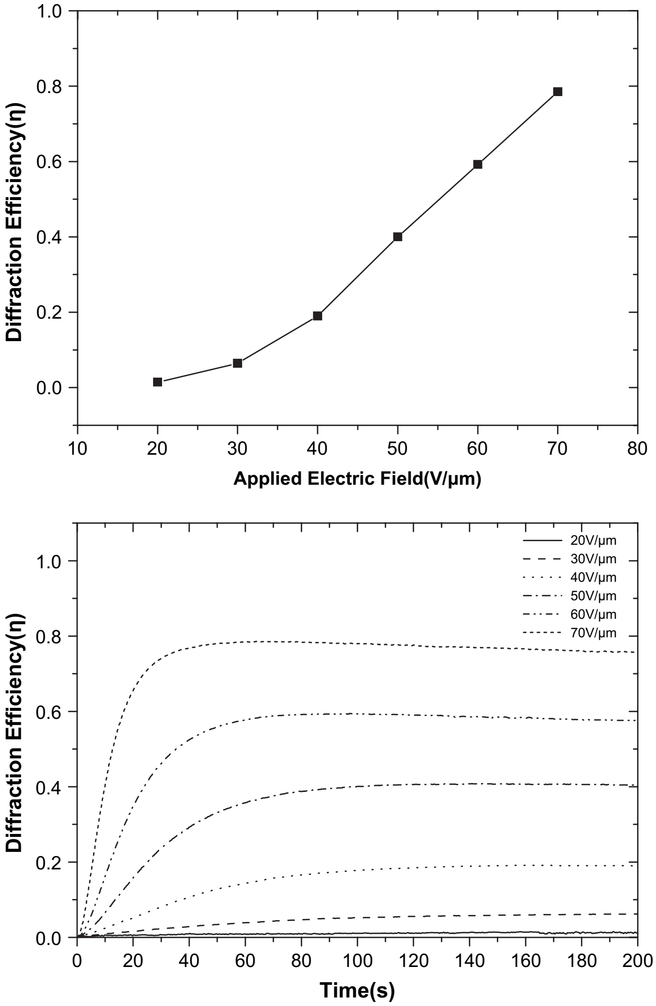


Fig. 3. FWM experimental results of **I** versus applied electric field (top). Grating dynamics of **I** (bottom).

Fig. 3 (bottom) illustrates the grating dynamics in **I**. The diffraction efficiency is defined as the intensity ratio of the first-order and the zero-order diffraction beams in the absence of one side of two beams. In this experiment, an electric field of 70 V/μm for **I** was applied to the sample, and a writing and a reading beam illuminated the samples. After a period of 200 s, a second writing beam was applied, and the diffracted reading beam monitored. The results of response time were the slow grating formation in this sample. Still now, the mechanism of the PR grating time in this composition is not understood. However, the morphology of composites and the interaction between the Cz-C6-DCST and the ECz are expected to play important roles. In another point of view, the most successful approach to photorefractivity with various response times in small molecules is the design of the molecular structure of material and the morphology of composite. Probably, this is because of the limit by reorientational enhancement effect in the polymer medium.

4. Conclusions

In summary, we have demonstrated a PR organic glass composite of good optical quality which has extended device lifetime, 78.5% device diffraction efficiency at 632 nm. The lifetime, reproducibility, and ease of manufacture of this composite offer significant advantages over present alternative composites of comparable efficiency. We have presented a quantitative evaluation of the holographic gratings produced in a newly synthesized material. It can be shown that with present materials the orientational effects of the side groups dominate the 'true PR' effect. It is to be expected that the temporal buildup and decay of the two gratings will be different, since the response time of the PR effect is given by the charge carrier dynamics and the response time of the orientational effects is given by molecular rotational parameters. For new materials it would be desirable that the true electronic PR effects dominate the orientational effects. Therefore, the photoconductive and the electro-optic properties of the present materials have to be further improved.

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