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The Research of Optimum Molar Ratio between Guest and Host Chromophores in Binary Chromophore System for Excellent Electro-Optic Activity

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A series of binary chromophore systems (BCSs) based on the electro-optic (EO) polymers **P1-P5** and guest chromophores **C1** and **C2** were designed and prepared. The poled films of these BCSs showed large EO coefficients (r_{33}=57~160pm/V), which were much higher than the sum of their individual component. The optimum molar ratio (OMR) between guest and host chromophores was first systematically explored by changing their molar ratios (N_g:N_h) in the following BCSs:(1) **C1/P2**; (2) **C1/P4**; (3) **C2/P1**; (4) **C1/P5**. Meanwhile, the influence of the types of the chromophores and the polymer main chains on the OMR was also studied. Finally, these results indicated that the BCSs showed the greatest r_{33} growth rates when the N_g:N_h was 1:1. Hence, the OMR in BCS was 1:1 and the types of the chromophores and the polymer main chains were found to have little influence on the OMR. At the OMR, the r_{33} values were even 2.1 times of the sum of their individual components. We gave the model for this phenomenon. The research of OMR in BCSs provided a promising way to further improve the EO coefficients.

Introduction

Organic electro-optic (EO) materials have shown commercial potential in high speed broadband waveguides for optical modulators, switches, sensors, and information processors.[1] Compared to conventional inorganic crystal materials, the organic EO materials have unparalleled advantages, such as high nonlinear optical (NLO) susceptibility, ultrafast response time, low dielectric constant and easy processing.[2] The approaches for NLO chromophores incorporated in EO materials include guest-host polymer systems,[3] chromophore-functionalized polymers (side-chain[4] and main-chain[5]), crosslinked systems,[6] dendrimers,[7] and self-assembled chromophoric superlattices.[8] However, to make the EO polymers possess the optical nonlinearity, the microscopic molecular first hyperpolarizability β must translate into the macroscopic EO activity efficiently. The relationship between the macroscopic EO coefficient (r_{33}) and the microscopic property (β) can be calculated by the following equation:[9]

$$r_{33} = 2Nf\beta < \cos^3\theta > /n^4 \qquad (1)$$

Where N is the chromophore number density, f is local field (Onsager) factor, n is the index of refraction and $<\cos^3\theta>$ is the order parameter for the alignment of chromophore. To realize large EO activity for dipolar organic materials requires the simultaneous optimization of β, $<\cos^3\theta>$ and N.[10] Unfortunately, in any materials, N couldn't be infinite large for a chromophore and there is always an optimal chromophore loading level. If N exceeds the optimal chromophore loading, the r_{33} value decreases due to the strong intermolecular dipole-dipole electrostatic interactions, because the strong electrostatic interaction seriously affects $<\cos^3\theta>$ value of the chromophores.[1b, 11]

Binary chromophore system (BCS) was reported in recent years, which usually depended on one chromophore as a guest doped into another chromophore-containing host materials.[12] BCS can significantly increase the loading density of chromophores in polymer matrices without causing obvious aggregation of chromophores.[12] More than that, BCS can effectively improve the poling efficiency and significantly increase the EO coefficient. The remarkably large EO activity displayed by BCS is even greater than the sum of their individual components.[13] However, many BCSs didn't show

anticpant r_{33} values. There were more factors affect the EO coefficients in BCS compared to the conventional polymer system. So many questions need to be explored, such as whether there is an optimum molar ratio (OMR) between guest and host chromophores in the BCS, what kinds of guest/host chromophore combinations can achieve the best EO coefficients and how does the guest and host chromophores work in the BCS to achieve super large r_{33} values, and so on. These are exactly what we want to figure out.

In this work, we focused on the first question. A series of binary chromophore systems (BCSs) based on the EO polymers **P1-P5** and guest chromophores **C1** and **C2** were prepared. Firstly, the BCSs that **C1** co-doped into **P1-P3** at a loading concentration of ~16.5wt% were prepared. The difference in the r_{33} growth rates of these BCSs indicated that the optimum molar ratio (OMR) between guest and host chromophores may exist in the BCS. Then, chromophore **C1** was doped into polymer **P2** with different concentration (BCSs **C1/P2**) to explore the OMR in the BCSs. It was found out that BCSs **C1/P2** showed greatest r_{33} growth rate when the molar ratio between guest and host chromophore ($N_g:N_h$) was 1:1. Therefore, the OMR in BCSs **C1/P2** was 1:1. Moreover, the OMR were also explored in BCSs **C1/P4** and **C2/P1** that with different host chromophore and guest chromophore, respectively. Furthermore, BCSs **C1/P5** were prepared to explore the OMR in the BCS that with different polymer main chain. Finally, we found the OMR in these BCSs was 1:1 and at the OMR, the r_{33} values were even 2.1 times of the sum of their individual components. Hence, the OMR provided a promising way to further improve the EO coefficients of the BCS. Besides, the phenomena that the BCSs possessed the large r_{33} values and the high loading density of the NLO chromophores were also explored.

Experimental

Materials

All the starting materials were purchased from Acros Organics, Fluka, or Aldrich and used as received unless otherwise stated. All the solvents were purchased from Beijing Chemical Reagents Company and distilled before use.

Instrumentation

The Ultraviolet-visible-Near Infrared (UV-vis-NIR) absorption spectra were obtained by Varian Cary 5000 spectrometer. ^{1}H nuclear magnetic resonance (^{1}H NMR) spectra were measured with an Advance Bruker (400 MHz) NMR spectrometer using tetramethylsilane (TMS, δ=0 ppm) as the internal standard. The fourier transform infrared (FT-IR) spectra were recorded by a Varian 3100 FT-IR spectrometer at a resolution of 2 cm^{-1} with a minimum of 64 scans. The number-average molecular weight (M_n) and weight average molecular weight (M_w) values were obtained by Gel permeation chromatography (GPC) analysis which was performed on a Waters high performance liquid chromatography (HPLC) system equipped with a 2690D

separation module and a 2410 refractive index detector. Polystyrene standards were used as calibration standards for GPC. Tetrahydrofuran (THF) was used as an eluent, and the flow rate was 1.0 mL/min. The thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) data were recorded by TA-instruments Q50 and Q10 analyzers with a heat rate of 10 ^{o}C/min under nitrogen atmosphere, respectively. The thickness of the films was measured with an Ambious Technology XP-1 profilometer. The refractive indices of the polymer films were measured by prism coupling device (Metricon Company) at 1310 nm.

Synthetic procedures

The chromophore 2, **C1** and polymers **P**, **P1-P3**, **P5** in scheme 1 were reported previously by our group. [14] The chromophore **C2** was reported in literature.[14d]

General procedure for the synthesis of polymer P4. Polyarylate **P4** was synthesized according to our previous work.[14b] **P** (0.5g, 1.14 mmol), chromophore **2** (0.0621g, 0.09mmol), 1,3-dicyclohexylcarbodiimide (DCC) (0.0206g, 0.10 mmol) and 4-(dimethylamino)-pyridinium-4-toenesulfonate (DPTS) (0.0029g, 0.01 mmol) were reacted in the mixture of 15 mL THF and 15 mL CH$_2$Cl$_2$ at room temperature in an atmosphere of dry nitrogen. After 24 h, 1 mL methanol and 0.1205 g (0.58mmol) DCC were added. Another 12 h later, the reaction mixture was filtered and dropped into methanol to precipitate the polymer. The product was redissolved and reprecipitated several times until the filtrate was colorless, and dried at 40 ^{o}C under vacuum for 24 h. Green polyarylate brached with chromophore **2** was obtained. (yield: 75%) ^{1}H NMR (400 MHz, DMSO-d_6, δ ppm): 8.77 (1H, Ar-H), 8.48 (2H, Ar-H), 7.83 (1H, Ar-H), 7.70 (0.10H, -CH=C), 7.42-7.12 (10.7H, Ar-H), 6.84 (0.10H, -C=CH),4.94 (0.2H, N-CH$_2$-Ph), 4.20 (0.2H, -COOCH$_2$-anthracene), 3.99 (0.2H, -CH$_2$-N),3.90 (1.5H, -COOCH$_3$), 3.74 (0.40H, -OCH$_2$), 3.18 (0.30H, -N-CH$_3$), 2.32 (1.2H, -CH$_2$-COO), 2.06 (1.2H, -C-CH$_2$), 1.98 (0.2H, -CH-), 1.65-1.23 (2.2H, -alkyl chain-H) 0.83 (0.6H, -CH$_3$). IR (thin film): ν = 2967 (s, -CH$_3$), 2227 (-CN), 1733 (-COO-) cm^{-1}.

Preparation of polymer films

The polymers and appropriate guest chromophores were dissolved in cyclopentanone (12.5 wt%). The solution was filtered through 0.22-μm syringe filters. The filtrate was spin-coated onto indium-tin oxide (ITO)-coated glass substrates. The resulting films were baked in vacuum at 40 ^{o}C overnight to ensure the removal of any residual solvent. The thickness of these films was measured to be 3-4 μm.

Poling and r_{33} measurements

To evaluate the EO activity of the BCSs, the prepared films were poled by corona poling at a suitable temperature (approximately 5 ^{o}C higher than the T_g) and voltage (12.5-13.0 kV) for 13-25 min to realize the noncentrosymmetric alignment

of the NLO chromophores. The poling voltage was removed after the samples were cooled to room temperature.

The EO coefficients of the poled films were determined by the simple reflection technique initially proposed by Teng and Man.[15] The r_{33} values were calculated by the following equation:[15]

$$r_{33} = \frac{3\lambda I_m}{4\pi V_m I_c n^2} \frac{(n^2 - \sin^2\theta)^{3/2}}{(n^2 - 2\sin^2\theta)} \frac{1}{\sin^2\theta} \qquad (2)$$

Where r_{33} is the EO coefficient of the poled polymer, λ is the optical wavelength, θ is the incidence angle, I_c is the output beam intensity, I_m is the amplitude of the modulation, V_m is the modulating voltage, and n is the refractive indices of the polymer films.

Results and discussion

Synthesis

The polymer **P4** was synthesized by the post-functionalization.[16] The prime advantage of this method is different types of chromophores can be introduced into the polymer backbone. The esterification reaction between **P** and chromophore **2** was catalyzed by 1,3-dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)-pyridinium-4-toenesulfonate (DPTS) at room temperature. This reaction is mild enough to the chromophores sensitive to the polymerization conditions.

P4 was characterized by[1]H-NMR, UV-vis-NIR, FT-IR, DSC, TGA and GPC.

The green polyarylate **P4** has good solubility in common solvents at room temperature, such as THF, CH_2Cl_2, $CHCl_3$, DMF, DMSO, and cyclopentanone. The other properties of **P4** were shown in Tab.1. The λ_{max} of **P4** in CH_2Cl_2 is 697 nm, which indicated that **P4** would exhibit good NLO property. In fact, the r_{33} value of **P4** was measured to be 33 pm/V, which is a well value considering the relatively low chromophore content. **P4** showed relatively high T_g of 145.5 °C, and the T_d of 360.2 °C indicated that **P4** had excellent thermal stability.

In the synthesis of **P1-P3**, it was found that in the catalysis of the DPTS, the esterification reaction was always companied by the ester exchange reaction, which produced the decrease in molecular weight and the increase in polydispersity of the polymer. Hence, in the synthesis of **P4**, the esterification reaction time between **P** and chromophore **2** was cut in half. And so did the esterification reaction between **P** and CH_3OH. As a result, in comparison with **P1-P3**, the weight-average molecular weight (M_w) of the **P4** was increased to 4.44×10^4 (the M_w of **P1-P3** was $3.63-3.98 \times 10^4$). And the polydispersity (M_w/M_n) of **P4** was decreased to 3.18, which of **P1-P3** was above 3.90. Therefore, it can be concluded that in esterification reaction, shortening the reaction time appropriately is helpful to obtain the polymers with lower polydispersity.
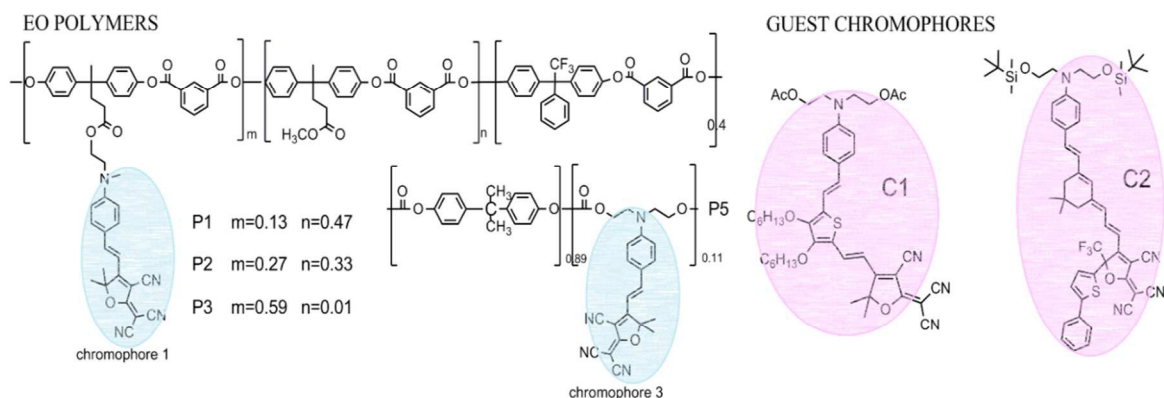
Scheme 1 The structures of the polymers and chromophores.
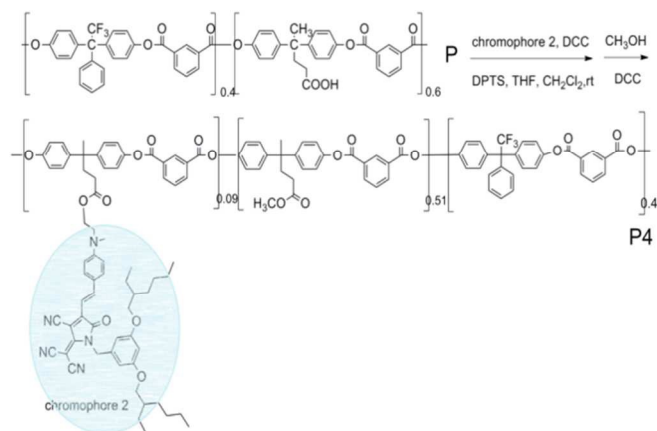
Scheme 2 The synthetic route of the polyarylate **P4**.

In order to facilitate the research, different types of host polymers (P1-P3, P4 and P5) were designed and synthesized. As shown in scheme 1 and 2, polyarylates **P1-P3** were polymers containing chromophore **1** with different loading concentration, and polyarylate **P4** contained chromophore **2**. Polycarbonate **P5** had different polymer main chain containing chromophore **3**. Chromophores **1** and **3** had the similar skeleton structures with tricyanofuran (TCF) type acceptors, while chromophore **2** had the different structure with tricyanopyrroline (TCP) type acceptors and large branched group in its acceptor which can both improve the solubility and thermal stability, and limit the intermolecular interactions of the chromophores as well. The guest chromophores **C1** and **C2** were synthesized as the guest chromophores. **C1** was thiophene-type chromophore and **C2** was CLD-type

chromophore with more electron-withdrawing phenylthienyl-CF$_3$-TCF acceptors. The hexyloxy groups in the thiophene-based bridge of **C1** made it more compatible with the polymer matrix. And so did the tertbutyldimethylsilyl groups in the donor of **C2**.

The optimum ratio

In our previous work, **P1-P3** presented well NLO and thermal properties. The BCSs 1-3 were prepared, in which the guest chromophore **C1** was co-doped into **P1-P3** at a loading concentration of ~16.5wt% (Tab. 2). The r$_{33}$ values of BCSs 1-3 were 62, 73 and 57 pm/V, respectively. Apparently, BCS 2 had the largest r$_{33}$ value. However, compared to the sum r$_{33}$ values of their individual components, the r$_{33}$ values of the BCSs 1-3 increased 88%, 12% and 10%, respectively. The BCS 1 has the largest growth rate of the r$_{33}$ value. The difference of them was only the molar ratio between guest and host chromophore (N$_g$:N$_h$), which was 1.01:1, 0.50:1 and 0.27:1, respectively. This implied that there may be an optimum molar ratio (OMR) between the guest and host chromophores in these BCSs to achieve the largest EO coefficients. Thus, a series of experiments were carried out, in which the concentration of the guest chromophore was changed while the concentration of the host chromophore was kept the same. So BCSs 4-7 (BCSs **C1/P2**) were prepared. **C1** was co-doped into **P2** at a weight loading level of 22.8%, 28.3%, 33.0% and 37.1% according to N$_g$:N$_h$ of 0.75:1, 1.00:1, 1.25:1, 1.50:1, respectively. We could clearly observe that when N$_g$: N$_h$ was 1:1, the BCS 5 had the largest growth rate of r$_{33}$ value. Therefore, the OMR did exist in these BCS, which was 1:1. This phenomenon is worth to further explore because it offers a promising way to maximize the EO coefficients in the BCS.

To confirm whether this phenomenon exists in other BCSs, another series of experiments were carried out. On basis of BCSs **C1/P2**, changes of the chromophores type can weaken or strengthen the electrostatic interactions between the chromophores in the BCSs (Tab. 3). Firstly, the type of the host chromophore was changed. Chromophore **2** (which the **P4** containing) was chosen for its large branched group in its acceptor which can effectively isolate the chromophores. Hereby, the electrostatic interaction between the chromophores in BCSs **C1/P4** was weaker than that in BCSs **C1/P2**. Therefore, BCSs 8-10 (BCSs **C1/P4**) with different concentration of guest **C1** were prepared. Guest chromophore **C1** was co-doped into **P4** according to N$_g$: N$_h$ of 0.75:1, 1.00:1 and 1.25:1, respectively. It turned out that, the r$_{33}$ value showed greater growth rate (up to 112%) than other concentration ratio when N$_g$:N$_h$ were 1:1 in BCSs **C1/P4**. This result told us that, the decreasing in electrostatic interaction between the chromophores in BCS barely had influences on the OMR.

Tab. 1 The properties of polyarylate **P4**.

polymer	$M_w{}^a$ (×10^4)	M_w/M_n	λ_{max} (nm)		$T_g{}^d$ (°C)	$T_d{}^e$ (°C)	Chromophore Content (wt%)	r$_{33}{}^f$ (pm/V)
			solution^b	film^c				
P4	4.44	3.18	697	697	145.5	360.2	13	33

^{a} Measured by GPC in THF on the basis of a polystyrene calibration. ^{b} λ_{max} of polymer solutions in CH$_2$Cl$_2$. ^{c} λ_{max} of spin-coated films. ^{d} Glass transition temperature, determined by DSC at a heating rate of 10 °C/min under nitrogen with a gas flow of 50 mL/min. ^{e} The 5% weight loss temperature, detected by the TGA analyses under nitrogen at a heating rate of 10 °C/min. ^{f} Measured by simple reflection technique at 1310 nm.

Tab. 2 The properties of the BCSs **C1/P1-P3**.

BCSs	EO Polymers			Guest C1		N$_g$:N$_h{}^c$	n^d	$T_g{}^e$ (°C)	r$_{33}{}^a$ (pm/V)	r$_{33}$ growth rate^f (%)
	Type	Host Chromophore Content (wt%)	r$_{33}{}^a$ (pm/V)	Content (wt%)	^{b}r$_{33}{}^a$ (pm/V)					
1	P1	9	20	16.5	13	1.01:1	1.596	105.5	62	88
2	P2	18	52	16.5	13	0.50:1	1.603	148.5	73	12
3	P3	33	37	16.5	13	0.27:1	1.621	158.0	55	10
4	P2	18	52	22.8	17	0.75:1	1.616	135.0	98	42
5	P2	18	52	28.3	19	1.00:1	1.627	128.6	129	81
6	P2	18	52	33.0	24	1.25:1	1.635	123.2	123	62
7	P2	18	52	37.1	27	1.50:1	1.639	118.0	110	39

^{a} Measured by simple reflection technique at 1310 nm. ^{b} The r$_{33}$ value of the guest chromophore **C1** was referenced to ref. 14f. ^{c} The molar ratios of guest/host chromophore. ^{d} The refractive indices of the polymer films were measured at 1310 nm. ^{e} Glass transition temperature, determined by DSC at a heating rate of 10 °C min-1 under nitrogen with a gas flow of 50 mL min-1. ^{f} The r$_{33}$ growth rate=[r$_{33}$(BCSs)/r$_{33}$(sum)-1]×100%.

Secondly, the type of the guest chromophore was changed. Compared to **C1, C2** was chosen for its larger dipole moment. Besides, **C2** had no isolated groups in its π-bridges. Thus, the electrostatic interaction between chromophores in BCSs **C2/P1** was much stronger than that in BCSs **C1/P2**. Furthermore, **C2** showed stronger EO activity than **C1** (120 pm/V vs 30 pm/V). So the much larger r$_{33}$ value may be got in BCSs **C2/P1** than that in **C1/P2**. Hence, BCSs 11-13 (BCSs **C2/P1**) were prepared, in which **C2** was co-doped into **P1** according to N$_g$:N$_h$ was 0.75:1, 1.00:1 and 1.25:1, respectively. Finally, the largest r$_{33}$ value 160 pm/V was got in BCSs **C2/P1**, which was larger than that in BCSs **C1/P2** (129 pm/V). It was found out that, the r$_{33}$ value also showed maximal growth rate when N$_g$:N$_h$ were 1:1 in BCSs **C2/P1**. As a result, the increasing in electrostatic interaction between the chromophores also barely had influences on the OMR.

Based on the results above, it can be concluded that the strength of the electrostatic interaction between chromophores had few influence on the OMR. Then, whether the polymeric environment in which the chromophores existed had influence on the OMR was explored in Tab. 4. It was known that there was interaction between chromophores and polymer chains, such as π-π interactions. This interaction may have influence on the OMR. To conform this, the polymer main chain was changed. So **P5** with lower density of benzene ring than **P2** was chosen to weaken the interaction between the polymer main

chains and chromophores. Meanwhile, the alkyl chains in the **P5** make it more flexible in the poling procedure. Thus, BCSs 14-16 (BCSs **C1/P5**) were prepared. **C1** was co-doped into **P5** according to N_g:N_h of 0.75:1, 1.00:1 and 1.25:1, respectively. As the results showed, the largest r_{33} value and the maximal growth rate of r_{33} value both appeared in BCS 15. And its molar ratio between guest and host chromophores happened to be 1:1. Therefore, it was proven that the polymer main chains had little influence on the OMR.

Tab. 3 The properties of BCSs **C1/P4** and **C2/P1**.

BCSs	EO Polymers			Guest Chromophores			N_g:N_h[c]	n[d]	T_g[e] (°C)	r_{33}[a] (pm/V)	r_{33} growth rate[f] (%)
	Type	Host Chromophore Content (wt%)	r_{33}[a] (pm/V)	Type	Content (wt%)	[b]r_{33}[a] (pm/V)					
8	P4	13	33	C1	9.9	6	0.75:1	1.604	125.4	60	54
9	P4	13	33	C1	12.7	9	1.00:1	1.619	107.5	89	112
10	P4	13	33	C1	15.4	11	1.25:1	1.625	97.5	92	109
11	P1	9	20	C2	15.3	105	0.75:1	1.620	138.5	132	6
12	P1	9	20	C2	19.4	120	1.00:1	1.638	133.5	160	14
13	P1	9	20	C2	23.1	110	1.25:1	1.649	128.5	115	-12

[a] Measured by simple reflection technique at 1310 nm. [b] The r_{33} value of the guest chromophore **C1** was referenced to ref. 14f. [c] The molar ratios of guest/host chromophore. [d] The refractive indices of the polymer films were measured at 1310 nm. [e] Glass transition temperature, determined by DSC at a heating rate of 10 °C min^{-1} under nitrogen with a gas flow of 50 mL min^{-1}. [f] The r_{33} growth rate=[r_{33}(BCSs)/r_{33}(sum)-1]×100%.

Tab. 4 The properties of BCSs **C1/P5**.

BCSs	Host P5		Guest C1		N_g:N_h[c]	n[d]	T_g[e] (°C)	r_{33}[a] (pm/V)	r_{33} growth rate[f] (%)
	Chromophore Content (wt%)	r_{33}[a] (pm/V)	Content (wt%)	[b]r_{33}[a] (pm/V)					
14	16	33	20.7	15	0.75:1	1.598	113.2	60	25
15	16	33	25.7	18	1.00:1	1.616	102.5	83	63
16	16	33	30.3	22	1.25:1	1.623	94.7	73	33

[a] Measured by simple reflection technique at 1310 nm. [b] The r_{33} value of the guest chromophore **C1** was referenced to ref. 14f. [c] The molar ratios of guest/host chromophore. [d] The refractive indices of the polymer films were measured at 1310 nm. [e] Glass transition temperature, determined by DSC at a heating rate of 10 °C min^{-1} under nitrogen with a gas flow of 50 mL min^{-1}. [f] The r_{33} growth rate=[r_{33}(BCSs)/r_{33}(sum)-1]×100%.

Hereby, in BCSs, the optimum value of N_g:N_h in BCS was about 1:1. This value was barely affected by the strength of the electrostatic interaction between the chromophores and the polymeric environment in which the chromophores existed.

In addition, it was found that in BCSs 5, 12 and 15, both the r_{33} values and the r_{33} growth rates were the largest, but in BCS 9 only the r_{33} growth rate was the largest. The largest r_{33} value of BCSs **C1/P4** appeared in BCS 10, and the N_g:N_h of which was 1.25:1. This was because the chromophore concentration in BCS 9 was very low. It didn't come to the top limit that the BCS can bear with. So the r_{33} values will increase with the increased concentration of the guest chromophore or the host chromophore or both chromophores appropriately. This was also the reason why the BCS 2 had larger r_{33} value than the BCS 1, even though the N_g:N_h of BCS 1 was 1:1. Exceeding the top limit, the more guest chromophores, the stronger the electrostatic interaction between the chromophores. This caused the significant r_{33} decrease in BCS 13.

The r_{33} growth rates

Fig. 1 showed the r_{33} growth rates of all the BCSs. The r_{33} growth rate was defined by the following equation on our own:

$$r_{33} \text{ growth rate} =[r_{33}(BCSs)/r_{33}(sum)-1]\times100\%$$
(3)

Where r_{33} (BCSs) are the r_{33} values of the BCSs, r_{33} (sum) are the r_{33} values of the sum of their individual components. Apparently, the r_{33} growth rates were largest at the N_g:N_h of 1:1, and almost all the r_{33} growth rates of the BCSs were greater than zero, which meant these BCSs showed obvious BCSs effect (r_{33} values are larger than the sum). Especially for BCSs with the guest **C1**, the largest r_{33} growth rates were obtained and the r_{33} values increased about 0.5-1.1 times of the sum of their individual components when N_g:N_h was 1:1. Even for **C2** with excellent EO property, the r_{33} value of the BCS almost increased 0.33 times. Before the OMR of 1:1, the r_{33} growth rates rose with the increase of N_g:N_h. After the OMR of 1:1, the larger values of N_g:N_h, the smaller r_{33} growth rates. Thus, the OMR can further improve the EO coefficients of the BCS, and

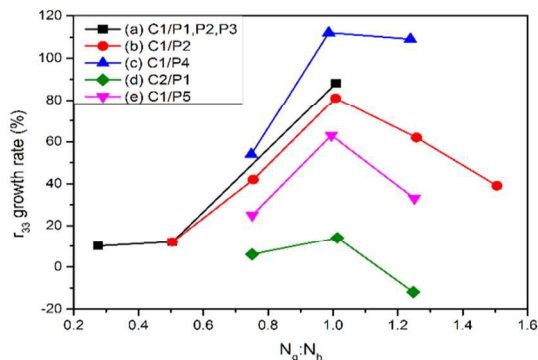it is promising to obtain super large EO coefficients by adjusting the $N_g:N_h$ to 1:1.

Fig. 1 The r_{33} growth rates of the polymeric films: (a) BCSs 1-3 that **C1** doped into **P1-P3**; (b) BCSs 2 and 4-7 that **C1** doped into **P2**; (c) BCSs 8-10 that **C1** doped into **P4**; (d) BCSs that 11-13 that **C2** doped into **P1**; (e) BCSs 14-16 that **C1** doped into **P5**.

NLO properties

The NLO properties of these polymeric materials were summarized in Tab.2-4. The BCSs showed the refractive indices ranged from 1.596 to 1.639, and the EO coefficients were in the range of 57 to 160 pm/V at 1310 nm.

Fig. 2 shows the r_{33} values of the EO polymer films. The r_{33} values of the BCSs **C1/P2**, **C1/P4** and **C1/P5** are much higher than that of **C1** doped into amorphous polycarbonate (APC). For example, the r_{33} value of the BCSs **C1/P2** was even 1.82 times of the sum r_{33} values of **P2** and **C1**. The largest r_{33} values of the BCSs **C2/P1** (160 pm/V) was also higher than that of **C2** (120 pm/V). Usually, in the conventional guest-host system or the side-chain system, the over loading of the chromophore will cause the aggregation of the chromophores and the decrease of the r_{33} value. But in these BCSs, the chromophore loading level is much higher than the individual systems, and the r_{33} values were much larger than the sum of the individual systems. This implies that there is another interaction between two chromophores to make them orientation.
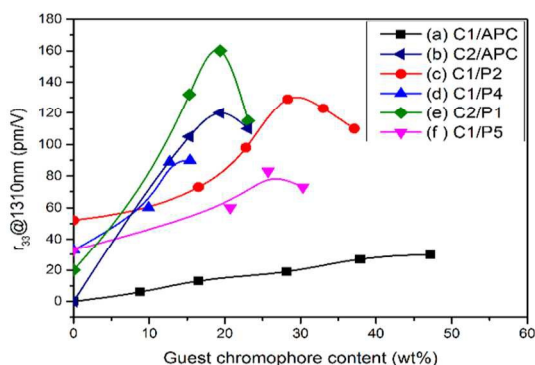

Fig. 2 The r_{33} values of the polymeric films: (a) guest chromophore **C1** doped into APC; (b) guest chromophore **C2** doped into APC; (c) BCSs 2 and 4-7 that **C1** co-doped into **P2**; (d) BCSs 8-10 that **C1** co-doped into **P4**; (e) BCSs 11-13 that **C2** co-doped into **P1**; (f) BCSs 14-16 that **C1** co-doped into **P5**.

The BCS 5 and BCS 9 were tested for the degree of chromophore orientation, because BCS 5 film which consisted of P2 and C1 with Ng:Nh of 1:1, and BCS 9 film which consisted of P4 and C1 with Ng:Nh of 1:1. The order parameter (Φ) for films can be calculated from the absorption changes according to the following equation: $\Phi=1-A/A_0$, in which A and A_0 are the respective absorptions of the polymer films after and before corona poling. The order parameter (Φ) of poled films was calculated. The Φ values of film BCS 5 and BCS 9 are 21.2% and 18.3%, respectively. These high Φ values indicated that the efficient poling was realized in the binary chromophores system with Ng:Nh of 1:1, and the degree of chromophore orientation perpendicular to the substrate becomes higher.

BCS model

The BCSs can be treated as the summation over two independent NLO-active entities, contributed respectively by two types of chromophores. Therefore, in a binary chromophore system loaded with dye I and dye II, the gas model gives an r_{33} value as:[17b]

$$r_{33}=(2/n^4)(E/5kT)[(Nf\mu\beta)_{dye-I}+(Nf\mu\beta)_{dye-II}] \qquad (4)$$

Where n is index of refraction, E is the poling field felt by the chromophore, k is the Boltzmann constant, T is the poling temperature (Kelvin), N, f, μ and β is the number density, local field (Onsager) factor, permanent (ground-state) dipole moment and first hyperpolarizability of the chromophores, respectively.

It was reported that, the guest chromophore and the host chromophores are prone to form some complexity.[17] Our results showed that the OMR in BCSs was 1:1, and it was barely affected by the types of the host chromophores, the guest chromophore and the polymer main chains. Therefore, it was speculated that the guest chromophore and the host chromophores form the complexity with the ratio of 1:1. In general, the two chromophore aggregations generally have head-to-head and head-to-tail arrangements as shown in Fig.3. In the Fig.3(a), although the electro-optic coefficient of the arrangement can be improved, the chromophores repel with each other because of the same charge. so the probability of existence for this aggregation type is relatively small. In the Fig.3(b), this arrangement of the two chromophores makes the electro-optic coefficient in BCSs very small. So, this complexity model of the two chromophores in the BCS can only be this structure in the Fig.3(c) or Fig. 4. The aggregation type in Fig. 3 (c) is a head-to-tail arrangement of two chromophores, the repulsion effect of the same charge is much weaker than that of the aggregation type in Fig. 3 (a), and the electro-optic coefficient is larger than the aggregation types in Fig. 3 (a) and Fig.3 (b).

The complexity can be treated as a new chromophore, so BCSs can increase the chromophore concentration in polymeric materials. Moreover, such a combination of chromophores can minimize the formation of antiparallel or head-to-tail centrosymmetric stacking between chromophores in solid states. Because of the complexity, the host and guest chromophores will efficiently promote each other to align in the poling procedure. The increase of the asymmetric alignment of the NLO chromophores means the increase of the poling-induced polar order parameter (poling efficiency), which leads to the greatly increase of macroscopic EO coefficients. At the OMR, the amount of the complexity was the largest. Before the OMR, the amount of the complexity increases with the increase of the guest chromophores. So the r_{33} growth rate increased. After the OMR, the aggregation of the guest chromophores becomes stronger with increase of guest chromophores, and the amount of the complexity is much lower. As a result, the r_{33} growth rate decreased.
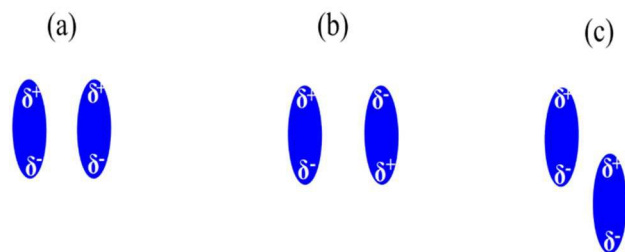

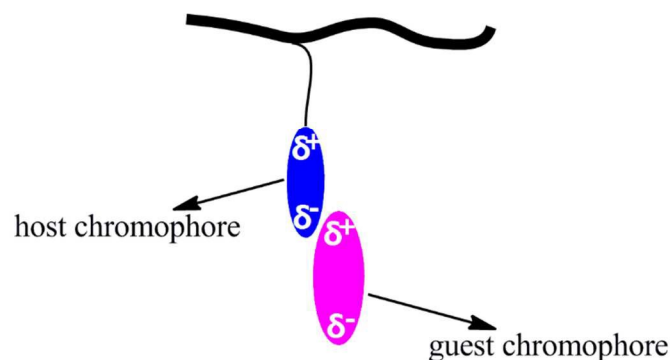**Fig. 3** The arrangement tpyes of the two chromophores.

Fig. 4 The complexity model of the host and guest chromophore in the BCS.

Thermal properties

The glass transition temperatures (T_g) of the BCSs were listed in the Tab.1-4. Almost all T_gs of the BCSs were above 100 ℃. The T_g of the BCSs decreased with more guest chromophores doped in the polymers. This was because the tacticity of the host polymer decreased and the interaction between the polymer chains was weakened when the guest chromophore was doped into the polymer. The decrease of T_g caused by **C1** was much larger than that caused by **C2**. This was due to **C1** had two isolated group in π-bridges, which can further decrease the tacticity of the host polymer. The magnitude of the decrease

of T_g became smaller with the increasing concentration of the guest chromophore in the BCSs.

In order to investigate the relaxation feature of the poling induced chromophores' dipole alignment, the temporal stability was studied through monitoring the r_{33} changes at evaluated temperature. Fig.5 showed the long-term temporal stability of BCS 5 (Tg is 128.6℃). The poled polymer BCS 5 was heated at 80 ℃ for 500 hours. After 500 hours, the value of r_{33} retained 81% of the initial value of BCS 5. The figure is as follows. Therefore, the temporal stability of the mixed polymer is better than the host-guest polymer (APC-C1), and is worse than the host polymer P2.
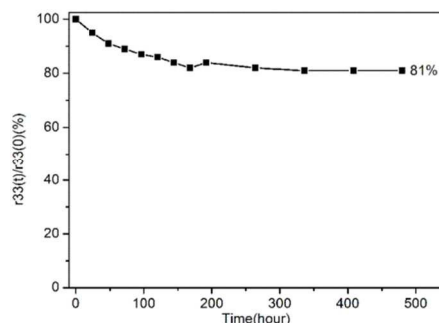

Fig. 5 The temporal stability of the BCSs 5 at 80℃ for 500 hours

UV-vis-NIR absorption spectrum

To further investigate the BCS, thin-film samples were prepared using increased spin speed per minute to afford thinner films. UV-vis-NIR absorption spectra were recorded for these BCSs and their related materials. As shown in Fig. 6A of the BCS **C1/P2** and its related materials, line (a) is the spectrum of film that **C1** was doped into APC with 10 wt%, line (b) is the spectrum of film of **P2** and line (c) is spectrum of film that **C1** was doped into **P2** with $N_g:N_h$ of 1:1. Some solvatochromic behaviour was also observed when a polarizable compound such as **C1** was introduced into a very polar environment like that of **P2**.[13] Similar treatments were performed for BCSs **C1/P4**, **C2/P1** and **C1/P5**, which were shown in Fig. 6B, 4C and 4D, respectively. It seems reasonable to assume that the UV-vis-NIR spectra of these BCSs can be accounted for the simple superposition of the independent spectra of their individual component materials. Therefore, there were no unexpected changes in the optical characteristics of the materials based solely on mixing.
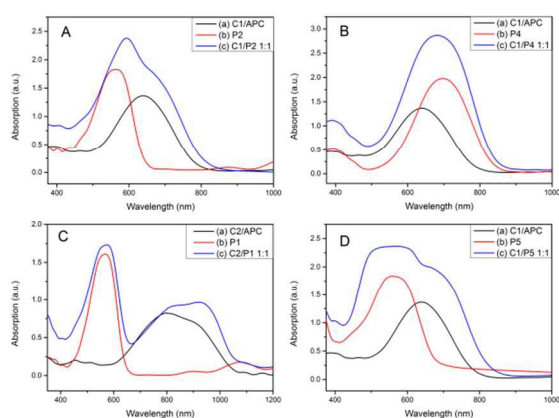
Fig. 6 UV-vis-NIR absorption spectra of the unpoled polymeric film of BCSs and related materials: A The spectra of **C1**/APC, **P2** and BCS **C1/P2**; B The spectra of **C1**/APC, **P4** and BCS **C1/P4**; C The spectra of **C2**/APC, **P1** and BCS **C2/P1**; D The spectra of **C1**/APC, **P5** and BCS **C1/P5**. Line (a) The spectrum of film that guest chromophore doped into APC (**C1** doped with 10 wt%, **C2** doped with 20 wt%,); Line (b) The spectrum of host polymer; Line (c) The spectrum of film that BCS with $N_g:N_h$ of 1:1.

Conclusions

We have employed a series of binary chromophore systems to increase the loading density of chromophores in polymer matrix without causing significant phase separation. All the BCSs showed good solubility, film-forming property and large EO activity. The remarkably large r_{33} values 57-160 pm/V were showed by these BCSs, which were greater than the sum of their individual components. Meanwhile, the host/guest chromophore molar concentration ratios in BCSs have optimum value, which was explored to be about 1:1. And the types of the host chromophores, guest chromophores and the polymer main chains were proved to barely have influence on it. The reason was that the guest chromophore and the host chromophore were prone to form some complexity with the ratio 1:1 in BCSs. Due to the complexity, the host and guest chromophores will efficiently promote each other to noncentrosymmetric alignment in the poling procedure, which leads to the greatly increase of the r_{33} values (up to 1.5-2.1 times of the sum).

Acknowledgements

Notes and references

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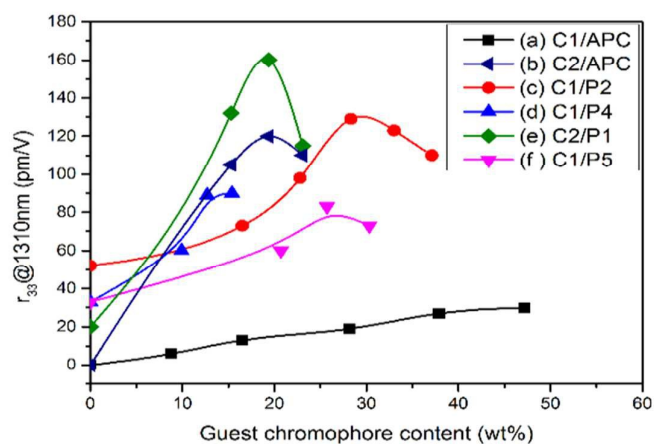
A series of binary chromophore systems (BCSs) based on the electro-optic (EO) polymers **P1**-**P5** and guest chromophores **C1** and **C2** were designed and prepared. The poled films of these BCSs showed the large EO coefficients (r_{33}=57~160pm/V), which were much higher than the sum of their individual component. The optimum molar ratio (OMR) between guest and host chromophores was first systematically explored by changing their molar ratios (N_g:N_h) in the BCSs. The research of OMR in BCSs provided a promising way to further improve the EO coefficients.