

# Synthesis and characterization of dendrimer encapsulated chromophore by one step method for electrooptics

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A dendritic chromophore was synthesized by one step method and doped in a high T<sub>g</sub> amorphous polycarbonate (APC) as a host for nonlinear optical (NLO) materials. The D- $\Pi$ -A core in the dendritic chromophore was wrapped by three dendrons. This conformation reduced the intermolecular interactions of the chromophore and made films containing dendritic chromophore easier to orient along the electric field. The poling conditions were investigated using simple reflection technique measurements. This material shows relatively higher EO activities ( $\gamma_{33}$ =334Pm/V). This chromophore also has good solubility in APC host and better thermal stability.

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## 1. Introduction

Organic second order nonlinear optical materials have been intensively studied in the past decade for their potential in high speed electro optic devices with very broad bandwidth and low driving voltages [1,2]. In spite of this, the development of EO materials has been hindered for several years because of the difficulties involved to achieve large EO coefficient. To further improve EO activity, research efforts have focused on developing shape-engineered chromophores with high first hyperpolarizabilities and increasing order within the matrices by controlling the nanoscale architecture of macromolecules. The spherical structure of dendrimers can result in higher solubility in polymeric hosts, lead to both higher chromophore loading density, and larger nonlinearity. Moreover, the NLO chromophores with high  $\beta$  value can be chemically bonded to dendrimers, which are further doped in polymer matrices. The highly branched structure of dendrimers provides the internal free volume for NLO chromophores, which can be site-isolate arranged through steric interaction. Thus the detrimental intermolecular electrostatic interaction can be reduced and large macroscopic nonlinearity will be realized [3-5].

Percec, V. et al. [6, 7] have proposed a strategy for the systematic design and synthesis of macromolecules with controlled backbone conformation, shape, and size, by a covalent coating of conventional polymer backbones with dendritic side groups which self assemble into spherical or cylindrical supramolecular dendrimers. The spherical

conformation is the better for poling and reducing the interaction among chromophore molecules. So the chromophore Lj-Dr-1 was designed and prepared according to paper 6, which gave us a very large  $\gamma_{33}$  value (334Pm/V). Some NLO-dendrimers have been reported before, and achieved higher electro-optic coefficient, but the synthesis is difficult, yield is low and the  $\gamma_{33}$  value was never improved for more than several times. This dendritic chromophore synthesized by one step, was doped in amorphous polycarbonate (APC). The  $\gamma_{33}$  values were obtained after a corona poling process. The effects of the molecular structure, loading density, and aggregation behavior of chromophores on the  $\gamma_{33}$  value were explored. The thermal stability and order parameter were also investigated.

## 2. Synthesis of dendritic chromophore Lj-Dr1

All the reagents were used as received unless stated. Chromophore Lj-1 was prepared according to the literature [8]. <sup>1</sup>H NMR spectra were determined by Varian Gemini 300 (300 MHz) NMR spectrometer (tetramethylsilane as internal reference). FT-IR spectra were recorded on BIO-RAD FTS-165 spectrometer; MS spectra were obtained on MALDI-TOF (Matrix Assisted Laser Desorption/Ionization of Flight) on BIFLEX III (Bruker Inc.) spectrometer. UV-vis spectra were performed on Hitachi U2001 photo spectrometer. TGA was determined by TA5000-2950TGA (TA co) with a heating rate of 10 °C

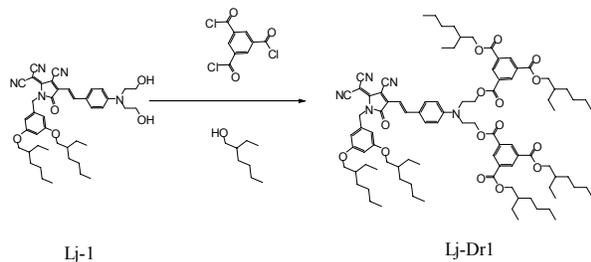
/min under the protection of nitrogen.

Trimesoyl chloride (0.158g, 0.6mmol) was added to the solution of chromophore Lj-1 (0.144g, 0.2mmol) in 50ml Acetonitrile. The mixture was stirred for 2h under an N<sub>2</sub> atmosphere at room temperature. Iso-octyl alcohol (0.234g, 1.8mmol) was then added to the mixture, and the solution was stirred for 2h. then solvent was removed, the crude product was purified by flash chromatography over silica gel using 20% ethyl acetate in hexane as eluent to afford 0.3g (97%) of chromophore Lj-Dr-1. MS (MALDI-TOF), m/z: 1553(M<sup>+</sup>); <sup>1</sup>H NMR(300 MHz, CD<sub>3</sub>COCD<sub>3</sub>),  $\delta$ : 0.86(t, 24H), 0.96(t, 12H), 1.31(m, 36H), 1.46(d, 12H), 2.01(m, 6H), 3.85(d, 4H), 4.22(t, 4H), 4.32(d, 8H), 4.75(t, 4H), 5.27(s, 2H), 6.42(s, 2H), 6.44(s, 1H), 7.13(d, 1H), 7.25(d, 2H), 7.78(d, 2H), 8.48(d, 1H), 8.67(s, 4H), 8.71(s, 2H). IR(KBr),  $\nu$ /cm: 2960(CH<sub>2</sub>, CH<sub>3</sub>), 2220(CN), 1730(COO), 1610(C=C), 1460(C-N); UV-Vis (CH<sub>3</sub>COCH<sub>3</sub>):  $\lambda_{\max}$  =683.5 nm.

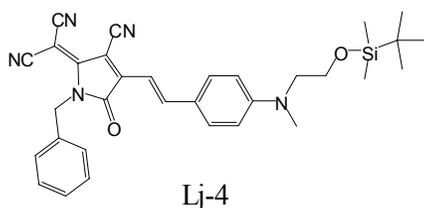
### 3. Results and discussion

#### 3.1 Synthesis of chromophore Lj-Dr-1

The structures of the push-pull chromophore Lj-Dr-1 was shown in Scheme 1. The chromophore Lj-Dr-1 was produced by a one-step procedure (yield: 97%). We produced the chromophore Lj-1 according to the related report.<sup>8,9</sup> The Trimesoyl chloride, acetonitrile and iso-octyl alcohol were purchased from Chemical reagent Beijing Co., Ltd. The reaction among trimesoyl chloride, iso-octyl alcohol and chromophore Lj-1 gave us a high yield of 97%, because of the stability of chromophore Lj-1 in acidic solution.



Scheme 1. Synthesis of chromophore Lj-Dr1.



Scheme 2. Structure of chromophore Lj-4.

#### 3.2 The NLO properties of the chromophores

Table 1. Physical properties of the chromophores.

	$\lambda/\text{nm}$		$\gamma_s$ (Pm/V)	Td (°C)	$\mu$ (D)
	acetone	Dichloromethane			
Lj-4	723	711	26	265	11.86
Lj-Dr-1	683.5	669.5	334	300	15.26

Thermal stability is an important requirement for the incorporation of new chromophores in poled polymer structures [10]. Table 1 gives the thermal decomposition temperature of the chromophore Lj-Dr-1 and Lj-4. both of them show good thermal stability with the onset decomposition temperature of 300 and 265 °C, and no weight loss was observed at lower temperatures. The dendritic chromophore is more stable than the chromophore Lj-4 (about 35 °C higher). This may be due to the dendritic moieties which prevent amino groups from reacting with acceptor cyano groups when being heated.

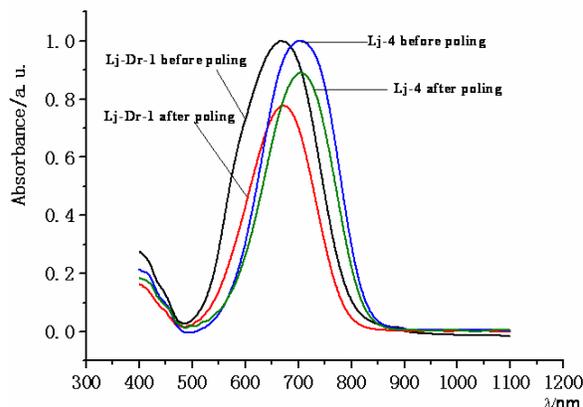


Fig. 1. Uv-Vis spectra of Lj-4 and Lj-Dr-1 before and after polarizing.

The values of maximum absorption of the chromophores in various solvents were also illustrated in Table.1. It can be seen that these chromophores show red shifts in stronger polar solvent (acetone) than in the weaker polar solvent (dichloromethane) and display positive solvatochromism as the polarity of the solvents increased. The shifts of the absorption maxima in different solvents show the effect of solvent on the energy gap between the ground state and excited state molecules, which reflect different electronic distribution in the molecules. DeMartino et al. have suggested that the high solvatochromic effects are related with a large second-order optical nonlinearity [11].

Normally, the  $\gamma_{33}$  value depends on the chromophore density in the films, so the films were prepared with the same loading density of 0.1 mmol/g and the poling process is completely same. The film with Lj-4 showed a little phase separation after poling, but the film with Lj-Dr-1 is in good condition. The EO coefficients ( $\gamma_{33}$ ) for two kinds of films are summarized in Table 1. It is found that the materials containing dendritic chromophores exhibited relatively higher EO activities than chromophore Lj-4. This is due to the dendritic moieties which make the chromophore molecular radius increase largely and the intermolecular interactions be effectively reduced, Fig. 1 proved this. The order parameter<sup>12</sup> of chromophore Lj-Dr-1 in the poled film is 22%, but the order parameter of chromophore Lj-4 is only 10%. It also indicates that the interaction among the dendritic chromophore molecules is less and the material is easier to be polarized.

### 3. Conclusions

A facile method was found to synthesize dendritic NLO-chromophore, and the yield was very high. The conformation of the dendritic chromophore can reduce the intermolecular electrostatic interaction effectively. High order parameter and high EO activities were measured ( $\gamma_{33}=334\text{Pm/V}$ ).

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