

Research Article

Preparation of the Inclusion Complex-Type Nonlinear Optical Polymer

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This study uses the inclusion complex method to import nonlinear optical (NLO) chromophores, disperse red1 (DR1), and spiropyran (SP), into the γ -CD cavity of the γ -cyclodextrin polymer (γ -CDP) to prepare orderly aligned nonphotocontrollable and photocontrollable nonlinear optical polymers. Calculations support the ultraviolet/visible analyses and suggest the formation of the 1 : 2 DR1/ γ -CDP and 1 : 2 SP/ γ -CDP inclusion complexes. Upon complexation, the DR1 and SP molecules are free to align themselves along an applied electric field and show high order parameters of approximately 0.48 and 0.20, respectively. Reversible photochromic reactions exhibit that the SP/ γ -CDP complex still retains the photochromic properties following corona poling.

1. Introduction

Nonlinear optical (NLO) material possessing optical modulation capabilities including changing optical phase, changing optical frequency, or coupling more than two light beams to increase or decrease frequency has recently become the most significant development goal for photonic devices [1, 2]. Through the development of NLO materials, photonics can be used as a future carrier of information and overcome transmission bottlenecks for current electronic transmission methods, including the resistive losses that occur with electrons moving through metal wires as the frequency of information increases [3].

Although general NLO organic molecules have excellent NLO properties, their commercial applications are limited because of the difficulty of their processing. By combining NLO molecules with polymers, the high NLO susceptibility, fast response time, low dielectric constant, small dispersion in refractive index, structural flexibility, and ease of material processing have brought NLO polymers to the forefront of NLO research [4]. NLO polymers can be divided into guest/host polymer [5–7] and covalently linked polymers (side- and main-chain polymers) [8–10]. Guest/host polymers blend NLO chromophores (guest) to the polymer matrices (host). They can achieve a higher noncentral symmetry

through poling, but are prone to phase separation [11]. Side- and main-chain polymers bond the NLO chromophores to the polymer chains covalently and exhibit good phase mixing. However, the mobility of the polymer chain hinders the alignment of NLO chromophores, influencing the efficiency of electric field poling [12, 13]. Crosslinking of the polymer which contains chromophore groups [14–16] or formation of interpenetrating polymer networks [17, 18] has been developed to reduce the mobility of the polymer segments; consequently, the materials require longer poling times and larger poling voltages [19, 20].

Disperse red 1 (DR1, Figure 1(a)) is very promising as NLO chromophore, because it is easy to create polar order of them by external electric field poling. To improve its processing and application characteristics, most studies have focused on the blending or covalent bonding methods to import it into the polymer [21–24]. Cui et al. [22] used a sol-gel process to copolymerize alkoxy silane dye and DR1 to prepare organic-inorganic hybrid materials. Aldea et al. [23] used the layer-by-layer electrostatic self-assembly structure to create multilayer thin film-based NLO materials. Tu et al. [24] explored the dynamic molecular behavior for mixing DR1 and poly(methyl methacrylate).

Spiropyran (SP, Figure 1(b)) plays a critical role in the photochromism field because the colorless SP form will

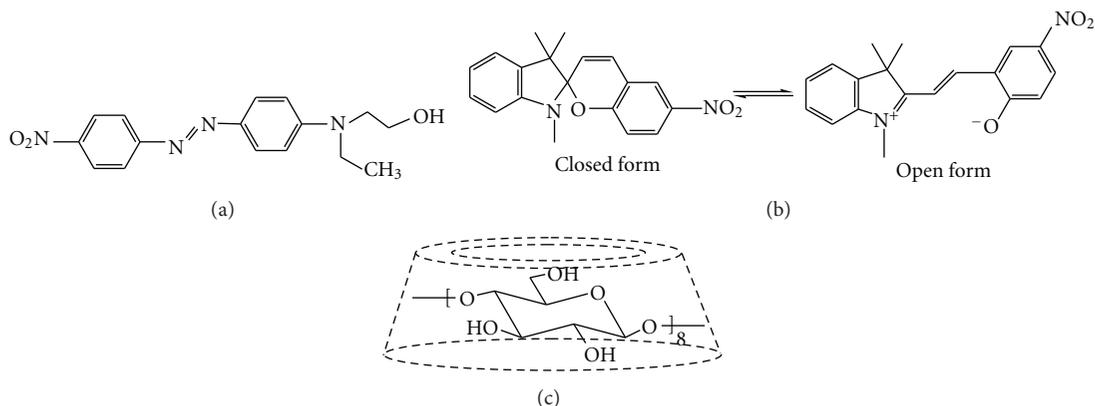


FIGURE 1: Schematic structures for (a) DR1, (b) SP, and (c) γ -CDP.

convert to a red-colored photomerocyanine (PM) under ultraviolet (UV) irradiation. The PM form can revert to the SP form either thermally or photochemically [25–27]. Typically, SP is included in polymer matrices to obtain various forms of solid-state photochromic materials to extend its commercial application range [28–30]. Kim et al. [28] prepared a series of cationic polymers using spirooxazines as side-chain groups. All of these synthesized photochromic polymer materials, whether in solution phase or solid-state thin films, have good photochromic properties.

Photomerocyanine (PMs) are comprised of strong electron donor and acceptor groups connected by a π -conjugated bridge. They possess delocalized π -electron systems capable of exhibiting charge transfer resonances, which leads to a preferential orientation of the molecules along the applied electric field [31–33]. Experimental values of dipole moments and first-order hyperpolarizability β were reported for various PMs [34–37]. Replacing the benzopyryl moiety by 1,3-diethylthiobarbituric acid, the indoline-based PM exhibits a negative β value ($\beta = -46 \times 10^{-30}$ esu) and a dipole moment of 7.4×10^{-18} esu [34]. Theoretically, considerable efforts have been directed toward the molecular engineering of such chromophore structures [38–40]. We used the density functional theory (DFT) calculation [41–43], CAM-B3LYP/6-31+G(d,p), and found that PM has a high dipole moment of approximately 2.8×10^{-30} esu and shows high second-order NLO properties with first hyperpolarizability of approximately 38.4×10^{-30} esu (commonly used stilbene-series NLO molecules are approximately $7 \times 10^{-30} \sim 38 \times 10^{-30}$). Because colorless SP form does not have NLO properties, different optical wavelengths can convert it between the two forms and produce second-order NLO property changes that can be applied to photocontrollable components for data storage or opto-optical switching [44].

Therefore, this study uses the inclusion complex method to separately import DR1 and SP into the γ -cyclodextrin (γ -CD) cavity of γ -cyclodextrin polymer (γ -CDP, Figure 1(c)) to prepare DR1/ γ -CDP and SP/ γ -CDP complexes for nonphotocontrollable and photocontrollable NLO polymers. Incorporation of chromophore in the cavity of γ -CDP increases the free volume surrounding the chromophore

and decreases the spatial constraint from polymer chains. Additionally, the physical bonding between chromophore and γ -CDP enables the materials to simultaneously possess the guest/host NLO material's advantage of being simple to prepare and easy to polarize and the covalently linked NLO material's advantage of having a stable phase mixing structure.

2. Experimental

2.1. Preparation of Inclusion Complexes. *N*-Ethyl-*N*-(2-hydroxyethyl)-4-(4-nitrophenylazo)aniline (Disperse red1, DR1) and γ -cyclodextrin polymer (γ -CDP) were purchased from Sigma-Aldrich, and 1'-3'-3'-Trimethyl-6-nitrospiro [2*H*-1-benzopyran-2,2'-indoline] (Spiropyran, SP) was purchased from TCI, respectively, and used as received. Solutions (250 μ L, 1×10^{-2} M) of DR1 and SP in ethanol were injected separately into 5 mL of aqueous γ -CDP (1×10^{-2} mol γ -CD/L) solution at 30°C with sonication for 10 min [45, 46]. After 24 h of stirring, the DR1/ γ -CDP and SP/ γ -CDP inclusion complexes were deposited separately by spin coating onto ITO (indium tin oxide) glass plates and dried at 40°C *in vacuo* overnight for Ultraviolet/Visible (UV/VIS, Hitachi U-3900) analysis. Because of the extreme light sensitivity of SP, all operations for SP/ γ -CDP complex preparation must be conducted in a dark room.

To calculate the complex stoichiometry, solutions of DR1 and SP (1×10^{-5} M) in ethanol were prepared separately. Samples of 0–7 mL γ -CDP solution with concentrations of 1×10^{-3} M were added to each 1 mL sample of DR1 or SP solution. The samples were then diluted to 10 mL by adding water.

2.2. Poling Process. External electrical field (corona) poling was used to break the symmetry of the inclusion complex. The corona field between -3 and -10 kV was applied for 15 min after the film was heated to the desired temperature of approximately 150–200°C [14, 24, 47]. Then the sample was cooled to room temperature under a continuous electrical field. During the poling procedure, the corona current was maintained at less than 50 μ A, and the distance between

the ITO and the needle was set at 1 cm. For the SP/ γ -CDP complex, the poling process had to be conducted under the irradiation of UV light because a high dipole moment value only appears after the formation of the PM form. The changes in the UV/VIS spectroscopic absorbance were used to examine the alignment of the γ -CDP-complexed NLO chromophore (DR1 and SP) before and after poling by order parameter Φ [48]:

$$\Phi = 1 - \left(\frac{A_f}{A_o} \right), \quad (1)$$

where A_o and A_f are the UV/VIS absorbance for the polymer film before and after poling, respectively. After the oriented arrangement of molecules, the UV/VIS absorbance is reduced, causing the Φ value to increase.

2.3. Quantum Chemical Calculations. The geometries of complexed compounds were firstly optimized using Parameterized Model number 3 (PM3) [49], and then the two-layered hybrid ONIOM method [50], ONIOM(B3LYP/6-31G+(d,p):PM3), was adopted to find the ground-state geometry. The high-level layer, DR1 and SP, and the low-level layer, γ -CD, were calculated by B3LYP/6-31G+(d,p) and PM3, respectively. For comparison, B3LYP/6-31G+(d,p) and PM3 alone were also used to optimize the geometrical structures of isolated DR1 (or SP) and γ -CD, respectively. All calculations were made using the Gaussian09 program package [51].

3. Results and Discussion

3.1. Stoichiometry of Inclusion Complexes. The stoichiometry of the inclusion complex was determined using the Benesi-Hildebrand method [52–54] from the UV/VIS data:

$$\frac{A_o}{\Delta A} = \frac{[1 + 1/(K \cdot [\gamma\text{-CD}]^n)]}{(\Delta\epsilon \cdot [\text{chromophore}])}, \quad (2)$$

where ΔA represents the difference between the absorptions of the chromophore (DR1 or SP) solution in the presence and absence (A_o) of γ -CD; $\Delta\epsilon$ denotes the difference between the molar absorption coefficients of chromophore/ γ -CD and chromophore; n is the molar ratio of γ -CD to SP; and $[\text{chromophore}]$ and $[\gamma\text{-CD}]$ are the concentrations of chromophore and γ -CD, respectively. The linear relationships of ΔA^{-1} against $[\gamma\text{-CD}]^{-2}$ for both DR1 and SP reveal the formation of 1:2 DR1/ γ -CD and 1:2 SP/ γ -CD complexes (Figure 2).

Quantum chemical calculations by using the two-layered hybrid ONIOM method were performed for each of the complexes of interest to yield geometries (Figure 2 inset) and energies that were determined exclusively by the inclusion processes. The calculations of binding energies revealed that for both DR1 and SP, the 1:2 γ -CD inclusion complexes (22.6 and 15.4 kcal mol⁻¹ for DR1/ γ -CD and SP/ γ -CD complexes, resp.) are more stable than the 1:1 γ -CD inclusion complexes (7.7 and 5.2 kcal mol⁻¹ for DR1/ γ -CD and SP/ γ -CD complex, resp.). This result agrees with experimental UV/VIS analyses:

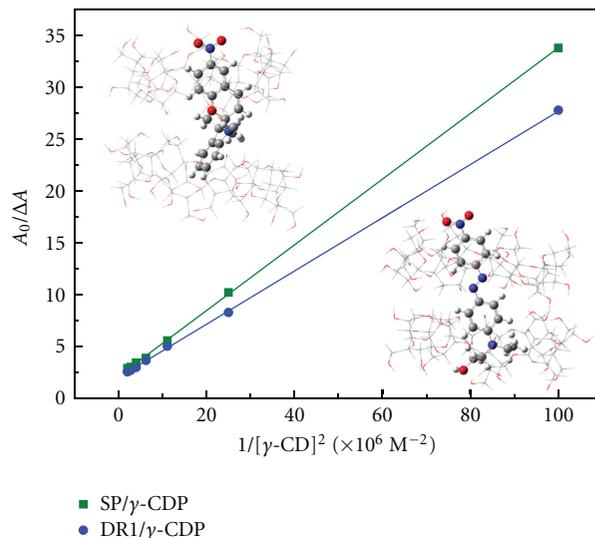


FIGURE 2: The linearity of the data when 1:2 complexation of DR1: γ -CD and SP: γ -CD is assumed. The insets show the optimized complexes.

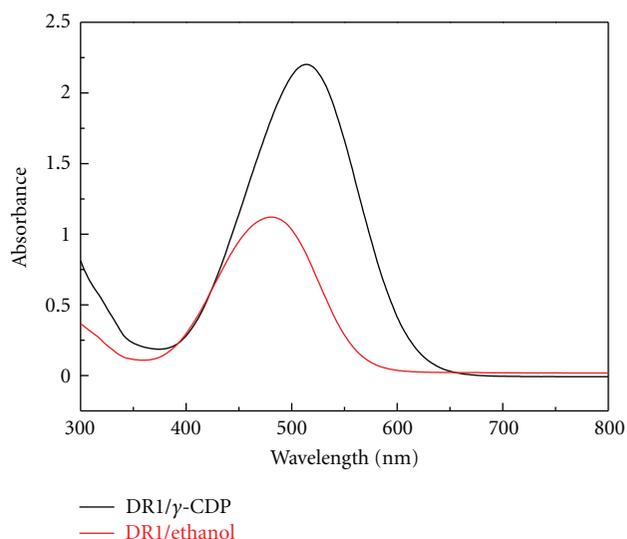


FIGURE 3: UV/VIS absorption spectra of DR1 in ethanol and in γ -CDP.

the hydrophobic γ -CD cavity encourages the end moieties of chromophore studied each entering one γ -CD cavity from the polar solvent.

3.2. Nonphotocontrollable NLO Materials. Figure 3 shows the UV/VIS spectra of DR1 in ethanol and in γ -CDP. After γ -CDP complexation, the absorption maxima of DR1 moved from 481 nm to 514 nm, thereby confirming the formation of the DR1/ γ -CDP complex. The increase in absorption wavelength upon complexation is attributable to the interaction of DR1 and γ -CDP. To achieve an overall noncentrosymmetry, the corona poling method was used to enable the orderly alignment of DR1 through an external electric field.

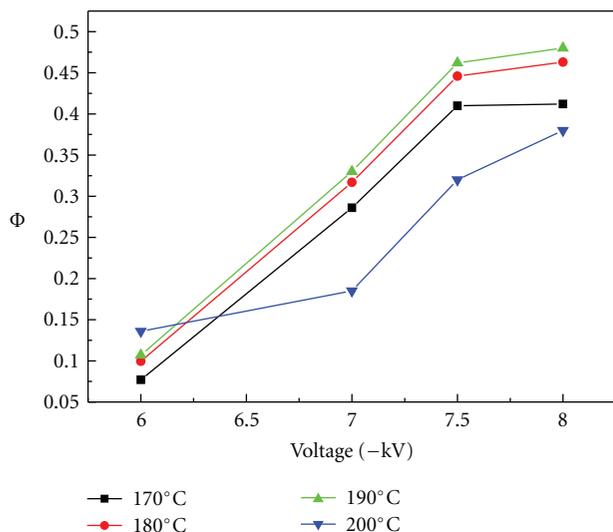


FIGURE 4: Effect of poling conditions on the order parameter (Φ) of DR1/ γ -CDP complex.

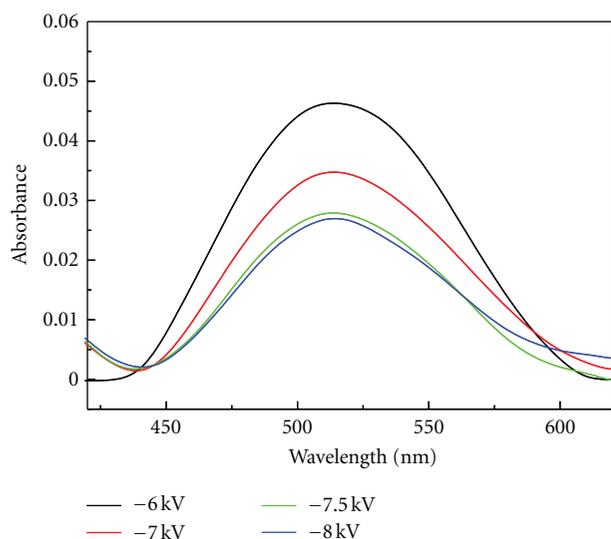


FIGURE 5: UV/VIS absorption spectra of DR1/ γ -CDP complex after electric-field poling.

The poling voltage (-6.0 , -7.0 , -7.5 and -8.0 kV), temperature (170 , 180 , 190 , and 200°C), and time (15 , 25 and 30 min) were altered, respectively, to determine the optimal poling conditions. After the oriented arrangement of molecules, the UV/VIS spectrum exhibits a decrease in absorption through which the order parameter (Φ) of the poled film can be estimated. The experimental results indicate that the Φ value increases with the poling time until 15 min. However, the Φ value was no longer affected after 15 min.

Nevertheless, the poling voltage and temperature range used in this study have a significant impact on the Φ value (Figure 4). As the poling temperature is fixed, the UV/VIS absorbance is reduced significantly (Φ value increased) with the increase of poling voltage (Figure 5), but the Φ value

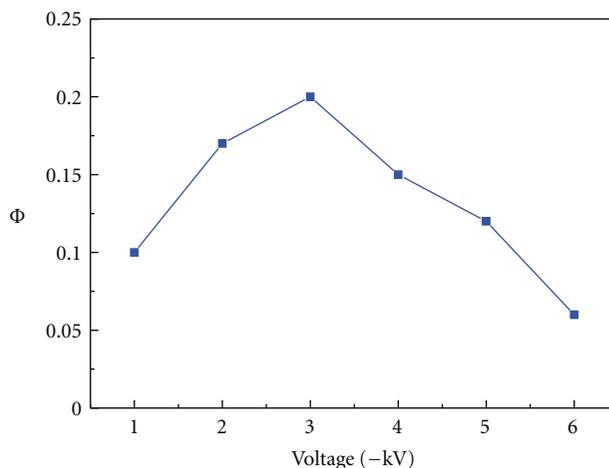


FIGURE 6: Order parameter (Φ) of SP/ γ -CDP complex at 150°C .

increases only slightly after the poling voltage is increased to -7.5 kV. At a fixed poling voltage (Figure 4), when the temperature increases from 170°C to 180°C , the Φ value changes more significantly, increasing approximately 12% (-8.0 kV) to 29% (-6.0 kV). If the temperature continues to increase until 190°C , the Φ value would increase accordingly (only slightly), at approximately 4% (-8.0 kV) to 8% (-6.0 kV). At a poling temperature of 200°C , the largest Φ value is obtained at a low-voltage of -6.0 kV, showing approximately twice the Φ value compared to other temperatures. However, the Φ value increased only slightly when the voltage continued to increase. The optimal operating conditions for DR1/ γ -CDP are -8.0 kV/ 190°C to obtain an Φ value of 0.48 , which is higher than the Φ value between 0.16 and 0.30 for DR1 doped poly(methyl methacrylate) [55, 56].

3.3. Photocontrollable NLO Materials. The UV/VIS absorption spectra for the prepared SP/ γ -CDP inclusion complex indicate that, after SP was combined with γ -CDP, the absorption maximum of SP moved from 337 nm to 382 nm, confirming the formation of the SP/ γ -CDP complex. The experimental results showed that the SP/ γ -CDP complex had a higher Φ value at a poling temperature of 150°C . At this temperature, the Φ value increased with poling voltage increases from -1.0 kV to -3.0 kV, but decreased as the poling voltage increased further from -3.0 kV to -6 kV (Figure 6). Among them, the poling voltage of -3.0 kV demonstrated the highest Φ value, at approximately 0.20 .

To clarify whether SP/ γ -CDP still retains photochromic properties after high voltage poling, the study applied repeated irradiation of 366 nm on the samples. The results indicated that after the materials absorbed UV light, a 568 absorption peak emerged, which was the absorption position of open-form PM. After the UV light was removed, the 568 absorption peak disappeared and the material returned to its original colorless state. Therefore, the SP/ γ -CDP retains photochromic properties after high voltage poling.

The Φ values of all poled polymer placed in a drying oven for 120 days under ambient temperature and atmospheric

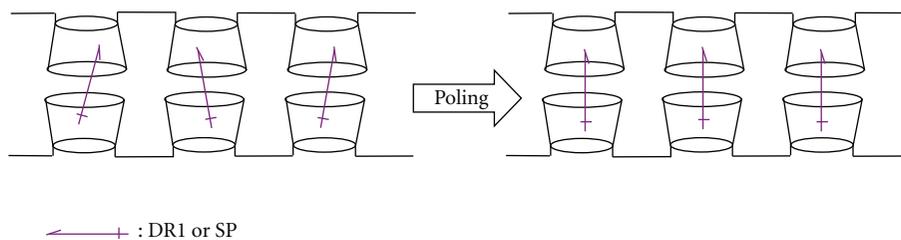


FIGURE 7: Schematics of aligned NLO chromophores in γ -CDP complexes.

pressure are maintained. This indicates that γ -CDP complexation produces excellent stability for the oriented arrangement of NLO chromophore. The hydrogen bonds between the hydroxyl groups laced on the rims of γ -CD increase the rigidity of the polymer chain preventing the relaxation of induced dipoles and further enhancing the stability of the poled complex (Figure 7). Additionally, the γ -CD cavity avoids the mobility of polymer segments interrupting the alignment of the NLO chromophore; therefore, the inclusion-complexed DR1 and SP molecules are free to align themselves along an applied electric field.

4. Conclusion

Nonlinear optical polymers with oriented and orderly alignment have been prepared by forming inclusion complexes of disperse red 1 (DR1) and spiropyran (SP) in the γ -cyclodextrin cavity of γ -cyclodextrin polymer (γ -CDP). Among them, the SP/ γ -CDP complex retains photochromic properties after poling and can be applied in photocontrollable NLO materials. Consistent with experimental ultraviolet/visible (UV/VIS) spectra, quantum chemical calculations provided valuable insight into the possible 1:2 inclusion geometries and the relative stabilities of the DR1/ γ -CD and SP/ γ -CD complexes. The UV/VIS spectral analyses demonstrate the correlation between poling voltage, poling temperature, poling time, and the NLO properties. The orderliness of the molecular alignment (order parameter Φ) within the material is significantly affected by the poling voltage and temperature. Voltage has a more significant effect than temperature.

Increasing voltage between -6.0 kV and -8.0 kV increases the Φ value of DR1/ γ -CDP at a fixed temperature. At a fixed voltage, the Φ value increases with temperature at the ranges of 170°C and 190°C . The highest Φ value of approximately 0.48 is obtained under the condition where the voltage is -8.0 kV and temperature is 190°C . When the temperature is 200°C , the Φ value obtained under the voltage of -6.0 kV is approximately double the Φ value obtained from any other temperatures. However, continued increases of voltage increments may cause material degradation.

SP/ γ -CDP still retains photochromic properties after high voltage poling, implying that γ -CDP provides adequate space to preserve the photochromic conversion of SP. The optimal operating conditions for SP/ γ -CDP are -3.0 kV/ 150°C to obtain an Φ value of 0.20. Materials maintained the same Φ value after poling for 120 days. This may be attributed to

the fact that the γ -CDP forms extensive hydrogen bonds in adjacent γ -CD and thereby increases rigidity, preventing the relaxation of induced dipoles and allowing the achievement of a high degree of stability.

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