

Quantitative Determination of the Chromophore Alignment Induced by Electrode Contact Poling in Self-Assembled NLO Materials

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The electrode contact poling is one of the efficient tools to induce a stable polar order of nonlinear optical (NLO) chromophores in the solid film. Self-assembled NLO chromophores with high electro-optic (E-O) activities were utilized for quantitative determination of the chromophore order induced under contact poling by spectroscopic changes. We found that NLO chromophores rarely decompose under the high electric field during contact poling. The absorption spectra were de-convoluted into a sum of Gaussian components to separate energy transitions for a binary composite system which contains a secondary guest chromophore **AJC146** in the self-assembled chromophore **HDFD**. Poling efficiency was significantly improved in the binary system compared to the individual components.

Key Words: Nonlinear optics. Chromophore. Self-assembly. Order parameter. Contact poling

Introduction

Organic second-order nonlinear optical (NLO) materials have been numerous investigated for their potential applications from electro-optic (E-O) modulators to THz generation applications.^{1,2} Recent advances in the use of highly efficient organic NLO materials with nano-scale architecture control have lead to significant breakthrough in the E-O devices exceeding those of inorganic materials by a factor of 5 ~ 6.^{3,4}

It is well known that second-order NLO properties originate from noncentrosymmetric alignment of dipolar NLO chromophores in a polymer matrix. A commonly used method to align the chromophore is through the application of an external electric field at elevated temperatures either by contact poling or corona poling methods.⁵ For the contact poling, a direct contact (DC) voltage applied between bottom and top electrodes produces a controlled electric field across the NLO polymer film. Chromophores will be aligned perpendicular to the surface plane of the sample. A single defect created during the film processing may introduce a short circuit, destroying the devices. However it is a preferred method because E-O coefficient (r_{33}) of the sample can be directly measured by simple reflection technique after the poling. In the corona poling a high voltage is applied to a thin wire or needle which is placed several millimeters above the film. Although poling efficiency is lower than that of the contact method, it has been used for studying the orientational order by the spectroscopic changes or Maker fringe technique.^{6,7}

We have developed novel NLO molecular glasses and their composites based on a reversible self-assembly of dendronized chromophores using the arene-perfluoroarene interactions (Ar-Ar^F) that can be reorganized into a stable acentric polar structure. One such composite glass showed an extremely large r_{33} of 327 pm/V at the wavelength of 1.31 μm after the contact poling.⁸ Although the results are very encouraging for

the organic materials, it is also important to evaluate orientational order to determine the efficiency and persistence of chromophore alignment after the poling.

We report, here, quantitative determination of the polar ordering for self-assembled chromophores induced under the contact poling by spectroscopic changes. In addition, a binary composite system which contains a secondary guest chromophore in self-assembled chromophores has been utilized to assess high E-O activities. These results will provide insight into the systematic optimization of E-O activities and guide the alignment efficiency of the poled organic E-O materials.

Experimental Section

HDFD and **AJC146** chromophores were designed and synthesized in our laboratories. Detailed synthetic procedures are described in the literature.⁸ All reactions were carried out under inert nitrogen atmosphere. Reliable and pinhole-free films can be prepared by spin-coating onto indium tin oxide (ITO) glass substrate from the 1,1,2-trichloroethane solution after the filtration through a 0.2 μm poly(tetrafluoroethylene) (PTFE) filter. Carefully controlled spin-coating speed and concentration of the solution were used for the suitable thickness of the film ranged from 0.3 μm to 2.0 μm . The films were then dried under high vacuum at 40 °C for 10 hrs to remove any residual solvent. UV/vis spectra were obtained on a Perkin-Elmer Lambda-9 spectrophotometer. Atomic Force Microscopy (AFM) was performed in the tapping mode using a Nanoscope III AFM (Digital Instruments) operating in ambient conditions at a scan rate of 0.5-1.0 Hz. Roughness measurements and cross-sectional analysis were performed using algorithm contained in the AFM software. The r_{33} values were measured using the simple reflection technique at the wavelength of 1.31 μm .⁹

Results and Discussion

Molecular structures of the chromophores studied are shown in Figure 1. For the chromophore, **HDFD**, phenyl and pentafluorophenyl rings have been incorporated as peripheral groups to form supramolecular self-assembled NLO chromophores by Ar-Ar^F. The core of the molecule is a CF₃-TCF-based (namely 2-dicyanomethylene-3-cyano-4,5-dimethyl-5-trifluoromethyl-2,5-dihydrofuran) conjugative structure, which is the skeleton of a well-established chromophore for guest-host E-O polymers.¹⁰

AJC146 is a newly developed and more efficient polyenic chromophore as a secondary guest¹¹ and can be doped in **HDFD**. The self-assembled chromophore and composite system were poled and characterized using device fabrication procedures as described in Figure 2. The conductive ITO and sputtered gold serve as electrodes used for poling and E-O modulation. For the poling process, DC voltage was turned on at the very beginning stage and slowly increased temperature with 5 °C/min was used to avoid possible film damage. We found that optimal poling temperature was around 70 °C corresponding to the glass transition temperature of **HDFD**. The films were then cooled to room temperature while the electric field was maintained. After measurement of r_{33} at 1.31 μm by simple reflection method for the poled films, the gold electrode was removed by KI etchant solution, which does not attack NLO materials. It is noted that films thermally treated without any electric field have been also used to compare surface morphology and absorption spectra.

The chromophore **HDFD** gave 108 pm/V of the r_{33} value applied by 100 V/μm of poling field strength. This result interpreted high chromophore ordering with improved dielectric strength induced from the formation of supramolecular self-assembly through the Ar-Ar^F interactions.¹² It is well known that well-ordered supramolecular materials through intermolecular forces can provide novel electronic and photonic properties.¹³ These poled thin films retained over 90 % of their original r_{33} values at 50 °C for a month. Further attempts to raise chromophore loading density and the r_{33} of these materials were conducted by adding more efficient **AJC146** guest chromophore to **HDFD** host chromophore. The resulting binary systems exhibited extraordinary high r_{33} values, 275 pm/V for the composite of **HDFD**:**AJC146** = 3:1 (wt.%), and 327 pm/V for the composite of **HDFD**:**AJC146** = 1:1 (wt.%).

One of the popular and simple approaches to quantitatively determine the degree of chromophore orientation is to measure the order parameter by absorption change. Most work has been performed from the corona poling. Knoesen and coworkers have described the axial orientation of the chromophores by the order parameter $\Phi = 1 - (A/A_0)$, where A_0 and A are respectively the absorbance maxima for the unpoled and poled samples at normal incidence.¹⁴ However, effects other than chromophore orientation can cause changes in the absorption spectrum during poling. Sublimation of the chromophore out of the polymeric host or thermal decomposition of the chromophore at the poling temperature can lead to reductions in the absorption not related to the poling order. In addition,

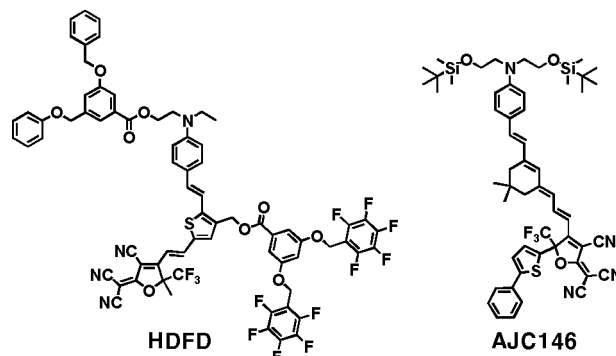


Figure 1. Molecular Structures for **HDFD** as a self-assembled chromophore and **AJC146** as a secondary guest chromophore.

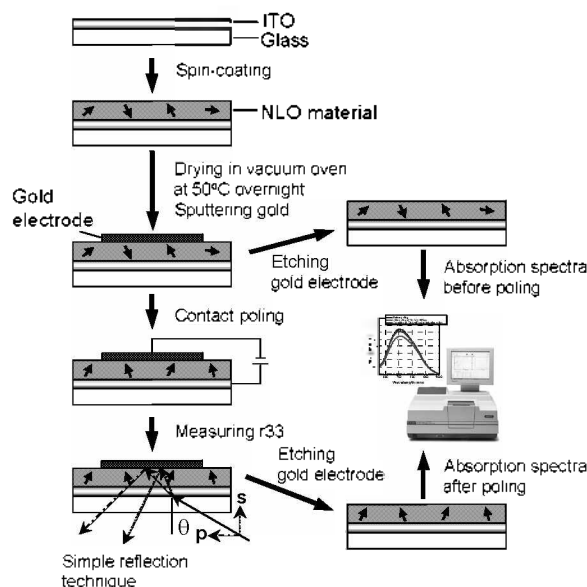


Figure 2. The schematic diagram of device fabrication procedures for the order parameter determination of dipolar chromophores.

the electric field applied during the poling process can lead to irreversible absorption changes. Furthermore, it is rarely reported the order parameter from contact poling due to the low alignment efficiency and poor surface quality after removing sputtered gold top electrode.¹⁵ Therefore, before we determine the polar order by an absorption change, it should address surface roughness change and degradation of the chromophores induced by high electric field for the contact poling.

Atomic force microscopy (AFM) was utilized to examine the morphology of the unpoled and poled films. The surface before sputtering a gold electrode was relatively flat and defects such as pinholes or aggregation were hardly observed. The surface roughness was estimated to be less than 1 nm by AFM shown in Figure 3. The remarkable film quality of **HDFD** chromophore itself is due to an extended solid structure through Ar-Ar^F interactions. A little of unevenly distributed defects were generated from the poled film applied with 75 V/μm of an electric field. The surface roughness of most area was found to be around 1 ~ 2 nm.

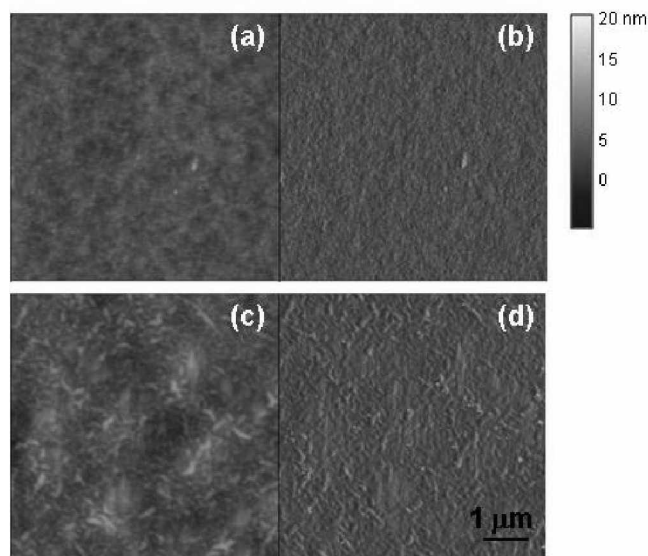


Figure 3. (a) Height and (b) phase AFM images of unpoled **HDFD** and (c) height and (d) phase images of poled **HDFD**.

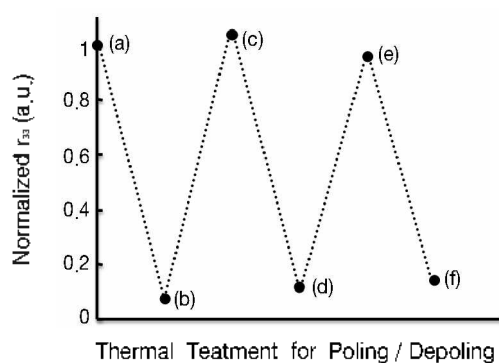


Figure 4. Thermal reversibility of E-O activities - (a) to (b), (c) to (d), (e) to (f), 70 °C by ramping rate of 5 °C/min without a voltage; (b) to (c), (d) to (e), 70 °C by ramping rate of 5 °C/min with 75 V/μm.

Although there is a little change for surface roughness of the poled film, it is still hard to indicate chromophore decomposition, which usually causes film bleaching during the poling process. We have thus performed multicycle poling and depoling treatment for the **HDFD** to verify thermal reversibility of E-O activities. Using 75 V/μm of an electric field by 5 °C/min of ramping rate to 70 °C, we have achieved 81 pm/V of r_{33} . After thermal depoling treatment with 5 °C/min of ramping rate to 70 °C without electric fields, the r_{33} only retained below 10% from the original value due to chromophore alignment relaxation. When the depoled film was again applied with 75 V/μm and increased to 70 °C, the r_{33} showed 78 pm/V, which was over 95% of the original value. The results of three cycles are shown in Figure 4. Therefore results suggest that there is minimal sublimation and decomposition of the chromophore during the poling process.

UV/vis absorption spectra of the **HDFD** with and without poling are shown in Figure 5a. The main absorption peak at 701 nm is due to the intramolecular charge-transfer band of

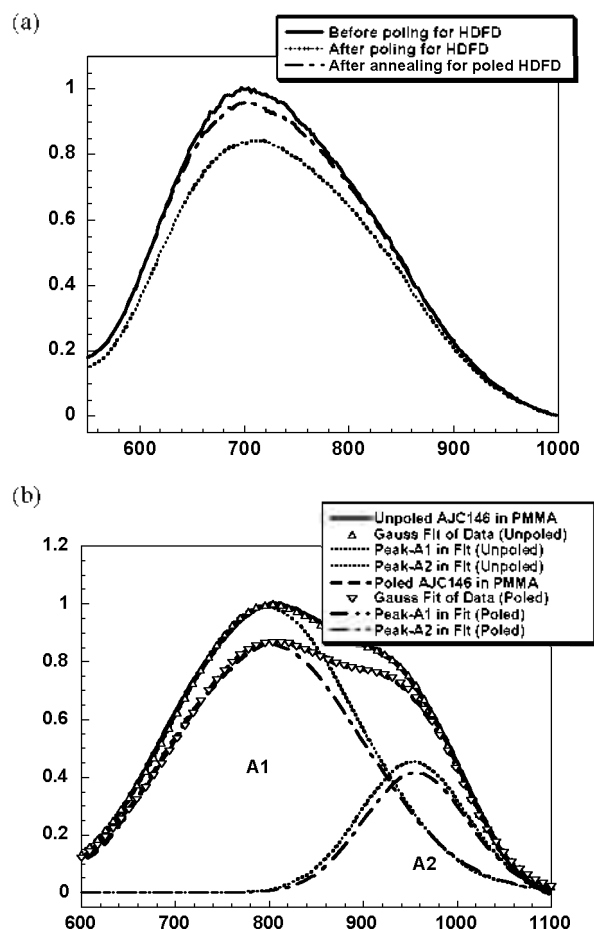


Figure 5. UV/vis absorption spectra: (a) the chromophore **HDFD** before poling, after poling and after thermal de-poling at 70 °C (b) **AJC146** in PMMA de-convoluted in two Gaussian components with the corresponding two-peak fittings superimposed onto the spectra.

the chromophores. The solid line was obtained with the film treated with heating to 70 °C without any electric field applied. The dotted line was obtained from the same film with 75 V/μm of the electric field. The decrease of the peak absorbance is caused by the alignment of the chromophore dipoles along the poling field direction, which is the incident light direction as well. From the absorbance change, the ordering parameter of the poled films was determined to be 0.17 with 81 pm/V of r_{33} . As thermal treatment proceeded again without the field for the poled film, the absorbance (dashed dotted line) was recovered over 95% due to the relaxation of the axially ordered chromophores. This is another clear indication that chromophores rarely decompose and reduced absorbance is purely from chromophore alignment by contact electric field.

A bathochromic absorption shoulder for chromophore **AJC146** (25 wt.%) in polymethylmethacrylate (PMMA) appears in the film, which suggests the favorable formation of acentric *J*-aggregates from chromophore **AJC146** (Figure 5b). The absorption spectra of the film can be de-convoluted into a simple sum of two Gaussian components¹⁶ to separate a main energy transition with an absorption shoulder centered at the wavelength of 799 nm and 951 nm. We found that the

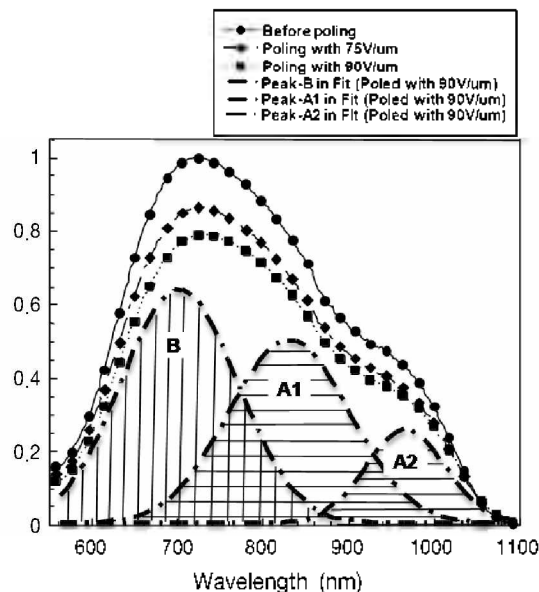


Figure 6. The absorption spectra for the composite of **AJC146** in **HDFD** before and after poling and their Gaussian de-convolution fitting curve.

Table 1. E-O activities and optical properties for **HDFD**, **AJC146** (25 wt.%) in **PMMA**, and **AJC146** (25 wt.%) in **HDFD**

Sample	E. Field (V/um)	r_{33}^a (pm/V)	Φ^b	Unpoled (Poled) λ_{max} (nm) ^c	Unpoled (Poled) Γ (nm) ^d	Unpoled (Poled) Area ^e
HDFD	75	81	0.17	700 (710)	202 (210)	256 (232)
				796 (800)	196 (217)	243 (217)
AJC146 in PMMA	100	120	0.13	953 (956)	112 (118)	64 (57)
			0.09	696 (696)	140 (141)	275 (202)
			0.25	836 (837)	144 (153)	213 (188)
AJC146 in HDFD	90	230	0.18	968 (972)	96 (98)	72 (57)
			0.22			

^aE-O coefficient measured by simple reflection at the wavelength of 1.31 μm ; ^bThe order parameter $\Phi = 1 - (A_0/A)$, where A_0 and A are the absorbance maxima for the unpoled and poled samples at normal incidence; ^cGaussian de-convoluted absorption maxima of thin films by UV-vis spectroscopy before and after poling; ^dThe full width at half-max of a Gaussian sub-peak in the absorption spectra before and after poling; ^eThe integrated area of a Gaussian sub-peak from the absorption spectra before and after poling.

film of **AJC146** in **PMMA** showed with 120 pm/V of r_{33} has two order parameters, 0.13 for the main peak and 0.09 for the shoulder peak. Further studies on the origin of the shoulder and its behavior are in progress. We have also performed a similar de-convolution of the spectra for binary glass of doped **AJC146** in **HDFD**. The ordering for the composite **HDFD** with doped **AJC146** was dependent on poling field strength as shown in Figure 6. Strong absorption bands covered from 600 nm to 1100 nm can be exactly de-convoluted into three distinct absorption peaks, i.e. peak B, A1, and A2. The first

peak, B, located in the high energy side of the spectrum is assigned as the charge transfer peak of self-assembled chromophore **HDFD** while A1 and A2 peaks are from doped **AJC146**.

We have not seen any increased broadening effect of absorption in this binary system respectively from their relatively consistent fractions of each spectrum. Both peak B and A2 even show band narrowing, and their full width at half-max (FWHM or Γ_s) are 24 nm and 12 nm which is smaller than those of **AJC146** in **PMMA**, respectively. Relevant parameter values of these de-convolutions can be compared in Table 1. It is noted that higher order parameters, $\Phi = 0.25$ for **HDFD** and 0.18 (A1 area), 0.22 (A2 area) for **AJC146** have also shown enhanced E-O activities up to 230 pm/V. The large E-O activities and enhanced order parameter of the binary composites suggest several critical structural facts about the approach: the self-assembly of **HDFD** based on the Ar-Ar^F interactions is robust enough not to be disturbed by the addition of guest chromophore: the dielectric properties were mainly dictated by the host self-assembly so that the poling field as high as 90 V/ μm could be applied to the composites: the poling efficiency of **AJC146** in self-assembled **HDFD** are significantly improved by the cooperative effect.

Conclusion

In summary we have demonstrated that the electrode contact poling is very efficient and induces a stable polar ordering in the films of self-assembled E-O glassy chromophores. Self-assembled NLO chromophores have been utilized for quantitative determination of the chromophore order induced under contact poling by spectroscopic changes. The enhanced order parameter in the binary composite has contributed to high E-O activities in self-assembled NLO materials. These results suggest that self-assembled chromophore matrix can help organize a doped chromophore and improve the polar order cooperatively.

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