

NONLINEAR OPTICAL PROPERTIES OF X-TYPE CHROMOPHORES AND THEIR DOPED FILMS*

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Abstract Two X-type chromophores, 2-[4-(4,5-di(4-nitrophenyl) imidazolyl) phenyl]-4,5-di(4-methoxyphenyl)-imidazole (DNIPDMOPI), 2-[4-(4,5-di(4-nitrophenyl)-imidazolyl) phenyl]-4,5-di(4-aminophenyl)-imidazole (DNIPDAPI), were synthesized and characterized. The results show that they possess good nonlinearity, considerable blue-shifted absorption (385 nm and 379 nm in THF) and high decomposition temperature (377 °C and 405 °C). These mean that the X-type chromophores possess a rather good nonlinearity-transparency-thermal stability trade-off. The multi-step corona-poling technique at elevated temperature and *in-situ* SHG measurements were used to obtain and evaluate the poled films of these chromophores doped in PMMA. The largest SHG signals appeared at 110–120 °C, which are 12.5 pm/V and 16.7 pm/V respectively. The dependence of poling induced orientation stability on temperature was measured by depoling experiments and the results indicate that the poling-induced orientation of the films is stable at about 100 °C. Theoretic analyses imply that better orientation stability arises from the X-type structure of chromophore. The X-type chromophore has two crossed intramolecular CT, both β_{xx} and β_{yy} can contribute to the second-order susceptibility, and the ratio of the tensorial components ($\gamma = \beta_{yy}/\beta_{xx}$) is about 1/3, so the orientation decay of the films induced by rising temperature will provide a certain compensation for the contribution of β_{yy} of chromophores.

Keywords Nonlinear optical, X-type chromophore

INTRODUCTION

Organic and polymeric NLO materials have attracted considerable attention in the past two decades because of their potential applications in photonics^[1]. Especially striking progress in the temporal orientation stability of the poled films through using the high glass transition temperature (T_g) chromophore-functionalized polymer, such as polyimides, polyurethanes, polyureas *etc.*^[2–4], holds great promise in the field of application. Recent research has provided an alternative strategy to improve the temporal orientation stability of poled films by especial structure configuration of chromophore, such as two-dimensional chromophore^[5]. In our previous work^[6], polyimide with one of the X-type chromophores preliminarily demonstrated the contribution from X-type configuration to orientation stability. To further understand the contribution, in this paper, other X-type chromophores and their doped films were given, as well as some theoretical analyses were given to explain the orientation stability.

Recently, Wang *et al.*^[7] reported the theoretical investigation of a series of tetra-substituted benzenes/pyrazines which can be described as 1,2-didonor-4,5-diacceptor-benzenes/2,3-didonor-5,6-diacceptor-pyrazines (abbr: X-type), which possess more appropriate β_{yy}/β_{xx} ratios and large $\mu\beta$ values. By extending the conjugation length and incorporating the thermally stable imidazole ring, chromophores with higher β values have been designed (cf. Fig. 1). The theoretical calculation results and some properties are given in Table 1. The results in this paper show that X-type chromophores possess good nonlinearity-transparency-thermal stability trade-off and

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also demonstrate the contribution of structure configuration of the chromophore to the orientation stability.

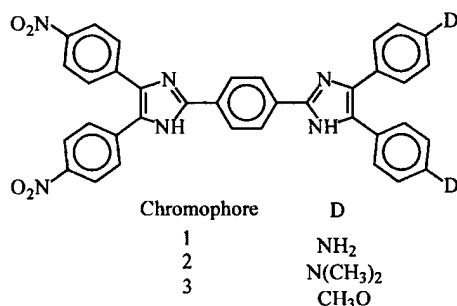


Fig. 1 The structure of X-type chromophores

EXPERIMENTAL

Two X-type chromophores were synthesized recently and they were characterized using a $^1\text{H-NMR}$ (Varian-200) spectrometer, a MS (AEI MS-50) instrument and elemental analysis (Heraeus Chen-RAPID). The results of the characterization were given as following:

DNIPDAP: m.p. $> 300^\circ\text{C}$. IR (KBr, cm^{-1}): 3384, 3214, 2913, 1613, 1599, 1515, 1342, 1289, 1181, 1110, 969, 855, 702. $^1\text{H-NMR}$ ($\text{DMSO-}d_6$, δ): 13.090 (s, 1H), 12.50 (s, 1H), 8.34 (d, 2H, $J = 9$ Hz), 8.23 (d, 2H, $J = 9$ Hz), 8.23 (d, 2H, $J = 9$ Hz), 8.18 (d, 4H), 7.85 (d, 2H, $J = 9$ Hz), 7.23 (d, 2H, $J = 9$ Hz), 6.55 (d, 2H, $J = 9$ Hz), 5.10 (br, s, 4H). $^{13}\text{C-NMR}$ ($\text{DMSO-}d_6$, δ): 147.5, 146.7, 146.1, 141.3, 137.5, 136.8, 130.8, 129.4, 128.8, 128.3, 128.0, 126.1, 125.7, 124.2, 124.0, 118.9. m/z (FAB), 635 (M^+). Anal. Calcd. For $\text{C}_{36}\text{H}_{26}\text{N}_8\text{O}_4 \cdot 2\text{H}_2\text{O}$ (%): C 64.47, H 4.51, N 16.70. Found (%): C 64.20, H 4.42, N 16.27. DNIPDMOPI: m.p. $> 300^\circ\text{C}$. IR (KBr, cm^{-1}): 3400, 2960, 1580, 1530, 1460, 1350, 1250, 1165, 1100, 960, 840, 700. $^1\text{H-NMR}$ ($\text{DMSO-}d_6$, δ): 8.45–8.20 (6H), 7.90 (d, 2H, $J = 9$ Hz), 7.85 (d, 2H, $J = 9$ Hz), 7.70 (d, 2H), 7.50 (d, 4H), 7.15 (d, 2H, $J = 9$ Hz), 6.95 (d, 4H), 3.85 (s, 6H). m/z (FAB), 664. Anal. Calcd. For $\text{C}_{38}\text{H}_{28}\text{N}_6\text{O}_6 \cdot 2\text{H}_2\text{O}$ (%): C 65.14, H 4.57, N 12.00. Found (%): C 65.31, H 4.44, N 11.34.

The doping film was formed by dissolving purified X-type chromophore, DNIPDMOPI and DNIPDAP together with PMMA in DMF. Dopant concentration was about 15% by weight ratio of chromophore with polymer, that is, the chromophore number density in both dopant polymers is about $0.16 \times 10^{21} \text{ cm}^{-3}$. The resulting solution was filtered through a $0.45 \mu\text{m}$ syringe PTFE filter. The filtered solution was spin coating onto an indium-tin oxide (ITO) coated glass slide to give doping films with a thickness of about $0.5\text{--}1.0 \mu\text{m}$. After the coating, the sample was dried under vacuum at 60°C for about 48 h to remove residual solvent.

The film was poled with corona-poling and *in-situ* measurement technique as described previously^[8]. The dependence of poling induced orientation stability on temperature was also studied using the same apparatus.

RESULTS AND DISCUSSION

Properties of Chromophores

As well known, to meet the requirement for applications in the field of organic/polymer nonlinear material, the nonlinearity-transparency-thermal stability trade-off for chromophores should be further comprehensively optimized. The chromophores reported in this paper can just meet it. As shown in Fig. 2, they show rather blue-shifted absorption peaks at 385 nm and 379 nm in THF, respectively. And they have high decomposition temperatures at 377°C and 405°C as shown in Fig. 3. At the same time, they possess good nonlinearity (cf. Table 1). So it is obvious that X-type chromophores exhibit rather good nonlinearity-transparency-thermal stability trade-off and such a multiple substitution strategy may be useful in searching for highly efficient NLO chromophores.

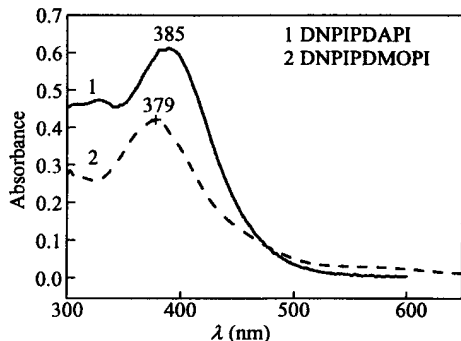


Fig. 2 UV absorption spectra of X-type chromophores

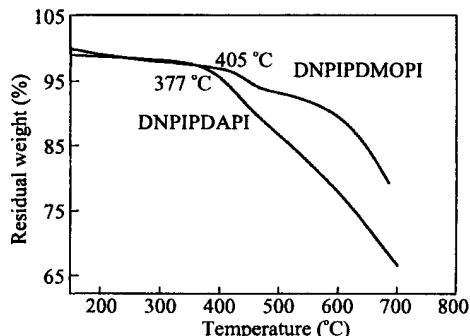


Fig. 3 TGA of X-type chromophores

Second Order NLO Coefficient d_{33} of the Doped Film

According to the discussion in Ref. [9], the order parameter Φ is directly proportional to the birefringence induced by interaction between dipoles and internal electric field, so it can be regarded as one of the important and useful parameters for monitoring the poling degree, which can be calculated from the decrease in absorbance of poled film before and after poling based on Eq. (1)

$$\Phi = 1 - (A/A_0) \quad (1)$$

Where A_0 and A are the observed absorbance of unpoled and poled film at the maximum absorption peaks, respectively.

Figure 4 shows the absorption spectra of poled and unpoled PMMA film doped with DNPIPDMOPI. Two electrochromic effects were observed on the poling: the peak intensity of absorption decreases and the wavelength of maximum absorption shifts towards longer wavelength. Based on Eq. (1), Φ value was calculated as about 0.29, indicating this doped film has good orientation.

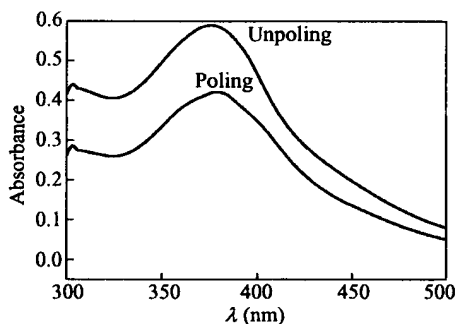


Fig. 4 The UV absorption spectra of DNPIPDMOPI/PMMA unpoled and poled film

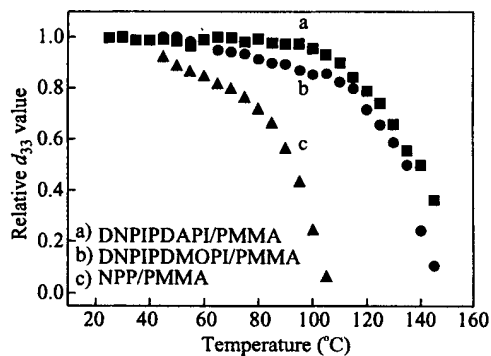


Fig. 5 Dependence of orientation stability of doped film on temperature; the heating rate is 5 K/min

In this paper, a multi-step corona-poling technique at elevated temperature and *in-situ* SHG measurements as described before were used to get and evaluate the poled films. Measurement of the second order NLO coefficient d_{33} for the film samples is based on Eq. (2)^[10].

$$\frac{d_{33,s}}{d_{11,q}} = \frac{\chi_s^{(2)}}{\chi_q^{(2)}} = \sqrt{\frac{I_s}{I_q}} \frac{l_{c,q}}{l_s} F \quad (2)$$

Where $d_{11,q}$ is d_{11} of quartz crystal which is 0.45 pm/v, I_s and I_q are SHG intensity of the sample and quartz respectively, $l_{c,q}$ is the coherence length of quartz, l_s is the thickness of sample and F is a correction factor, which is equal to 1.2 approximately when $l_s \ll l_{c,q}$. The results show that the largest SHG signal appeared at 110–120 °C, and was 12.5 pm/v and 16.7 pm/v, respectively.

The Dependence of Orientation Stability on Temperature

The dependence of poling induced orientation stability on temperature was measured by depoling experiments in which the decay of the SHG intensity was monitored as a function of temperature. Figure 5 shows the relative d_{33} versus temperature for the doped film on raising temperature at a rate of 5 K/min. For comparison, the doped film of NPP in PMMA was employed in this paper, as shown in Fig. 5(c). It can be seen clearly that the orientation stability of X-type chromophore in PMMA is much better than that of NPP in PMMA.

Just as discussed before^[5-11], the better orientation stability is due to the structure of chromophore. For the traditional one-dimensional chromophores, such as NPP, β_{xxx} (2218) is far larger than β_{xyy} (-222), which means that β_{33} comes mainly from the contribution of the β_{xxx} . But for the X-type chromophore, which has two crossed intramolecular CT, both β_{xxx} and β_{xyy} contribute to the second-order susceptibility, and the ratio of the tensorial components ($\gamma = \beta_{xyy}/\beta_{xxx}$) is about 1/3 (as shown in Table 1), which is obviously different from that of NPP, so that the contribution of β_{xyy} to β_{33} for X-type chromophore can not be neglected. Hence when the orientation coming from the β_{xxx} decays due to the rising temperature, β_{xyy} will be moved accordingly due to the structure of chromophore. Then the d_{33} of the film can be compensated partly as shown in Fig. 6, which is based on the chromophore DNPIPDAP1.

Table 1. The properties of the X-type chromophores

Chromophore	1 ^[8]	2	3
$\mu\beta_0$ (esu) $\times 10^{48}$	554.8	734.4	343.1
λ (nm)	385*	413	376*
T_m (°C)*	> 300	> 300	> 300
T_d (°C)*	377	-	405
β_{xxx}, β_{xyy}	-6124, -2153	-9538, -2356	-5675, -1768
$r = \beta_{xyy}/\beta_{xxx}$	0.35	0.25	0.31

* Experimental results

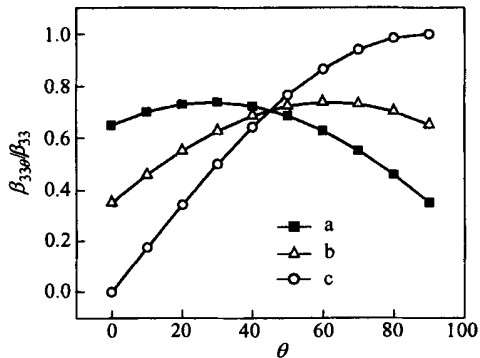


Fig. 6 The dependence of β_θ/β on θ , (a) θ is the angle between the β_{xyy} and the face of film based on the X-type chromophore; (b) θ is the angle between the β_{xxx} and the face of film based on the X-type; (c) θ is the angle between the β_{xxx} and the face of film based on 1D chromophore (such as NPP)

Figure 6 shows clearly that the dependence of β_{33} for X-type chromophore on θ is less than that for 1D chromophore, such as NPP. So that the decay of SHG activity (d_{33}) is slow, which means the orientation stability of the SHG activity (d_{33}) is good.

CONCLUSION

In this paper, the X-type chromophores were synthesized and the NLO property of its doped film with PMMA was measure. The results of the dependence of poling-induced orientation stability on the temperature show that

the doping film has better poling-induced orientation stability than that of NPP in PMMA. This is another example to show the contribution of structure configuration of the chromophore to the orientation stability.

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