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# **Crosslinkable Nonlinear Optical Dendrimers** Synthesized by Diels-Alder Reaction

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Crosslinkable NLO dendrimers based on azobenzene-type chromophores were synthesized by a Diels-Alder reaction. Their thermal and optical properties were investigated before and after poling at a high temperature. We found that the dendrimers retained good thermal stability up to 260 °C after curing at 130 °C for 10 min based on thermal analysis. Through in-situ poling and curing processes, the highest NLO activity of the dendrimers was  $d_{33} = 1.7 \times 10^{-6}$  esu at 1064 nm, which was determined by a Maker fringe experiment.

Keywords: Second-Order Nonlinear Optics, Dendrimer, Crosslinking, Diels-Alder Reaction, Poling.

# **1. INTRODUCTION**

Organic second-order nonlinear optical (NLO) materials have been extensively studied for their potential applications for information technologies in telecommunications, computing, network sensing, and THz generation/detection.<sup>1-6</sup> It is well established that dipolar NLO chromophores consisting of electron donor and acceptor groups contribute to large second-order optical nonlinearity arising from their intramolecular charge transfer and need to be assembled into a noncentrosymmetric lattice in order to obtain macroscopic nonlinearity. A major challenge for designing efficient dipolar NLO chromophores is the optimization of the  $\pi$ -conjugation length as well as the strength of electron donors and acceptors.<sup>7,8</sup> It is also highly desirable to covalently incorporate NLO chromophores into polymer networks and harden the matrix through a crosslinking reaction to improve both their thermal and mechanical properties.<sup>9–11</sup> High performance NLO polymers were recently demonstrated by Diels-Alder reaction for postfunctionalization and lattice hardening to improve NLO properties and thermal stability.<sup>12–15</sup> It involves a ring forming coupling reaction between a dienophile and a conjugated diene, and can be generally described by a symmetry allowed concerted mechanism that does not include reactive radical or ionic intermediate species.

On the other hand, dendrimers are a relatively new class of macromolecules and are different from conventional linear, crosslinked, or branched polymers. Their globular,

reported that NLO dendrimers can significantly improve optical nonlinearity by reducing electrostatic interaction between NLO chromophores.21,22 Multiple NLO chromophore building blocks can be placed into the dendrimers to construct a precise molecular architecture with a predetermined chemical composition. The most important advantage of NLO dendrimers is their capability of maximizing chromophore concentration without phase separation and aggregation. Here we describe the synthesis and characterization of crosslinkable NLO dendrimers facilitated with a Diels-Alder reaction (Fig. 1). In order to conduct Diels-Alder reactions for the NLO dendrimer, maleimide- and anthryl-containing NLO chromophores were prepared. Through in-situ poling and curing processes, the highest NLO activity showed  $1.7 \times 10^{-6}$  esu of second harmonic generation coefficient  $(d_{33})$  at 1064 nm by a Maker fringe experiment. 2. EXPERIMENTAL DETAILS

monodisperse structures can lead to interesting characteristics and unusual physical properties.<sup>16-20</sup> It has been

#### 2.1. Chemicals

All reagents were purchased from commercial sources and used without further purification unless otherwise noted. 3-Maleimidopropionic acid (MPA),<sup>23</sup> 4-(anthracen-9-ylmethoxy)-4-oxobutanoic acid (AMBA),<sup>24</sup> (2-amino-5-nitrophenyl)methanol (ANM),<sup>25</sup> and 4-(dimethylamino) pyridinium-4-toluenesulfonate (DPTS)<sup>26</sup> were synthesized according to the literature methods. The reaction solvents, such as dichloromethane and tetrahydrofuran, were freshly

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Fig. 1. Crosslinked NLO network by Diels-Alder reaction.

distilled prior to use. All reactions were carried out under an inert nitrogen atmosphere.

## 2.1.1. Synthesis of (E)-2,2'-(4-((2-(hydroxymethyl)-4-nitrophenyl)diazenyl)phenylazanediyl) Diethan-Ol (DR-OH)

Ice-cooled solution containing ANM (0.5 g, 3.0 mmol) and 3% HCl solution (30 mL) was added dropwise to sodium nitrite (0.28 g, 4.0 mmol) in water (4 mL). *N*-phenyldiethanolamine (0.54 g, 3.0 mmol) in 7% HCl solution was then added. The resulting mixture was stirred for 2 hours at 5 °C and then neutralized with 10% NaOH solution. A deep red precipitate was collected and washed three times with ethanol/water (1:3) to give DR-OH (Yield: 85%). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  8.41 (*d*, 2 H), 8.32 (*d*, 2 H), 8.23 (*d*, 2 H), 7.65 (*d*, 2 H), 7.03 (*d*, 2 H), 5.39 (*t*, 3 H), 4.79 (*t*, 3 H), 3.76 (*t*, 3 H), 3.54 (*t*, 3 H).

## 2.1.2. Synthesis of Maleimide-Containing Chromophore DRMI

DCC (0.2 g, 0.10 mmol) with a catalytic amount of DPTS was added to the solution of DR-OH (0.10 g, 0.30 mmol) and MPA (0.14 g, 0.80 mmol) in THF (30 mL). The reaction mixture was allowed to stir at room temperature for 6 hours under the nitrogen atmosphere. After filtration of the resultant urea, the solution was concentrated under reduced pressure. The crude product was purified by column chromatography using ethyl acetate and hexane (2:1) as an eluent to afford DRMI (Yield: 73%). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  8.41 (*d*, 2 H), 8.32 (*d*, 2 H), 8.23 (*d*, 2 H), 7.65 (*s*, 2 H), 7.03 (*d*, 2 H), 6.94 (*s*, 2 H), 5.34 (*s*, 2 H), 4.31 (*t*, 2 H), 3.87 (*t*, 2 H), 3.63 (*t*, 2 H), 2.61 (*m*, 4 H).

#### 2.1.3. Synthesis of Anthryl-Containing Chromophore DRAN

This was synthesized with a similar procedure as described for compound DRMI using DR-OH (0.10 g, 0.30 mmol) and AMBA (0.80 g, 3.00 mmol) instead of DR-OH and MPA. The crude product was purified by column chromatography using ethyl acetate and hexane (2:1) as an

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Crosslinked NLO network

eluent to afford DRAN (Yield: 85%). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  8.41 (*d*, 2 H), 8.32 (*d*, 2 H), 8.23 (*d*, 2 H), 7.89 (*d*, 4 H), 7.65 (*d*, 2 H), 7.03 (*d*, 2 H), 6.14 (*s*, 1 H), 5.78 (*s*, 2 H), 5.34 (*s*, 2 H), 2.64 (*t*, 2 H).

#### 2.1.4. Synthesis of DR-2G

The solution of DRMI (0.12 g, 0.15 mmol) in THF (80 mL) was refluxed and stirred for 1 hour to dissolve the DRMI completely. DRAN (0.03 g, 0.02 mmol) in 20 mL of THF was slowly added to the reaction mixture and kept reflux for overnight. The crude product was purified by chromatography using ethyl acetate and methanol (9:1) as an eluent to afford DR-2G (Yield: 35%). H-NMR (300 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  8.41 (*d*, 2 H), 8.32 (*d*, 2 H), 8.23 (*d*, 2 H), 7.65 (*d*, 2 H), 7.31 (*d*, 2 H), 7.19 (*t*, 3 H), 6.94 (*s*, 2 H), 5.94 (*s*, 2 H), 5.34 (*s*, 1 H), 4.31 (*t*, 2 H), 2.51 (*t*, 2 H). MALDI-TOF-MS (matrix, 2-(4-hydroxyphenylazo)benzoic acid (HABA)): calcd for C<sub>188</sub>H<sub>167</sub>N<sub>25</sub>O<sub>56</sub> 3672.47; found 3670.64 [M<sup>+</sup>].

#### 2.2. Characterization

<sup>1</sup>H NMR spectra (300 MHz) were taken on a Varian 300 spectrometer and mass spectra were recorded on a JMS-AX505WA mass spectrometer. UV/vis spectra were obtained on a Perkin-Elmer spectrophotometer. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed on a TA instruments Q50 at a ramping rate of 10 °C/min under a nitrogen atmosphere. Atomic force microscopy (AFM) was performed using a Digital Instruments Nanoscope IV operated in tapping mode (~350 kHz frequency, Si tip).

#### 2.3. Film Preparation and SHG Measurements

Pinhole-free films were prepared by spin-coating onto indium tin oxide (ITO) glass substrates from cyclopentanone solution (12 wt% of solid contents) after filtration through a 0.2  $\mu$ m of poly(tetrafluoroethylene) (PTFE) filter. The substrate was dried under high vacuum at 40 °C for overnight to remove residual solvents. The thickness of the films were found to be around  $0.8 \sim 1.2 \ \mu\text{m}$ . For second harmonic generation (SHG) measurements, the films were poled at 130 °C for 30 minutes under an applied voltage of 6 kV with a corona electrode using a tungsten needle. A *Q*-switched Nd:YAG laser ( $\lambda = 1064 \text{ nm}$ ), with a pulse width of 10 ns and a repetition rate of 10 Hz, was used as the fundamental light source and *Y*-cut quartz was used as a reference. SHG coefficients,  $d_{33}$ , were derived from analysis of a Maker fringe method.<sup>27</sup>

# 3. RESULTS AND DISCUSSION

The synthetic scheme of maleimide-containing DRMI and anthryl-containing DRAN chromophores is shown in Scheme 1. The hydroxy-functionalized chromophore, DR-OH, was reacted with an acid compound, MPA or

AMBA, to afford DRMI or DRAN, respectively. The resulted N-acrylurea and anhydride byproduct can be removed by repetitive precipitation after a catalyzedesterification reaction. The crosslinkable NLO system is able to be generated from blending with a 1:1 mixture of DRMI and DRAN. After spin-coating the mixture solution onto glass substrates, the highly reactive anthracene groups in DRAN react with maleimide groups in DRMI at elevated temperatures. Through this solid phase Diels-Alder reaction, it forms a chromophore-embedded network system. A multi-arm NLO dendrimer, DR-2G, was synthesized by a solution reaction between DRAN and an excess of DRMI also facilitated with the Diels-Alder reaction (Scheme 2). The structure and purity of all intermediates and final compounds have been verified by <sup>1</sup>H NMR, UV/vis and mass spectroscopy, and thermal analysis.



Scheme 1. Synthesis of anthryl-containing DRAN and maleimide-containing DRMI chromophores.

**RESEARCH ARTICLE** 



Scheme 2. Synthesis of a DR-2G dendrimer.

DR-2G has excellent solubility in common organic solvents, such as acetone, ethyl acetate; tetrahydrofuran, vertice to the solution of the s

Figure 2 shows the UV-vis absorption spectra of a thin film for DRMI/DRAN (1:1 mixture). The main absorption peak at 476 nm is due to the intramolecular chargetransfer band of the chromophores. The solid line was



**Fig. 2.** UV-vis absorption spectra of a thin film for DRMI/DRAN (1:1 mixture) upon increasing a time at 130 °C.

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obtained from the as-prepared film. The typical absorption bands for the anthracene moiety are observed at 354, 372, and 392 nm. As seen from Figure 2, upon increasing the time at 130 °C, these bands are reduced by the Diels-Alder cycloaddition reaction between the anthryland maleimide-functionalized chromophores. These bands have completely disappeared within 5 minutes during annealing, indicating the high reactivity of the Diels-Alder reaction in the solid state. It was found that the UV-vis absorption spectra of DR-2G blended with DRAN showed similar behavior during annealing at 130 °C. Interestingly, DR-2G has a higher absorption coefficient than DRMI and DRAN, as listed in Table I. This is probably due to reducing chromophore aggregation for the DR-2G dendrimer in the solution and solid states.

Thermal analysis of DRMI/DRAN (1:1 mixture) and DR-2G/DRAN (1:2 mixture) by DSC exhibited an exothermic transition above 130 °C, at which temperature Diels-Alder cycloaddition and a crosslinking network were induced. Upon the second heating of these samples,

Table I. Thermal and optical properties of DRMI, DRAN, and DR-2G.

a 1	<b>T</b> (1)(2)	The (a C)			
Sample	$T_g^u$ (°C)	$T_d^{v}$ (°C)	$\lambda_{\max\_sol}^c$ (nm)	$\varepsilon^{a}$ (L/mol·cm)	
DRMI	_	218	460	$3.1 \times 10^{4}$	
DRAN	78	204	470	$2.9 \times 10^4$	
DR-2G	56	230	465	$3.8 \times 10^4$	

*Notes*: <sup>*a,b*</sup> Determined by DSC and TGA curves at a heating rate of 10  $^{\circ}$ C · min under nitrogen atmosphere; <sup>*c*</sup> Absorption maxima in dichlromethane; <sup>*d*</sup> Absorption coefficient.



Fig. 3. TGA thermograms of DRMI, DRAN, and DRMI/DRAN (1:1 mixture) at a heating rate of 10 °C/min under nitrogen.

we did not observe any significant thermal transition up to 250 °C before decomposition of the chromophores. They were very tough and were completely insoluble in any organic solvent. The initial decomposition temperature ( $T_d$ ) with 5% of weight loss was measured by TGA for DRMI, DRAN, DRMI/DRAN (1:1 mixture), and DR-2G/DRAN (1:2 mixture). As shown in Figure 3, the  $T_ds$  of DRMI and DRAN were found to be at 218 °C and 204 °C, respectively. The cured crosslinked networks of DRMI/DRAN (1:1 mixture) and DR-2G/DRAN (1:2 mixture) significantly enhanced their thermal stabilities over 50 °C compared with DRMI and DRAN.

The NLO properties of DRMI/DRAN (1:1 mixture) and DR-2G/DRAN (1:2 mixture) were studied by the SHG method. To induce noncentrosymmetric polar order, the thin films were treated with corona poling (external field of 6 kV) at 130 °C for 30 minutes. Starting from a soft and very soluble composite film, the poled/cured network film became very tough and gained good solvent resistance due to Diels-Alder crosslinking. Both poling fields and times were varied to optimize the polar order and crosslinking. Although the UV-vis absorption spectra showed effective crosslinking network induced within 5 min, we found improved poling efficiency as increased time until 30 min. Furthermore we did not observe any NLO activity of crosslinked films applied with the voltage let than 5 kV of poling fields.

Due to such a high voltage applied at a high temperature, the poled films may possess unevenly distributed surface morphology. Therefore, we examined the film surface by AFM before and after poling. As shown in Figure 4(a), the AFM image of the DRMI/DRAN (1:1 mixture) before the poling shows a highly uniform film with a surface roughness of  $1\sim2$  nm. We observed aggregates evenly distributed with a size of  $10\sim30$  nm and aligned to the poling direction (Fig. 4(b)). However, there is little change for the surface roughness of the poled film. This result differs from previous studies that show numerous hills



Fig. 4. AFM images of the DRMI/DRAN (1:1 mixture) film (a) before and (b) after poling.

and valleys in the surface structure of corona-poled polymers and suggest that crosslinked network films may be more stable under poling. UV-vis absorption spectra before and after poling for the DRMI/DRAN (1:1 mixture) are shown in Figure 5. The solid line was obtained from the film treated with heating to 130 °C without any external field applied. The dashed line was obtained from the same film with the corona poling applied with 6 kV at 130  $^\circ\mathrm{C}$ for 30 minutes. The decrease of the peak absorbance is caused by the alignment of the chromophore dipoles along the poling direction, which is the incident light direction as well. 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.<sup>28</sup> From the calculation, the estimated order parameter was 0.38 for DRMI/DRAN (1:1 mixture). It is noted that DR-2G/DRAN (1:2 mixture) exhibited the order parameter of 0.22. The reduced value suggests a high

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Fig. 5. UV-vis absorption spectra of the DRMI/DRAN (1:1 mixture) film before and after poling.

concentration of the maleimide exterior moieties in the DR-2G accelerated Diels-Alder reaction with DRAN at lowered temperatures resulted in a poor poling order.

SHG measurements were performed at a fundamental wavelength of 1064 nm with a Q-switched Nd-YAG laser and OPO. The SHG intensity of the films was measured using a standard Maker fringe technique. Figure 6 shows the relationship between the SHG intensity and the incident angle for DRMI/DRAN (1:1 mixture). The SHG coefficients can be calculated from the angular dependence of the SHG intensity compared to a Y-cut quartz as a reference signal. To obtain the  $d_{31}$  and  $d_{33}$  values, both s-polarized and p-polarized IR laser beams were directed at the samples. The NLO properties of DRMI/DRAN (1:1 mixture) and DR-2G/DRAN (1:2 mixture) are summarized in Table II. The values of  $d_{31}$  and  $d_{33}$  for DRMI/DRAN (1:1 mixture) were  $3.6 \times 10^{-7}$  and  $1.7 \times 10^{-6}$  esu, respectively. However we found a reduced order parameter and lowered SHG coefficient ( $d_{33} = 1.1 \times 10^{-6}$  esu) for DR-2G/DRAN (1:2 mixture). Since the ratio of  $d_{33}/d_{31}$ is predicted to be about 3 in the isotropic model, 3.4 of



Fig. 6. Angular dependence of SHG signal intensity for the DRMI/ DRAN (1:1 mixture) film.

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**Table II.** Thermal, optical, and NLO properties of DRMI/DRAN (1:1 mixture) and DR-2G/DRAN (1:2 mixture).

Sample	$T_d^a$ (°C)	$\lambda^{b}_{\max\_film}$ (nm)	$oldsymbol{\phi}^{c}$	$d_{31}^d$ (esu)	$d_{33}^d$ (esu)
DRMI/DRAN (1:1 mixture)	260	476	0.38	$3.6 \times 10^{-7}$	$1.7 \times 10^{-6}$
DR-2G/DRAN (1:2 mixture)	263	481	0.22	$3.2 \times 10^{-7}$	$1.1 \times 10^{-6}$

*Notes.* <sup>*a*</sup>Determined by TGA curves at a heating rate of 10 °C · min under nitrogen atmosphere; <sup>*b*</sup>Absorption maxima in a thin solid film; <sup>*c*</sup>Order parameter; <sup>*d*</sup>SHG coefficients derived from the analysis of a Maker fringe technique.

 $d_{33}/d_{31}$  for DR-2G/DRAN (1:2 mixture) is in good agreement. Evaluation of high-temperature and temporal alignment stability of the crosslinked NLO films is on progress by using various poling and annealing conditions.

### 4. CONCLUSION

We have successfully synthesized two crosslinkable NLO dendrimers, DRMI/DRAN (1:1 mixture) and DR-2G/DRAN (1:2 mixture). Through the solid phase Diels-Alder reaction, they formed chromophore-embedded network systems. Their thermal and optical properties were investigated before and after poling at a high temperature. The cured crosslinked networks significantly enhanced their thermal stability more than 50 °C compared with DRMI and DRAN. For the DRMI/DRAN (1:1 mixture), the highest NLO activity was  $d_{33} = 1.7 \times 10^{-6}$  esu with an order parameter of 0.38, which was obtained from *in-situ* poling and curing processes.

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