High-Performance Switching of Bulk Quadratic Nonlinear Optical Properties with Large Contrast in Polymer Films Based on Organic Hydrogen-Bonded Ferroelectrics

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ABSTRACT: Highly controllable photoelectric switches are urgently demanded in the field of nonlinear optics. In the present work, high-performance quadratic molecular nonlinear optical (NLO)-switches based on organic hydrogen-bonded ferroelectric materials, showing large contrasts (up to ~68%), tunable reversibility, and superior switching "on-off" time, were first prepared from the highly oriented thin polymer films, which overcome the stability problems of the conventional photochromic counterparts and throw light on the further research of NLO-switching materials from the emerging field of organic molecular ferroelectrics.

INTRODUCTION

Controllable organic nonlinear optical (NLO) materials have been extensively investigated due to their wide application in optical communication, data storage, and signal processing.1−3 One of their unique advantages in comparison to the inorganic counterparts is that the molecular-level NLO activities can be converted between diverse states by external stimuli4−8 and several organic and organometallic compounds have been utilized to modulate second-harmonic effects.7,9 For example, photoswitching of NLO properties was achieved in solutions containing dipolar photochromic metal complexes.10 Such NLO-switching generally depends on reversible modification of molecular hyperpolarizability using chemical methods, such as photochromism,11,12 redox reaction,13,14 and proton-transfer process.15 Whereas, in solid-state materials, centrosymmetric crystallization of NLO-active moieties extends the disadvantage to the bulk switchable NLO properties (i.e. second-harmonic generation, SHG).16−18 Dalton et al. reported that dipole−dipole interactions among chromophores make it difficult to achieve a high degree of noncentrosymmetric order and to incorporate these molecules into a host material with effective NLO activities.19−21 Under these conditions, satisfying the desirable demands of NLO properties, process-compatibility along with sufficient electric, mechanical, and environmental endurance, still remains a great challenge.22

Solid-state NLO-switching materials should possess several essential figures of merit, including high contrast, superior reversibility, and easy compatibility, etc. One of the previously common strategies is to prepare polymer films containing the NLO-active components.23−25 For instance, the cross-linked polymers containing organic chromophores26 and photochromic azobenzenes27 were fabricated as the electro-optic switches. However, the nonequilibrium nature of photochromic systems (including polymer films and crystals) severely suppresses the reversibility of NLO changes, affording only a limited number of “on”/“off” cycles.28−30 As a new designing principle, phase transition compounds with centric-to-a-centric structure changes were recently introduced as appealing candidates for solid-state NLO-switches,31−33 which could allow switchable NLO activities.

Organic molecular ferroelectrics, showing ferroelectric-to-paraelectric phase transitions, have caught our attention due to advantages of lightness, nontoxicity, and easy processing.34 Although a few hydrogen-bonded organic ferroelectrics are recently found to show attractive properties,35,36 such as croconic acid, β-diketone enol, and carboxylic acid, there are some drawbacks specific to each compound for fabrication of thin films. For instance, croconic acid is corrosive and needs a strong acid for crystallization, while other candidates are often unstable against air oxidation or thermally fragile.37 To the best of our knowledge, NLO-switching of polymer films based on organic hydrogen-bonded ferroelectrics is still unexplored, although the SHG method has been used to detect ferroelectric phase transitions. Herein, we first prepared highly oriented polymer films of poly(acrylic acid) (PAA, rich in H-bonding acceptors) and the organic hydrogen-bonded ferroelectric

Supporting Information

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bis(imidazolium)-l-tartrate (I, Scheme 1).\textsuperscript{38} The imidazole cation of I carries a large dipole moment (3.61 D) as a proton carrier, while the l-tartrate moiety behaves as proton-acceptor, forming a proton-conductive system. Strikingly, such an organic array exhibits remarkable NLO-switching behaviors, including large contrast, highly tunable reversibility, and superior switching “on-to-off” time, which overcomes the NLO-signal attenuation problems arising in the conventional photochromic counterparts and which will throw light on further research on molecular ferroelectric NLO-switches.

**RESULT AND DISCUSSION**

**Synthesis and experimental section.** Polymer films were prepared by the spin coating method from aqueous solutions containing poly(acrylic acid) (PAA, Mw ≈ 100,000) and I (with the weight percent of about 20%). For the preparation of polymer films, several layers were deposited on the quartz substrates repeatedly with the rotary rate of 2000–3000 rpm. Finally, the obtained films were annealed at 80 °C for ~1 h for the SHG experiments. The surface morphologies of thin films were observed by SEM (JSM-6700F), and the thickness was measured to be about 5 μm. SHG-switching experiments were performed on an unexpanded laser with a low divergence (Nd:YAG, 1064 nm, 5 ns, 1.6 MW peak power, 10 Hz repetition rate). The instrument model is FLS 920, Edinburgh Instruments, and temperature can be controlled in the range of 100–600 K, while the laser is Vibrant 355 II, OPOTEK. The NLO numerical coefficients of I were compared with that of KDP (μ\textsubscript{KDP} = 0.39 pm/V).

**Characterization of organic molecular ferroelectric.** In order to scrutinize the intrinsic spontaneous polarization (P\textsubscript{s}) of I, we first investigated its physical properties involving the structural polarity (Figure 1). Structure analysis shows that I is an ionic compound consisting of one l-tartrate anion and two imidazolium cations. It undergoes a structural phase transition at the phase-transition point (T\textsubscript{c}) from the paraelectric space group of P2\textsubscript{1}2\textsubscript{1}2\textsubscript{1} to the ferroelectric P2\textsubscript{1}. Below the T\textsubscript{c}, ferroelectric responses are clearly observed in I. Measurement of ferroelectric hysteresis loops and pyroelectricity affords the P\textsubscript{s} value as ~1.1 μC/cm\textsuperscript{2}, which is slightly larger than that of potassium sodium tartrate tetrahydrate (P2\textsubscript{1}2\textsubscript{1}2\textsubscript{1}O H-bonds, Table S1) give rise to a margin of total dipole moment (Figures 1c and 1d). The shifts or displacements of protons in those H-bonds with respect to its structural polarity, as well as the reversal of polarization, from the origin of P\textsubscript{s} the absence of atomic disordering may be reminiscent of the underlying displacement or reorientation of protons, although it is difficult to determine their precise atomic positions. There are two different motifs of O–H···O and N–H···O H-bonds in I, as denoted in Figure 1c, which create a chain-like configuration along the polar b-axis. In its paraelectric phase (PEP), the components of dipole moments are canceled out, due to the structural instabilities of O–H···O and N–H···O H-bonds (hopping or disordering of protons); in contrast, electric polarization is achieved due to the settlement of H-bonds in the ferroelectric phase (FEP). The inhomogeneous displacements of H-bonds (the D–A distances: 2.747 to 2.737/2.728 Å for O–H···O H-bonds; 2.698 to 2.706/2.675 Å, 2.706 to 2.708/2.699 Å for N–H···O H-bonds, Table S1) give rise to a margin of total dipole moment (Figures 1c and 1d). The shifts or displacements of protons in those H-bonds with respect to its channel-like framework, compared to zero shift in PEP, result in the ferroelectricity of I. This transfer will favor its NLO activities. As expected, the SHG efficiency of I displays a gradual enhancement to be saturated (~2.5 × KDP), revealing its potential as a bulk NLO material.\textsuperscript{42} Moreover, bulk crystals of I have a high transmittance in the transmission spectral range of 270–1300 nm (more than 80%) and a large laser-induced damage threshold (4.6 GW/cm\textsuperscript{2}), which will be advantageous for the NLO-switching (Figures S1–S3). Overall, all these promising photoelectric properties of I greatly motivate us to study its SHG-switching properties and prepare thin ferroelectric polymer films as NLO-switches.

**Surface characterization and NLO-switching properties of highly oriented polymer films.** Utilizing strong
hydrogen-bonding interactions, transparent ferroelectric polymer thin films were deposited on substrates (Figure 2), which had been modified with the precursor PAA layers. Like the preparation of other polymer films, morphology and microcrystal dimension are mainly decided by the solution properties and subsequent treatments. Here, crystal growth for polymer films was slowly controlled under an optimized condition of 45 °C. The SEM morphology images in Figure 2c display that sheet-like nucleation is formed on the functional layers, and all the microcrystals are well-distributed in a highly oriented assignment (Figure S4). The orientation of the as-prepared films was further investigated by the grating incidence X-ray diffraction. The results demonstrate that there are only (10–1), (20–2), and (30–3) diffraction peaks (in Figure 2d), which agree well with the simulated results from its single-crystal structure. Such an observation solidly confirms the occurrence of highly oriented ferroelectric polymer films with the large lattice constants, and it might enhance the NLO-switching activities.

Since surface and dimensional effects commonly bring unexpected influence, ferroelectric polymer films may also exhibit different properties from that of crystalline materials. Therefore, we first performed contrastive NLO experiments on polycrystalline samples of 1. The key results indicate that its collected SHG signals are about 2.5 times that of KDP, i.e., the quadratic NLO coefficient as ~0.98 pm/V (Figure 3a). Both polycrystalline samples and polymer films demonstrate a similar decline of SHG signals. For polycrystalline samples, SHG intensity decreases about 70% between two states (SHG-on and SHG-off), as shown in Figure 3a. However, it should be emphasized that polymer films exhibit a high switching-contrast of ~68%. Such a figure-of-merit is comparable with many other polymer films containing photochromic crystals and with Langmuir–Blodgett (LB) films of organo-metallic complexes, whereas the switching-induced irreversible changes of initial chromophore alignment in LB films severely limit the number of “on”/“off” cycles. For instance, only two switching cycles were repeated in the LB films, with the 50% decrease of SHG intensities. For the case of 1, the strong hydrogen-bonding interactions are formed between PAA layers and functional layers, which enhance the directional alignment of dipoles and lead to stability of SHG-switching. As shown in Figure 3b, SHG-switching of polymer films is completely reversible and shows no obvious fatigue after many switching cycles. In this context, such highly oriented polymer films not only maintain comparable properties of crystalline samples but also overcome the reversibility problems arising in the conventional polymer films. In terms of structural flexibility and diversity of organic...
compounds, our present work is likely to stimulate an innovative pathway to design new ferroelectric devices; particularly, the easy compatibility of polymer films would afford an effective modulation of bulk NLO responses as smart photoelectronic elements.

For comparison, the NLO-switching properties of bulk crystal were also investigated, which show a large switching-contrast and excellent reversibility (in Figure S5). In addition to a similar variation trend, it is noteworthy that both crystals and polymer films demonstrate weak SHG signals at the low NLO state (defined as the SHG-off state). This observation of nonzero SHG information reveals that the NLO-switching of 1 is not a totally “on/off” type, which coincides fairly well with its symmetry breaking from the space group of $P2_12_12_1$ to $P2_12_1$.

For a deeper understanding of such an exceptional switching process, theoretical calculation of the first hyperpolarizability tensors ($\beta_{ijkl}$) was performed by density functional theory (DFT) using the hybrid functional B3LYP with the 6-31+G(d) mode. The calculated results at different states are $\beta_{on} = 39 \times 10^{-30}$ and $\beta_{off} = 5.8 \times 10^{-30}$ esu, respectively (in Table S2). Therefore, the ratio of $\beta_{on}/\beta_{off}$ can be estimated as 6.72, which agrees fairly well with our experimental switching-contrast of 85% performed on the bulk crystal (the ratio equals to $\sim 6.67$, Figure S5). Further structural analyses disclose that the anionic moiety makes a critical contribution to its NLO-switching responses in comparison with that of cations (Table S2).

Switching time ($\tau$), another important merit figure for NLO-switchable devices, strongly depends on the nature of chosen materials and external conditions. For instance, if the thermal diffusivity of the NLO material is well-matched with that of the polymer substrate, a short “on/off” time could be achieved. Here, the thermal conductivity of 1 is measured to be $\sim 0.5 \text{Wm}^{-1}\text{K}^{-1}$. (see Figure S6). This value indicates its excellent compatibility with the substrate of PAA, which will be quite advantageous for the NLO-switching in polymer films. Another crucial element is the external heater, of which the heating/cooling rate affords a driving influence for the NLO-switching time. We measured the $\tau$ values of 1 at different cooling rates and obtained a short time of $\sim 4$ s with the heating rate of 0.833 K/s (Figure 4a). This figure is slightly inferior to waveguide thermo-optic switches and vertical digital thermo-optic switches in polymers (10 ms) but comparable with that of thermal-induced NLO-switching in organic–inorganic compounds. Emphatically, such a responsive behavior is much superior to many other molecular NLO-switches using the different mechanisms, such as the photochromic organometallics (30 min), electron-transfer photochromic complexes (35 min), and liquid ferroelectric materials (300 s), etc. In this context, it is believed that such an order of magnitude would suggest its potentials for possible NLO-switching.

**Relationship between quadratic NLO-switching and ferroelectric polarization.** For the ferroelectric materials, the second-order phase transition can be well-described using Landau theory. When an external electric field ($E$) is applied, the Gibbs free energy ($G$) with order parameter ($Q$) can be written as below: the above expression is written as

$$G = G_0 + \frac{1}{2}aQ^2 + \frac{1}{4}bQ^4 + \frac{1}{6}cQ^6 + dQ + \frac{1}{3}eQ^3$$

$$+ \frac{1}{5}fQ^5 - EQ$$

(1)

where $a$ is linearly correlated with temperature factor, $a = a_0(T - T_d)$. Since 1 belongs to the noncentrosymmetric space group ($P2_12_12_1$) in PEP, the odd items should not be ignored. The G value reaches its maximum when the condition is

$$\frac{\partial G}{\partial Q} = aQ + bQ^3 + cQ^5 + d + eQ^2 + fQ^4 - E = 0$$

(2)

and

$$\frac{\partial^2 G}{\partial Q^2} = a + 3bQ^2 + 5cQ^4 + 2eQ + 4fQ^3$$

(3)

For 1, its order parameter is the electric displacement $D = D_E + P_e$, where $D_E$ is the electric displacement induced by the external electric field. Since $\partial G/\partial D = E$ and $\partial^2 G/\partial D^2 = 1/\epsilon$, the above expression should be

$$\frac{1}{\epsilon} = a + 3bD^2 + 5cD^4 + 2eD + 4fD^3$$

$$+ 4fP^4 + 5cP^6 + ... + \left(2e + 6bP + 12fP^3 + 20cP^5 \right)D_E$$

$$+ ... \right)D_E + \left(3b + 12fP + 30cP^3 \right)D_E^2 + ...$$

(4)

In the quasistatic frequency range, NLO coefficients contain the contributions from both ionic and electronic polarization, while, at the optical frequency, they contain contributions only from the electronic polarization. The refractive index can be written as $n^2 = n_1^2/n_2^2$ and thus, eq 4 is described as

$$\frac{1}{n_t^2} = \frac{1}{n_i^2}$$

$$= \left(2e_0v + 6e_0bP + 12e_0fP^3 + 20e_0cP^5 + ... \right)D_E$$

$$+ \left(3e_0b + 12e_0fP + 30e_0cP^3 \right)D_E^2$$

$$= \chi^{(2)}D_E + \chi^{(3)}D_E^2$$

(5)
where $n_b$ is the refractive index without external electric field and $\chi^{(2)}_{D_b}$ and $\chi^{(3)}_{D_b}$ indicate the distortion of refractive index ellipsoids induced by the external electric field. At the lower frequency range, $\chi^{(2)}_{D_b}$ and $\chi^{(3)}_{D_b}$ describe the linear (Pockels) electro-optic effect and quadratic (Kerr) effect, respectively. At optical frequencies, these terms denote the NLO susceptibilities. If ignoring high-order terms, we can obtain the formulas of $\chi^{(2)} = 6\varepsilon_0 b P_c + 2\varepsilon_0 b$ and $\chi^{(3)} = 12\varepsilon_0 P_c + 2\varepsilon_0 b$. Since $b$ and $c$ are temperature-independent, it is clearly shown that the thermal behaviors of second-order nonlinearity $\chi^{(2)}$ are linear with $P_c$. Emphatically, $\chi^{(2)}$ has a nonzero value of $2\varepsilon_0 b$ when $I$ locates in PEP ($P_c = 0$, low NLO state). Such derived results agree fairly well with its noncentrosymmetric space group of $P2_12_12_1$ and further confirm our experimental results; namely, its NLO-switching is not a totally “on/off” type.

The schematic diagram in Figure 4b shows that the generation of $P_c$ makes a critical contribution to the SHG-switching of $I$. In the SHG-off state, the positive charge centers coincide with the negative ones and the polarization is eliminated in whole. Under this circumstance, its NLO-active moieties are arranged in a nonpolar phase, corresponding to the low quadratic NLO response ($\chi^{(2)} = 2\varepsilon_0 b$). While $I$ approaches the SHG-on state, the noncoincidence of positive and negative charge centers creates the vectors of molecular dipole moments and then molecular alignments are located in a highly polar state, leading to its high NLO state ($\chi^{(2)} = 6\varepsilon_0 b P_c + 2\varepsilon_0 b$). To the best of our knowledge, although there is extensive research on temperature-dependent SHG effects and SHG imaging in inorganic oxides and ferroelectrics, this finding provides the first concrete example of polymer films as the SHG-switch using organic molecular ferroelectrics.

\section{Conclusion}

In summary, we have demonstrated the high-performance switching of NLO properties in highly oriented polymer films based on organic hydrogen-bonded molecular ferroelectrics, including the large contrasts, remarkable tunable reversibility, and superior switching “on-to-off” time. This system of polymer films overcomes the stability problem of conventional photochromic polymer films and guarantees the efficient switching of bulk quadratic NLO response. As a new-type switching system, our work constitutes a concrete platform for the externally controllable NLO-active materials and provides a significant step toward further research of NLO-switching materials from the emerging field of organic ferroelectrics.

\section{Associated Content}

\subsection{Supporting Information}

Figures S1–S7 (SHG intensities, UV–vis–NIR transmission spectra, photograph of laser-induced damage pattern, SEM images, SHG-switching, thermal diffusivity coefficient, and project coordinates of I) and Tables S1 (hydrogen bonds in I) and S2 (calculated results of hyperpolarizability tensors). The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.5b01716.

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\subsection{Notes}

The authors declare no competing financial interest.

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