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1,3-Bis(dicyanomethylidene)indane-Based Second-Order NLO Materials

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Organic polymeric second-order nonlinear optical (NLO) materials are very promising for applications in photonic devices, such as electrooptic modulators and frequency doublers, due to their large optical nonlinearities, high laser damage thresholds, low dielectric constants, and excellent processibilities.[1-3] To meet the requirements for photonic applications, two important issues must be addressed. First, the materials must have large, nonresonant second-order optical nonlinearities. Second, the materials must exhibit excellent temporal and thermal NLO stability. In addressing the first issue, chromophores with large microscopic second-order optical nonlinearities and high loading densities in polymer matrixes are desired. In addressing the second issue, NLO chromophores stable at high temperatures and in a strong electric poling field are required. In this paper, we report preliminary studies of incorporating a strong electron acceptor, 1,3-bis(dicyanomethylidene)indane (BDMI),[4] in second-order nonlinear optical materials.

Figure 1 shows the general scheme of synthesizing difunctional aminophenylenethienylidene-1,3-bis(dicyanomethylidene)indane (APT-BDMI) chromophores. 1,3-Bis(dicyanomethylidene)indane (BDMI) was synthesized according to the literature procedure.[4] Diethyl 2-thienylmethylenephosphonate was synthesized from the respective 2-(chloromethyl)thiophene in an Arbusov reaction. 2-(Chloromethyl)thiophene was prepared by chlorination of 2-thiophenemethanol by either thionyl chloride or concentrated hydrochloric acid.

To synthesize the difunctional APT-BDMI chromophore, we chose bis(hydroxyethyl)aniline (**1**) as the donor unit, due to its hydroxyl groups for use in the fabrication of polymers as well as its commercial availability in high purity. We used thiophene as the bridge unit due to its advantages relative to the phenyl group.[5] 1,3-Bis(dicyanomethylidene)indane (BDMI) was employed as the acceptor due to its excellent electron-withdrawing strength[4] and its ability to produce chromophores with impressive optical nonlinearities.[6] Furthermore, consideration of other critical and practical parameters such as ease of synthesis and chemical stability (both under ambient and materials processing conditions, i.e., elevated temperatures under a poling electric field) make BDMI chromophores attractive candidates for device quality electrooptic materials.

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(5) Jen, A. K.-Y.; Rao, V. P.; Wong, K. Y.; Drost, K. J. *J. Chem. Soc., Chem. Commun.* **1993**, 90.

(6) Marder, S., private communication. The dimethylamino analogue of chromophore **6** of Figure 1 has a dipole moment $\mu = 6.0 \times 10^{-18}$ esu, and a first hyperpolarizability $\beta = 1024 \times 10^{-30}$ esu at 1.907 μm, so $\mu\beta = 6144 \times 10^{-48}$ esu.

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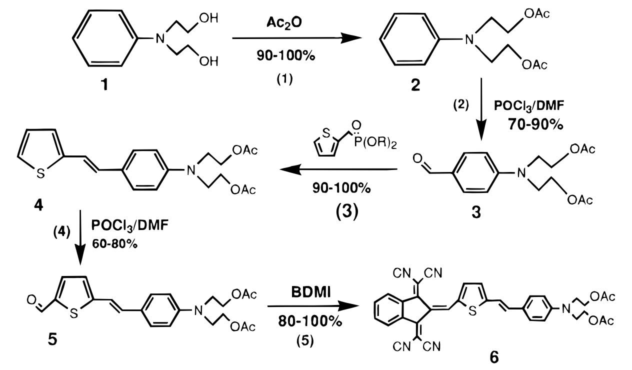

Figure 1. Synthetic scheme of acetate protected difunctional aminophenylenethienylidene-1,3-bisdicyanomethylideneindane (APT-BDMI) push–pull nonlinear optical chromophore **6**.

The preparation of BDMI materials as shown in Figure 1 is described as follows. Acetate protection of the hydroxyl functional groups of bis(hydroxyethyl)-aniline (**1**) is carried out by reaction with neat acetic anhydride (step 1). Contrary to the typical use of 1 equiv of pyridine (as a base) in this type of reaction, we have found that quantitative conversion to the diacetate **2** is possible without any base. This may be due to the aniline species itself acting as a base in the reaction. The product **2** was obtained in a sufficiently pure state by simply removing the excess acetic anhydride and side-product acetic acid by vacuum evaporation. The acetate protecting groups are stable to the subsequent harsh Vilsmeier–Haack formylation conditions (steps 2 and 4), which is applied to the sufficiently pure crude diacetate products. The Horner–Emmons reaction (step 3) of the aldehyde **3** with diethyl thienyl-2-methylenephosphonate resulted in the phenylenethiophene species **4**, but this was accompanied by partial deprotection of the acetate protecting groups (due to the strong bases present). Reprotection of the crude product mixture with acetic anhydride afforded the diacetate **4**. The aldehyde **5** was condensed with the BDMI acceptor in acetic anhydride to give the BDMI chromophore **6** in excellent yield. ^1H of **6** (ppm in $CDCl_3$, 7.24 ppm peak used as reference): 2.04 (s, 6H), 3.67 (t, $J = 5.8$ Hz, 4H), 4.25 (t, $J = 5.8$ Hz, 4H), 6.75 (d, $J = 8.3$ Hz, 2H), 7.01 (d, $J = 16.1$ Hz, 1H), 7.08 (d, $J = 4.0$ Hz, 1H), 7.13 (d, $J = 16.2$ Hz, 1H), 7.42 (d, $J = 8.5$ Hz, 2H), 7.58 (d, $J = 4.0$ Hz, 1H), 7.75 (m, 2H), 8.54 (m, 2H), 8.62 (s, 1H). ^{13}C of **6** (ppm in DMSO-d_6, 40.0 ppm peak used as reference peak): 183.82, 170.87, 158.65, 153.66, 148.42, 140.27, 139.69, 138.33, 133.58, 130.61, 129.08, 126.41, 124.31, 122.05, 118.42, 118.31, 116.81, 112.33, 103.23, 61.50, 49.33, 21.15. FAB MS 625. Calculated 625. The visible absorption peak of **6** in dichloromethane is at 690 nm. Thermal analysis of **6** demonstrates its melting point around 190 °C and decomposition (weight loss) temperature of 290 °C as shown in Figure 2.

To examine the general performance (i.e., optical nonlinearity and chemical stability at elevated temperatures) of BDMI based chromophores in thin-film polymer matrixes, especially under the influence of poling electric fields, we pursued some initial poling studies. Thin films of chromophore **6** doped in poly(methyl methacrylate) (PMMA) were spin coated onto indium tin oxide (ITO) coated glass slides. Thicknesses of the polymer films were from 1 to 5 μm. The doped PMMA films were poled in situ as described elsewhere.[7] A corona needle tip to ITO glass slide distance of 1 cm was used. This set up has a maximum applied voltage of 9 kV from the corona poling needle to the slide ITO plane. The in situ measurement allows the monitoring of the nonlinear optical signal while the sample is being heated and poled. This provides information on the condition where the best poling occurs. For chromophore **6**/PMMA composite films, the optimal poling temperature can be as high as 90 °C for a completely dried film.

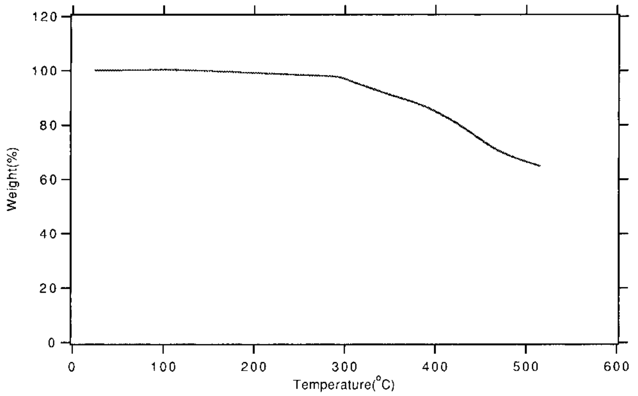

Figure 2. Thermal gravimetric analysis (TGA) of chromophore **6**. Weight loss starting at 290 °C demonstrates thermal degradation.

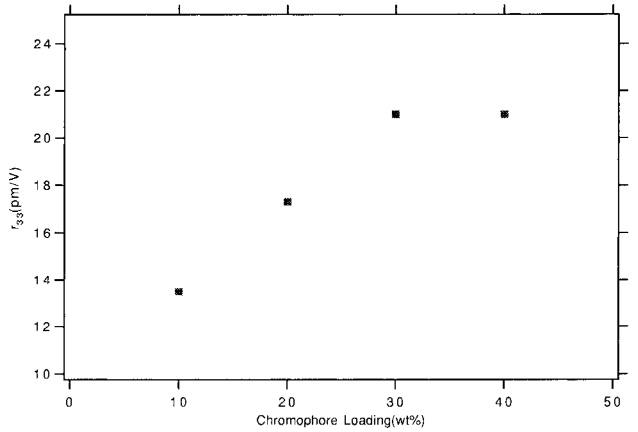

Figure 3. Electrooptical coefficients r_{33} (pm/V) measured at 1.06 μm for different chromophore **6** weight loading densities in PMMA films.

The electrooptic coefficient r_{33} value of each film was measured 10–30 min after the poling field (typically 9 kV) was removed from the film at room temperature. An attenuated total reflection (ATR) technique[8] was used to measure r_{33} at a wavelength of 1.06 μm. For films of 30 and 40 wt % doped loading density, we measured maximum r_{33} of 21 pm/V. For one film of 10 wt % doped loading density, an r_{33} of 13.5 pm/V was obtained, while for films of 20 wt % doped loading density, a maximum r_{33} of 17.3 pm/V was obtained. Figure 3 demonstrates the measured r_{33} values for different chromophore **6** loading densities in PMMA film. For the 20 wt % films, we estimated that the poling efficiency was around 15% based on the chro-

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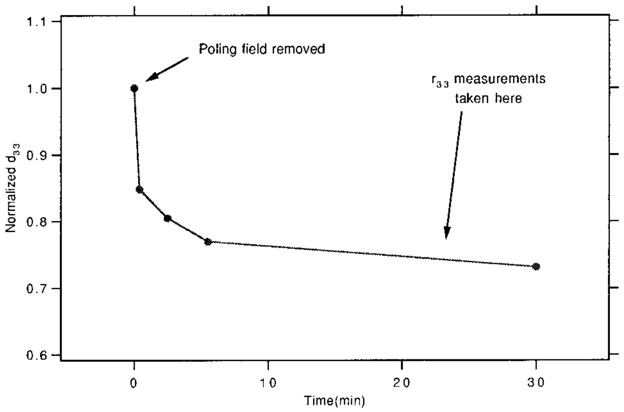

Figure 4. Typical 30 min second-order optical nonlinearity (d_{33}) decay after the electric poling field removed from the chromophore **6**/PMMA composite film.

mophore molecular weight, loading density, average bulk nonlinear signals, and the estimated chromophore first hyperpolarizability value.[6]

The 40 wt % composite film possessed a lower nonlinearity value than expected. This may have been due to a number of reasons, such as (1) poor poling efficiency or chromophore alignment due to stronger intermolecular interactions caused by either the chromophore's large dipole moments or steric hindrance, (2) chromophore aggregation in the films due to surpassing the solubility parameter of the chromophore in the host polymer, and (3) solubility saturation (i.e., the actual loading density was less than 40 wt % due to chromophore solubility saturation in the solvent, with removal of suspended undissolved chromophore during filtration of solutions of the composite).

Since the quality of the films varies from one to another, the measured r_{33} values are only a rough estimate. However, we believe the data in this range may be used for relative comparison. One thing to point out is that our r_{33} measurements were usually performed 10−30 min after the poling field was removed from the films, and so the values obtained were those of the material after initial chromophore dipole relaxation. Invariably, the nonlinearity had decayed to about 60−80% of the maximum signal after this time. Figure 4 shows a typical temporal decay of the poling induced nonlinearity during the 30 min period after removing the poling field. Thus, it can clearly be seen that the r_{33} values we have obtained are by no means the maximum values that may be obtained from these systems. We still have considerable opportunity for further improving of the nonlinearity of these systems either by chemical methods, such as lattice hardening to lock in the poling-induced dipolar alignment, or by physical methods, such as improving poling efficiency.

In summary, the difunctional aminophenylenethienylidene-1,3-bis(dicyanomethylidene)indane (APT-BDMI) based second-order nonlinear optical chromophores have been synthesized via a multistep synthetic route. The starting materials of this multistep synthetic scheme are inexpensive, and all steps can be pursued conveniently with conventional synthetic organic methods, i.e., no special equipment or reagents are required. The BDMI-based second-order NLO chromophores studied here demonstrate excellent chemical stability under ambient and poling conditions (no observable chromophore degradation under even the maximum poling field of 9 kV), and the chromophore can be efficiently poled at low loading densities in the polymeric composite systems we studied. The electrooptic coefficient r_{33} of 21 pm/V at 1.06 mm for a 30−40 wt % chromophore-doped PMMA thin film was the value measured at approximately 60−80% of retention of the maximum poling signal. This implies that stabilization of the poling-induced chromophore alignment will produce materials with device-quality electrooptic coefficients. This preliminary study demonstrates that BDMI-based materials have excellent potential for electrooptic applications. Current work involves covalent incorporation of BDMI-based chromophores into a variety of polymer systems, the optimization of poling protocols for these materials, and stabilization of the nonlinearities by various lattice hardening methods. Nonlinear characterization of covalent BDMI polymers are currently underway and will be reported separately.

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