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The effect of the molecular structure of the chromophore on the photorefractive properties of the polymer systems with low glass transition temperatures

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Seven chromophores with different dipole moments and polarizability anisotropies were synthesized by varying conjugation bridges, such as polyene, thiophene, indole, and benzene combined with strong electron-donor and electron-acceptor groups. The birefringence of photorefractive materials containing 30 wt% of chromophore was observed to be in the range of 0.45×10^{-3} to 5.0×10^{-3} at an electric field of 70 V μm^{-1}, depending on the chromophore structure. The photorefractive material containing a polyene-based chromophore exhibited the highest photorefractive property, followed by those containing thiophene-based, benzene-based and indole-based chromophores. It was observed that, within material systems used in this study, photorefractive properties of guest–host systems were *linearly* proportional to the orientational birefringence.

Introduction

The photorefractive effect refers to the spatial modulation of the refractive index of material due to the light-induced redistribution of charge.[1,2] Under the illumination of non-uniform light formed by the interference of two coherent laser beams, a spatially oscillating space-charge field is formed arising from the generation and the redistribution of photo-induced charges. The refractive index of material is subsequently modulated *via* an electro-optic effect.

Polymeric photorefractive materials have been intensively studied due to the potential applications such as optical data storage and information processing, since the first discovery of the photorefractive effect in 1991 by IBM researchers.[3] Of the many polymeric photorefractive materials reported so far, the low glass transition temperature (T_g) guest–host system based on a photoconducting polymer doped with a nonlinear optical chromophore exhibits the most promising results.[4–7] Photorefractive properties of low T_g polymer systems are observed to be much better than expected based merely on the Pockels effect, which is largely ascribed to the *in situ* reorientation of the chromophore under a spatially modulated electric field.[8] Consequently, a chromophore which can maximize the orientational birefringence has been preferred to one which can exhibit a large Pockels effect.[6,9–14] It was observed that the photorefractive composite based on the methyl *N*-(2-butyl)-2,6-dimethylpyridin-4(1*H*)-ylidene(cyano)acetate (2BNCM) chromophore, which possesses both high dipole moment (μ) and large polarizability anisotropy ($\Delta\alpha$) but negligible hyperpolarizability (β), exhibited the one of the best performances reported so far.[12] The composite containing the 2,5-dimethyl-4-(*p*-nitrophenylazo)anisole (DMNPAA) chromophore showed better photorefractive properties than one containing the 3-fluoro-4-(*N,N*-diethylamino)-β-nitrostyrene (F-DEANST) chromophore, which was suggested to be due to the higher contribution of orientational birefringence on the total refractive index modulation of the DMNPAA system than the F-DEANST system.[13,14]

In this work, we synthesized several chromophores in order to study the relationship between chromophore structure and photorefractive properties systematically and provide the polymeric material with high efficiency. Since it was suggested that the dipole moment and the polarizability anisotropy are the key parameters of a chromophore for photorefractive applications,[8–14] we attempted to vary μ and $\Delta\alpha$ of the chromophore by changing the conjugation bridge, electron donor and electron acceptor. The electro-optical properties and photorefractive properties of the materials were determined under identical experimental conditions.

Experimental

Materials

Poly[methyl(3-carbazol-9-ylpropyl)siloxane] (PSX-CZ) was synthesized by the previously described methods[15] and 2,4,7-trinitrofluoren-9-one (TNF) purchased from Kanto Chem. Co. Inc. was purified prior to use. The preparations of 2-{3-[(*E*)-2-(dibutylamino)ethen-1-yl]-5,5-dimethylcyclohex-2-enylidene}malononitrile (DB-IP-DC), 2-(4-piperidinobenzylidene)malononitrile (P-BZ-DC), 2-[4-(dibutylamino)benzylidene]malononitrile (DB-BZ-DC) and 2-[4-(diethylamino)benzylidene]malononitrile (DE-BZ-DC) chromophores were carried out following the synthetic routes reported previously.[16,17] 2-(2-Piperidino-5-thenylidene)-malononitrile (P-TH-DC), 2-[1-(2-ethylhexyl)indol-3-ylmethylene]malononitrile (EH-IN-DC), and 4-[1-(2-ethylhexyl)indol-3-ylmethylene]-3-phenylisoxazol-5-one (EH-IN-IO) chromophores were prepared as described in the following paragraph. Chemical structures of the molecules were characterized by NMR spectrometry (Varian Mercury 400 MHz) and FT-IR spectrometry (Perkin-Elmer, Paragon 500). The absorption maxima (λ_{max}) and the melting points of chromophores were determined by UV–VIS spectrophotometry (Optizen 2120) and a melting point apparatus (Electro-thermal 9100), respectively.

Synthesis of 2-(2-piperidino-5-thenylidene)malononitrile (P-TH-DC). Piperidine (6.7 g, 80.6 mmol), potassium carbonate (2 g), Aliquat® 336 (phase-transfer catalyst, 2 drops) and dimethylformamide (200 ml) were stirred under nitrogen atmosphere at ambient temperature for 2 hours and then

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5-bromothiophene-2-carbaldehyde (2.5 g, 13.1 mmol) was added. After stirring the mixture at 110 °C for 4 days, it was poured into 450 ml of water. The reaction product was extracted with ethyl acetate. The crude product was obtained by drying the extracted organic layer over $MgSO_4$, followed by removing ethyl acetate. It was purified by silica gel column chromatography using a mixed solvent eluent (hexane : ethyl acetate = 7 : 3 v/v). After the solid product was further purified by recrystallization from a mixed solvent of THF and hexane, 5-piperidinothiophene-2-carbaldehyde was obtained as a brown solid. Yield: 83%, mp: 92.5 °C, λ_{max}: 369 nm, ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H (ppm) = 1.69 (m, 6H, 3 × CH_2), 3.33 (t, 4H, 2 × CH_2), 6.05 (d, 1H, $H_{thienyl}$), 7.45 (d, 1H, $H_{thienyl}$), 9.48 (s, 1H, H_{ald}). ^{13}C-NMR ($CDCl_3$, 400 MHz) δ_C (ppm) = 23.55, 24.95, 50.88, 103.76, 126.31, 140.11, 168.13, 179.96. FT-IR (KBr pellet, cm^{-1}) 1751 (C=O), 2756 (C–H_{ald}).

Malononitrile (1.2 equiv.) was added to the mixture of the 2-piperidinothiophene-5-carbaldehyde (1.0 equiv.), piperidine (catalyst, 2 drops), and ethanol (20 mL). The reaction was carried out at 60 °C for 3 hours. After cooling the reaction mixture to room temperature, the precipitated chromophore was collected by filtration. The product was washed thoroughly with methanol and then purified by recrystallization from ethanol. Yield: 82%, mp: 140 °C, λ_{max}: 463 nm, ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm) = 1.68 (br s, 6H, 3 × CH_2), 3.57 (br t, 4H, 2 × CH_2), 6.60 (d, 1H, $H_{thienyl}$), 7.71 (br d, 2H, $H_{thienyl}$), 7.97 (s, 1H, -CH=). ^{13}C-NMR ($CDCl_3$, 400 MHz) δ_C (ppm) = 23.48, 25.17, 51.53, 105.28, 116.19, 116.97, 119.36, 148.20, 169.82. FT-IR (KBr pellet, cm^{-1}) 2207 (C≡N).

Synthesis of 2-[1-(2-ethylhexyl)indol-3-ylmethylene]malononitrile (EH-IN-DC). To a solution of indole-3-carbaldehyde (10 g, 68.9 mmol) and sodium hydride (1.7 g, 70.8 mmol) in DMF (150 mL) was added 2-ethylhexyl bromide (13.3 g, 68.9 mmol) under nitrogen atmosphere. The mixture was stirred at room temperature for 24 hours and poured into 400 mL of water. The product was extracted with ethyl acetate. After solvent removal, the oily reaction product, 1-(2-ethylhexyl)indole-3-carbaldehyde, was further purified by silica gel column chromatography. The elusion solvent was hexane : ethyl acetate (30 : 70 by v/v). Yield: 79%, λ_{max}: 295 nm, ^{1}H-NMR ($CDCl_3$, 400 MHz) δ_H (ppm) = 0.91 (m, 6H, 2 × CH_3), 1.30 (m, 8H, 4 × CH_2), 1.94 (m, 1H, CH), 4.04 (d, 2H, NCH_2), 7.32 (m, 3H, H_{phenyl}), 7.65 (d, 1H, H_{phenyl}), 8.28 (m, 1H, H_{phenyl}), 9.97 (s, 1H, H_{ald}). ^{13}C-NMR ($CDCl_3$, 400 MHz) δ_C (ppm) = 10.63, 14.11, 23.03, 23.97, 28.62, 30.64, 39.65, 51.19, 110.12, 117.81, 121.95, 122.66, 123.71, 125.31, 137.30, 138.62, 184.20. FT-IR (KBr pellet, cm^{-1}) 1729 (C=O), 2761 (C–H_{ald}).

1-(2-Ethylhexyl)indole-3-carbaldehyde (1.0 equiv.) was reacted with malononitrile (1.2 equiv.) to yield EH-IN-DC under the same reaction conditions used for the synthesis of the P-TH-DC chromophore. Yield: 83%, mp: 105 °C, λ_{max}: 398 nm, ^{1}H-NMR ($CDCl_3$, 400 MHz) δ_H (ppm) = 0.91 (m, 6H, 2 × CH_3), 1.30 (m, 8H, 4 × CH_2), 1.94 (m, 1H, CH), 4.07 (d, 2H, NCH_2), 7.36 (m, 3H, H_{phenyl}), 7.65 (d, 1H, H_{phenyl}), 7.93 (m, 1H, H_{phenyl}), 8.34 (s, 1H, NCH=). ^{13}C-NMR ($CDCl_3$, 400 MHz) δ_C (ppm) = 10.43, 13.92, 22.84, 23.75, 28.29, 30.32, 39.39, 51.54, 71.31, 110.02, 110.91, 115.23, 115.36, 117.97, 122.96, 124.09, 127.35, 134.38, 136.13, 149.48. FT-IR (KBr pellet, cm^{-1}) 2219 (C≡N).

Synthesis of 4-[1-(2-ethylhexyl)indol-3-ylmethylene]-3-phenylisoxazol-5-one (EH-IN-IO). 1-(2-Ethylhexyl)indole-3-carbaldehyde (1.0 equiv.) was reacted with 3-phenylisoxazol-5-one (1.2 equiv.) under the same reaction conditions used for the synthesis of EH-IN-DC. Yield: 81%, mp: 75 °C, λ_{max}: 437 nm, ^{1}H-NMR ($CDCl_3$, 400 MHz) δ_H (ppm) = 0.84 (m, 6H, 2 × CH_3), 1.30 (m, 8H, 4 × CH_2), 1.99 (m, 1H, CH), 4.12 (d, 2H, NCH_2), 7.23–7.72 (m, 9H, H_{phenyl}), 7.99 (s, 1H, H_{phenyl}), 9.65 (s, 1H, =CH-). ^{13}C-NMR ($CDCl_3$, 400 MHz) δ_C (ppm) = 10.58 (CH_3), 14.06 (CH_3), 22.98, 23.94, 25.67, 28.53, 30.56, 39.51, 51.79, 67.92, 108.70, 111.15, 112.37, 118.04, 123.03, 124.00, 128.49, 128.51, 128.87, 128.95, 130.27, 136.79, 139.71, 141.55, 163.72, 170.99. FT-IR (KBr pellet, cm^{-1}) 1729 (C=O).

Sample preparation

The guest–host systems employed in the current study were based on photoconducting carbazole-substituted polysiloxane (PSX-CZ) doped with chromophores (30 wt%) and 2,4,7-trinitrofluoren-9-one (TNF, 1 wt%). However, in the case of polymeric systems containing P-TH-DC and EH-IN-IO chromophores, 5 wt% of liquid plasticizer, butyl benzyl phthalate (BBP, Aldrich Chem. Co.), was added in order to enhance the mobility of the chromophore at the measuring temperature of 25 °C. Note that in the case of low T_g materials, *in situ* poling is performed at the measuring temperature. Thus, in order to assure sufficient mobility of the chromophore, the glass transition temperature of the materials must be controlled to be lower than or at least in the vicinity of the measuring temperature.

In order to prepare the sample, the mixture of PSX-CZ, TNF, and chromophore was dissolved in dichloromethane, and the solution was filtered through a 0.2 μm filter. The polymer composite was cast on an indium tin oxide (ITO) glass plate, dried for 6 hours at ambient temperature and subsequently heated in an oven at 90 °C for 24 hours to completely remove the residual solvent. Then, the polymer was softened by placing it on a hot plate at 100 °C and then covered with the second ITO coated glass. The thickness of the film was controlled by Teflon spacers between two ITO glass plates. All samples prepared in this study exhibited long-term stability. They retained optical clarity for a year when stored at room temperature, which was also confirmed by recording the UV–VIS spectra.

Measurements

The electro-optical properties of the polymer sample were determined by transmission ellipsometric methods.[18] The sample tilted by 45° was placed between the polarizer and the analyser with the polarization set to +45° and −45°, respectively. The electric-field induced birefringence (Δn) of the material was determined from the variation of the transmitted intensity (T) through crossed polarizers upon the application of electric field, as described by eqn. (1)

$$T = \sin^2\left(\frac{2\pi}{\lambda} l \Delta n\right) \qquad (1)$$

where λ is wavelength and l is length of light path.

The photorefractive properties of the sample were characterized at the wavelength of 632.8 nm (He–Ne laser) by the two-beam coupling (2BC) method.[2,7] A p-polarized laser beam with an intensity of 20 m W cm^{-2} was used as a writing beam. Two coherent laser beams were used to irradiate the sample in the tilted geometry with incidence angles of 30° and 60° with respect to the sample normal. The asymmetric energy coupling between two laser beams was evaluated by the gain (γ) defined as $\gamma = I_2^{(I_1 \neq 0)}/I_2^{(I_1 = 0)}$, where I_1 and I_2 are the pump beam and signal beam, respectively. The gain coefficient (Γ) was calculated from the measured value of gain (γ), as given by eqn. (2)[19]

$$\Gamma = \frac{1}{L}\left[\frac{\ln \beta\gamma}{\ln(1+\beta-\gamma)}\right] \qquad (2)$$

where L is the beam path length and β is the intensity ratio of the incident laser beams.

The glass transition temperature (T_g) of the polymer was determined by differential scanning calorimetry (Perkin Elmer, DSC7) at a heating rate of 10 °C min^{-1} The glass transition temperatures of DB-IP-DC, P-BZ-DC, DE-BZ-DC, DB-BZ-DC, and EH-IN-DC systems (PSX-CZ : TNF : chromophore = 69 : 1 : 30 w/w) were 27 °C, 25 °C, 20 °C, 5 °C, and 15 °C, respectively. The plasticized P-TH-DC and EH-IN-IO systems (PSX-CZ : TNF : BBP : chromophore = 69 : 1 : 5 : 30 w/w) both showed the same glass transition temperature of 23 °C.

Results and discussion

Influence of chromophore structure on electro-optical properties of guest–host system

Fig. 1 shows the chemical structures of chromophores synthesized in this work. The chromophore structures were varied by using different types of conjugation bridges such as polyene, heteroaromatic ring, and benzene combined with electron donors and electron acceptors.

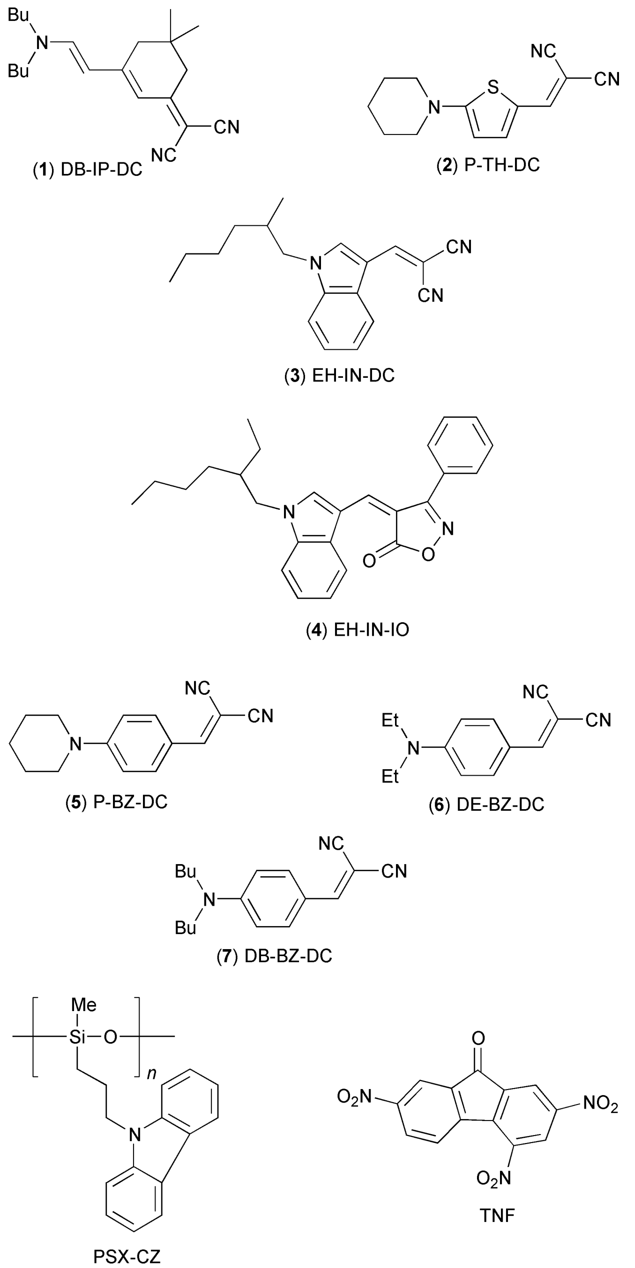

Fig. 1 Chemical structures of photoconducting polymer, sensitizer and optically nonlinear chromophores: DB-IP-DC: 2-{3-[(*E*)-2-(dibutylamino)ethen-1-yl]-5,5-dimethylcyclohex-2-enylidene}malononitrile; P-TH-DC: 2-(2-piperidino-5-thenylidene)malononitrile; EH-IN-DC: 2-[1-(2-ethylhexyl)indol-3-ylmethylene]malononitrile; EH-IN-IO: 4-[1-(2-ethylhexyl)indol-3-ylmethylene]-3-phenylisoxazol-5-one; P-BZ-DC: 2-(4-piperidinobenzylidene)malononitrile; DE-BZ-DC: 2-[4-(diethylamino)benzylidene]malononitrile; DB-BZ-DC: 2-[4-(dibutylamino)benzylidene]malononitrile; PSX-CZ: poly[methyl(3-carbazol-9-ylpropyl)siloxane]; TNF: 2,4,7-trinitrofluoren-9-one.

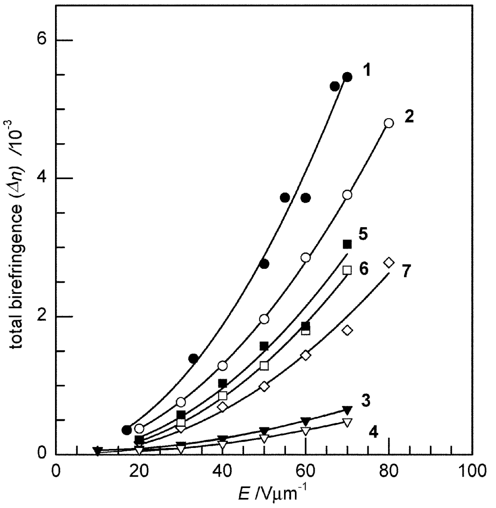

Fig. 2 Electro-optical properties of guest–host systems at various electric fields: (1) DB-IP-DC system; (2) P-TH-DC system; (3) EH-IN-DC system; (4) EH-IN-IO system; (5) P-BZ-DC system; (6) DE-BZ-DC system; (7) DB-BZ-DC system.

The electro-optical properties of the guest–host systems containing 30 wt% of chromophore were characterized by transmission ellipsometric measurement at various applied fields. As given in Fig. 2, the birefringence (Δn) of the photorefractive materials is increased quadratically with an electric field in the order of EH-IN-IO < EH-IN-DC < DB-BZ-DC < DE-BZ-DC < P-BZ-DC < P-TH-DC < DB-IP-DC systems. Polyene-based chromophore, DB-IP-DC, exhibits the highest electro-optical property, followed by thiophene-based, benzene-based, and then indole-based chromophores irrespective of electron donors and electron acceptors. This observation reflects that the contribution of the conjugation bridge of the chromophore to the electro-optical properties is more important than those of electron-donor and electron-acceptor groups.

It is to be noted that the birefringence (Δn) determined by transmission ellipsometric methods is governed by the combined contributions of orientational birefringence and Pockels effect. In the case of the current chromophores used in this work, the contribution of orientational birefringence on the total birefringence is estimated from the calculated molecular parameters of the chromophores. Dipole moment (μ), molecular polarizability (α), and hyperpolarizability (β) of chromophore were calculated using the semi-empirical method, MOPAC 6 with PM3 approximation method for geometry optimization.[20] The figure-of-merit (F) of a chromophore used in a photorefractive material is generally described as follows:[11,14]

$$F=\left(\frac{2\mu^2\Delta\alpha}{9kTM}+\frac{\mu\beta}{M}\right) \tag{3}$$

where M is the molecular weight of the chromophore. The first term of eqn. (3) is related to the orientational birefringence while the second term corresponds to the Pockels effect. In Table 1, figures-of-merit of both terms, F_{BR} and F_{Pockels}, for the current chromophores are presented. The calculated results show that F_{BR} is an order of magnitude larger than F_{Pockels}. Furthermore, the total birefringence (Δn) of guest–host systems determined experimentally is observed to be linearly proportional to the calculated value of F_{BR}, as given in Fig. 3. Thus, it may be suggested that the contribution of the orientational birefringence to the total birefringence is usually much larger

Table 1 Dipole moment (μ), polarizability anisotropy ($\Delta\alpha$) and hyperpolarizability (β) calculated from MOPAC 6 and estimated figures-of-merit of chromophores

Chromophore	μ/ 10^{-30} C m	$\Delta\alpha$/ 10^{-40} C m^2 V^{-1}	β/ 10^{-50} C m^3 V^{-2}	$F_{BR}{}^{a}$/ 10^{-77} C^2 m^4 mol V^{-2} kg^{-1}	$F_{Pockels}{}^{b}$ 10^{-77} C^2 m^4 mol V^{-2} kg^{-1}
DB-IP-DC	26.7	71.3	12.7	84.9	1.05
P-TH-DC	23.0	56.7	9.3	66.5	0.87
P-BZ-DC	21.5	52.8	7.0	55.2	0.64
DB-BZ-DC	20.1	54.4	8.4	41.8	0.59
DE-BZ-DC	19.7	52.3	7.4	48.2	0.65
EH-IN-DC	24.9	30.6	2.9	33.9	0.24
EH-IN-IO	24.9	18.4	1.8	15.4	0.11

$^{a}F_{BR} = (2/9)M^{-1}\mu^2\Delta\alpha\, k^{-1}T^{-1}$. $^{b}F_{Pockels} = M^{-1}\mu\beta$.

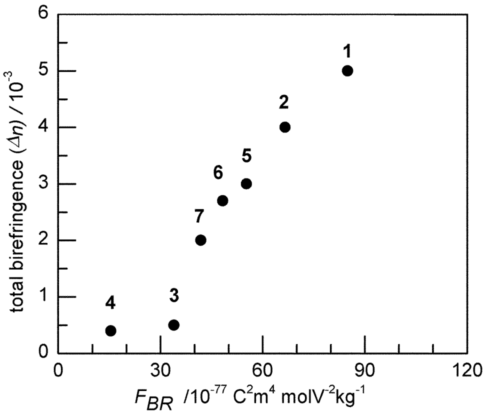

Fig. 3 Calculated F_{BR} of chromophore *versus* total birefringence (Δn) of guest–host systems determined at 70 V μm^{-1} from transmission ellipsometric measurements. An explanation of the numbers is given in Fig. 2.

than that of the Pockels effect for the chromophores in low T_g materials used in this study, as found in the literature.[10,11,14]

The influence of chromophore structure on birefringence of the guest–host system, as presented in Fig. 2, can be explained based on the results of Table 1 as follows. In the cases of DB-IP-DC and P-TH-DC systems, the high electro-optic properties may be due to a large dipole moment as well as a high polarizability anisotropy of chromophores associated with the effective conjugation along the polyene or heteroaromatic ring. In contrast, P-BZ-DC, DE-BZ-DC, and DB-BZ-DC chromophores containing benzene as a conjugation bridge possess lower dipole moments and polarizability anisotropies than DB-IP-DC and P-TH-DC chromophores, since the high resonance-stabilization energy of the benzene ring limits charge transfer along a π-conjugation bridge. The indole-based chromophores exhibit the lowest electro-optical effect, indicating the importance of polarizability anisotropy on electro-optical properties. Note that the dipole moments for the indole-based chromophores are larger than those of the benzene-based chromophores, while the polarizability anisotropy ($\Delta\alpha$) of the former is much lower than that of the latter.

Photorefractive properties of guest–host systems

Photorefractive properties of various systems were characterized by the gain coefficient determined by the two-beam coupling method. At the external field of 70 V μm^{-1}, the values of the gain coefficient (Γ) of guest–host systems containing DB-IP-DC, P-TH-DC, P-BZ-DC, DE-BZ-DC, DB-BZ-DC, EH-IN-DC, and EH-IN-IO chromophore were 280 cm^{-1}, 230 cm^{-1}, 150 cm^{-1}, 140 cm^{-1}, 120 cm^{-1}, 30 cm^{-1}, and 27 cm^{-1}, respectively. The gain coefficients of the photorefractive materials obtained at 70 V μm^{-1} are plotted against

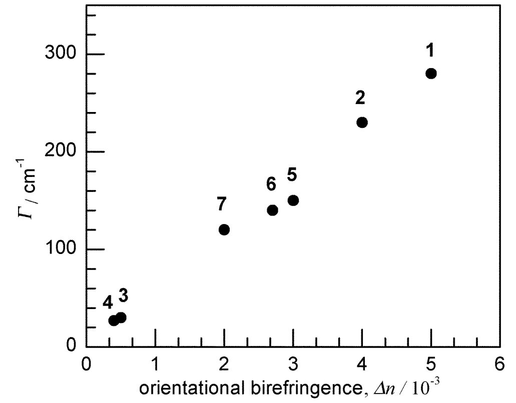

Fig. 4 Gain coefficient *versus* birefringence (Δn) of guest–host system at 70 V μm^{-1}. An explanation of the numbers is given in Fig. 2.

the birefringence values (Δn) determined from transmission ellipsometric method and the results are given in Fig. 4. The DB-IP-DC system gives rise to the best photorefractive property whereas the EH-IN-IO system gives rise to the lowest gain coefficient, which is in good agreement with their electro-optical properties. The gain coefficients of the guest–host systems are observed to be linearly proportional to Δn, indicating the significant contribution of the orientational birefringence to the photorefractive property. It should be noted that the gain coefficient of a photorefractive material depends on the magnitudes of the space-charge field and phase shift, in addition to the electro-optical activity. However, when the experimental conditions, such as photoconducting medium, chromophore concentration, the applied field and viscosity of the medium are identical, the photorefractive properties of guest–host systems seem to be determined largely by the magnitude of the orientational birefringence. Otherwise, the close relationship between the orientational birefringence and photorefractive properties may not necessarily be satisfied, as found in the literature.[14]

The variations of two-beam coupling gain coefficients (Γ) with an electric field are given for DB-IP-DC, P-TH-DC, P-BZ-DC, DE-BZ-DC and EH-IN-DC systems in Fig. 5. The photorefractive properties of the guest–host systems are increased quadratically with the applied electric field. The excellent photorefractive properties of the DB-IP-DC and P-TH-DC systems are noteworthy. Even at the moderate electric field of 50 V μm^{-1}, the gain coefficient of DB-IP-DC system is 180 cm^{-1}, which is a sufficiently high value for practical applications. In the case of the P-TH-DC system, the gain coefficient is as high as 340 cm^{-1} at the applied field of 90 V μm^{-1}. When compared to the well-known photorefractive system containing 2,5-dimethyl-4-(*p*-nitrophenylazo)anisole (DMNPAA) chromophore,[4] the DB-IP-DC and P-TH-DC systems exhibit better photorefractive properties. The gain

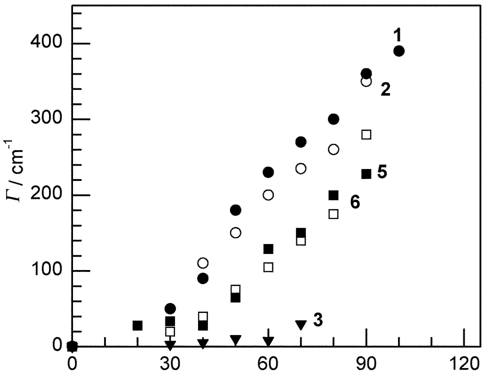

Fig. 5 Photorefractive properties of guest–host systems at various applied electric fields. (filled circles) DB-IP-DC system; (open circles) P-TH-DC system; (filled triangles) EH-IN-DC system; (filled squares) P-BZ-DC system; (open squares) DE-BZ-DC system.

coefficient of the poly-(N-vinylcarbazole) (PVK) composite doped with 2,5-dimethyl-4-(p-nitrophenylazo)anisole (50 wt %), plasticizer ethylcarbazole (16 wt%), and sensitizer 2,4,7-trinitrofluoren-9-one (1 wt%) was 220 cm^{-1} at the applied electric field of 90 V µm^{-1}.

Conclusion

In this work, we investigated the influence of chromophore structures on the photorefractive properties of low T_g guest–host systems. The DB-IP-DC and P-TH-DC systems showed large orientational birefringences due to both large dipole moments and high polarizability anisotropies of chromophores associated with the effective conjugation along the polyene and heteroaromatic ring, respectively. These polymeric systems gave rise to the excellent photorefractive properties. The gain coefficients of DB-IP-DC and P-TH-DC systems were 360 cm^{-1} and 340 cm^{-1} at the electric field of 90 V µm^{-1}, respectively. In contrast, the guest–host systems containing indole-based chromophores exhibited the lowest gain coefficients among the materials used in this work, probably due to the low birefringence associated with the low $\Delta\alpha$ of the indole moiety. When the photorefractive properties of guest–host systems are compared under identical experimental conditions, the gain coefficients of the materials were observed to be *linearly* proportional to orientational birefringence within the materials used in the current study.

Acknowledgement

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References

1 W. E. Moerner and S. M. Science, *Chem. Rev.*, 1994, **94**, 127.
2 P. Günter and J.-P. Huignard, in *Photorefractive Materials and Their Applications*, Springer-Verlag, Berlin, 1988, vol. 1 and 1989, vol. 2.
3 S. Ducharme, J. C. Scott, R. J. Twieg and W. E. Moerner, *Phys. Rev. Lett.*, 1991, **66**, 1846.
4 K. Meerholtz, B. L.Volodin, Sandalphon, B. Kippelen and N. Peyghambarian, *Nature*, 1994, **371**, 497.
5 E. Hendrickx, J. Herlocker, J. L. Maldonado, S. R. Marder, B. Kippelen, A. Persoons and N. Peyghambarian, *Appl. Phys. Lett.*, 1998, **72**(14), 1679.
6 B. Kippelen, S. R. Marder, E. Hendrickx, J. L. Maldonado, G. Guillemet, B. L. Volodin, D. D. Steele, Y. Enami, Y. J. Yao Sandalphon, J. F. Wang, H. Rockel, L. Erskine and N. Peyghambarian, *Science*, 1998, **279**, 54.
7 D. Wright, M. A. Diaz-Garcia, J. D. Casperson, M. DeClue, W. E. Moerner and R. J. Twieg, *Appl. Phys. Lett.*, 1998, **73**, 1490.
8 W. E. Moerner, S. M. Silence, F. Hache and G. C. Bjorklund, *J. Opt. Soc. Am. B.*, 1994, **11**, 320.
9 S. R. Marder, B. Kippelen, A. K.-Y. Jen and N. Peyghambarian, *Nature*, 1997, **388**, 845.
10 R. Wortmann, C. Poga, R. J. Twieg, C. C. Geletneky, R. Moylan, P. M. Lundquist, R. G. DeVoe, P. M. Cotts, H. Horn, J. E. Rice and D. M. Burland, *J. Chem. Phys.*, 1996, **105**, 10637.
11 B. Kippelen, F. Meyers, N. Peyghambarian and S. R. Marder, *J. Am. Chem. Soc.*, 1997, **119**, 4559.
12 P. M. Lundquist, R. Wortmann, C. Geletneky, R. J. Tweig, M. Jurich, V. Y. Lee, C. R. Moylan and D. M. Burland, *Science*, 1996, **274**, 1182.
13 Sandalphon, B. Kippelen, K. Meerholz and N. Peyghambarian, *Appl. Opt.*, 1996, **35**, 2346.
14 C. Moylan, R. Wortmann, R. J. Twieg and I.-H. McComb, *J. Opt. Soc. Am. B*, 1998, **15**, 929.
15 P. Strohriegl, *Mackromol. Chem. Rapid Commun.*, 1986, **7**, 771.
16 H. Chun, I. K. Moon, D.-H. Shin and N. Kim, *Chem. Mater.*, 2001, **13**, 2813.
17 M. A. Diaz-Garcia, D. Wright, J. D. Casperson, B. Smith, E. Glazer and W. E. Moerner, *Chem. Mater.*, 1999, **11**, 1784.
18 R. Bittner, T. K. Daubler, D. Neher and K. Meerholz, *Adv. Mater.*, 1999, **11**(2), 123.
19 P. Günter, *Phys. Rep.*, 1982, **93**, 199.
20 C. A. van Walree, O. Franssen, A. W. Marsman, M. C. Flipse and L. W. Jenneskens, *J. Chem. Soc., Perkin Trans. 2*, 1997, 799.