

고분자 태양전지에서의 고분자 유전상수 증가에 따른 재결합 손실 감소

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Reduced Recombination Losses with Enhanced Dielectric Permittivity of Donor Polymers in Polymer Solar Cells

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초록: 본 연구에서는 나이트릴 그룹을 작용기로 가지는 고분자에 전기장을 가해주어 고분자의 분극도를 높여 고분자의 유전상수를 증가시키는 연구를 진행하였다. 전자주게 고분자의 유전상수를 증가시켜 재결합에 의한 손실을 효과적으로 감소시킬 수 있었고 이로 인해 고분자 태양전지의 개방전압을 증가시킬 수 있음을 보고하였다. 이러한 결과로부터 고분자 태양전지에서 고분자의 유전상수가 가지는 중요성 및 외부 전기장에 의한 고분자의 배열을 이용한 응용분야에 대한 중요성을 밝혔다.

Abstract: In this work, we have demonstrated that the electric field assisted poling of the donor polymer possessing conformationally labile nitrile groups increases dipolar polarization and dielectric permittivity. We find that the enhanced dielectric permittivity of the donor polymer reduces non-geminate recombination losses in bulk-heterojunction (BHJ) solar cells (SCs), resulting in increased open circuit voltage (V_{oc}) compared with unpoled devices. This result reveals the importance of dielectric permittivity of polymers and also signifies the promising applicability of electric field assisted poling for high dielectric polymers in BHJ SCs.

Keywords: polymer solar cell, dielectric permittivity, electric field assisted poling, charge dynamics, charge recombination.

Introduction

Suppressing recombination of charge carriers, caused by Coulombic attraction between electron and hole, is critical for efficient photocurrent generation in organic solar cells.¹⁻⁴ Since the dielectric permittivity of conventional organic semiconducting polymers and small molecules is relatively low ($\epsilon_r \sim 3$), photon absorption leads to excited states (excitons) with high binding energies on the order of $E_b \sim 0.5$ -1.0 eV. These excitons

require more than the thermal energy available at room temperature ($kT \sim 0.025$ eV) to ionize into free charges. This is in contrast to excitations in inorganic semiconductors where the dielectric permittivity is typically higher ($\epsilon_r > 10$) and the exciton binding energies are smaller than kT . Nevertheless, since excitons of conjugated organic materials can be potent oxidizing or reducing agents, heterojunction (HJ) architectures that pair appropriate excited state charge donors with complementary ground state charge acceptors have been introduced to achieve efficient photoinduced charge transfer.⁵ Unfortunately, photogenerated electrons and holes in HJ experience a strong Coulombic attraction to one another due to poor charge screening in these active materials having low

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dielectric permittivity. Thus, increasing the dielectric properties of the active layer can be a potentially compelling strategy to reduce the Coulombic attraction of charge carriers and concomitantly suppress recombination losses. Ideally, suppressing exciton binding energy in semiconducting donor polymers by increasing dielectric permittivity can rule out the need of acceptor materials, which can be the most potent game-changer for solar cells over the next decades. Recently, few attempts have been reported to increase the dielectric permittivity of semiconducting polymers by introducing non-ionic polar side-chains such as nitrile⁶ or oligo(oxyethylene) groups.^{7,8}

The permanent dipoles in these polar side-chains should be able to freely rotate and reorient owing to their flexibility and the rapid motion of polar groups in the GHz - MHz frequency domain.⁷ Since non-geminate recombination occurs within ns- μ s regime, increasing dielectric constant by introducing permanent dipoles can be used to control non-geminate recombination dynamics. While increasing dielectric permittivity by incorporating polar side-chains remains very attractive, further control of dipolar polarization with reorientation of dipole moment by applying external stimuli still remains unexplored.

Here, we demonstrate the viability of using electric field assisted poling on a model donor polymer possessing conformationally labile polar groups to increase dipolar polarization and dielectric permittivity. We show that electric field assisted poling of the donor polymer enhances dielectric permittivity and reduces non-geminate recombination in bulk-heterojunction solar cells (BHJ SCs), resulting in longer carrier lifetimes and increased open circuit voltage (V_{OC}) compared to unpoled devices.

Experimental

Materials Synthesis. PC₇₁BM were purchased from Rieke Metals, Inc. All other chemicals were purchased from Aldrich

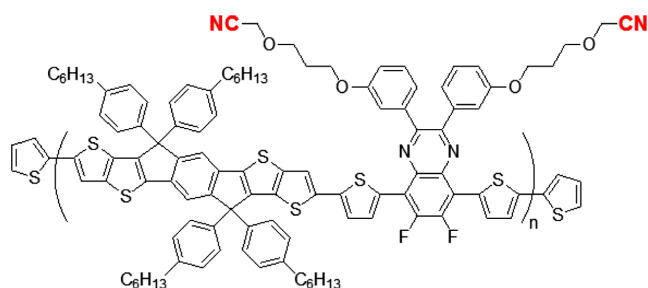


Figure 1. Chemical structure of PIDTT-QxOCN.

Chemical Corporation. The polymer, PIDTT-QxOCN shown in Figure 1, was synthesized by copolymerizing the ladder-type indacenodithieno[3,2-b]thiophene (IDTT) with a quinoxaline-based (5,8-bis(5-bromothiophen-2-yl)-6,7-difluoro-2,3-bis(3-cyanomethoxy-propoxyphenyl)quinoxaline) (detailed synthetic procedure will be published elsewhere).

Fabrication and Characterization of Solar Cells. Indium-tin oxide (ITO) coated glass substrates were cleaned in ultrasonic baths with typical solvents and detergent and then further cleaned by oxygen plasma. PC₇₁BM and PIDTT-QxOCN was spin-coated (0.9 k rpm) on the PEDOT:PSS layer in a glove box and annealed at 110 °C for 10 min. The preparation of PEDOT:PSS and bis-FPI (fullero-pyrrolidinium iodide) layer were reported elsewhere.⁹⁻¹¹ A metal electrode was vacuum-deposited. The J-V characteristics of the solar cell devices were tested using a Keithley 2400 SMU. Thermally stimulated current (TSC) experiment was performed using Keithley 4200 and probe station. Step voltage and delay time were 0.15 mV and 50 ms, respectively. Temperature was increased by 0.3 °C/sec for poling process.

Results and Discussion

In general, the macroscopic dielectric permittivity is defined as the sum of all of the microscopic polarizations (atomic, electronic, dipolar or orientational, and interfacial or Maxwell-Wagner polarizations) of a bulk material under an external electric field. These microscopic polarizations occur when the frequency is lower than the reciprocal of their relaxation time. Thus, the dielectric permittivity of PIDTT-QxOCN in the GHz - MHz frequency region mainly originates from the relaxation

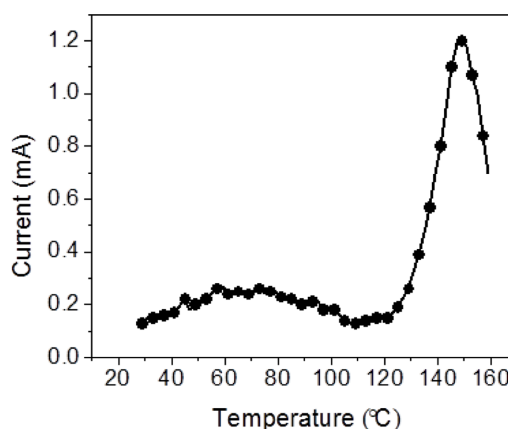


Figure 2. Thermally stimulated current of ITO/PIDTT-QxOCN/Au device with the external electric field of 20 MV/m.

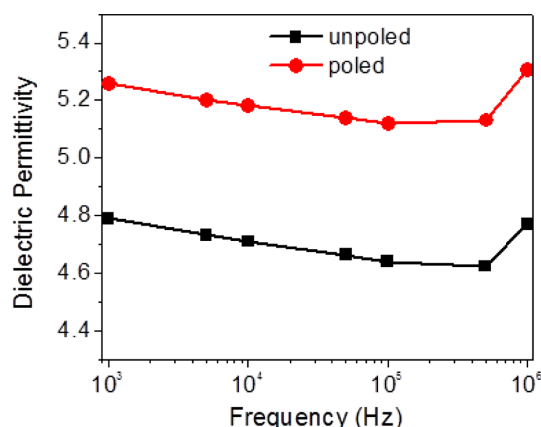


Figure 3. Dielectric permittivity with respect to frequency for poled and unpoled PIDTT-QxOCN films.

of polar side-chains and the local polarization along its main backbone. To investigate the transition behavior of PIDTT-QxOCN film, we performed TSC measurements. The polymer was spin-coated on ITO substrates and annealed at 110 °C for 10 min. A 100 nm Au was then thermally deposited with a shadow mask. Figure 2 shows the TSC data from 30 to 160 °C. The maximum current peak under an external electric field (20 MV/m) was observed between 130 and 160 °C, which mainly originated from the glass transition (α -relaxation) of PIDTT-QxOCN. The broad peak observed from 40–100 °C is probably associated with the rotational motion (β -relaxation) of the phenyl side-groups on IDTT and quinoxaline units including reorientation of polar alkyl chains (γ -relaxation). It is also well known that the polar side-groups can be oriented together with the segmental motion of the main backbone.¹² This cooperative motion occurs near the glass transition temperature.

To study the poling effect on the dielectric permittivity of PIDTT-QxOCN, we performed capacitance-voltage (C-V) measurement with ITO/polymer/Al structures by assuming a parallel plate capacitor ($C = \epsilon_r \epsilon_0 A/d$, where C , A , and d are the capacitance, the active area of device, and the thickness of polymer films, respectively.). Figure 3 shows the dielectric permittivity extracted from C-V measurement as a function of frequency. We observed that the poled PIDTT-QxOCN films show higher dielectric permittivity ($\epsilon_r \sim 5.3$) compared to the unpoled films ($\epsilon_r \sim 4.8$) at 1 MHz. This enhanced dielectric permittivity is attractive, especially in BHJ systems, for decreasing both Coulomb attraction between the electron and hole ($E_b = q^2/4\pi\epsilon_0\epsilon_r r_0$) and non-geminate recombination rate ($k_{\text{rec}} = q\mu/\epsilon_0\epsilon_r$),¹³ where q , ϵ_0 , r_0 , and μ are the elementary charge, the permittivity of free space, the separation distance

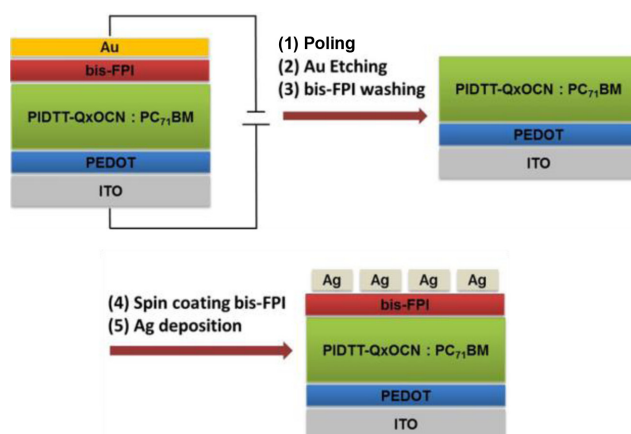


Figure 4. Electric field assisted poling process of BHJ films and the device architecture of the conventional single-junction solar cells.

between electron and hole, and the charge mobility, respectively. Below, we show how the dielectric enhancement controls the recombination kinetics in BHJ SCs fabricated with the PIDTT-QxOCN donor polymer.

Figure 4 shows the poling process and the device architecture of the conventional BHJ SCs. First, a PEDOT:PSS layer was spin-coated onto the ITO substrate and then annealed at 150 °C for 15 min. The active layer (ca. 100 nm) was spin-coated from the blend solution of 5 mg/mL PIDTT-QxOCN and 20 mg/mL PC₇₁BM in 1,2-dichlorobenzene, followed by annealing at 120 °C for 10 min. Subsequently, a bis-FPI layer (10 nm) was spin-coated from methanol solution (2 mg/mL). After annealing at 110 °C for 5 min, an Au layer (100 nm) was vacuum deposited on the entire active layer without a shadow mask. After electric field assisted poling, the deposited Au was removed using Au etchant. Note that we used bis-FPI to protect the active layer from the corrosive Au etchant. The bis-FPI layer was then washed away using methanol and then spin-coated again on top of the active layer as an electron transporting layer. Lastly, Ag was deposited by thermal evaporation with a shadow mask.

Figure 5(a) shows a typical TSC spectrum of the BHJ devices during electric field assisted poling. Thermal annealing, in general, expedites molecular ordering and annihilation of structural defects, but it alone is not enough to facilitate the orientational polarization of heterogeneous matter. For efficient poling of the BHJ films, a 100 MV/m electric field was applied to the BHJ devices at room temperature. The sample was heated gradually to 140 °C and then cooled rapidly to room temperature under the applied electric field. A rapid increase in leakage current was observed at 140 °C from the BHJ films,

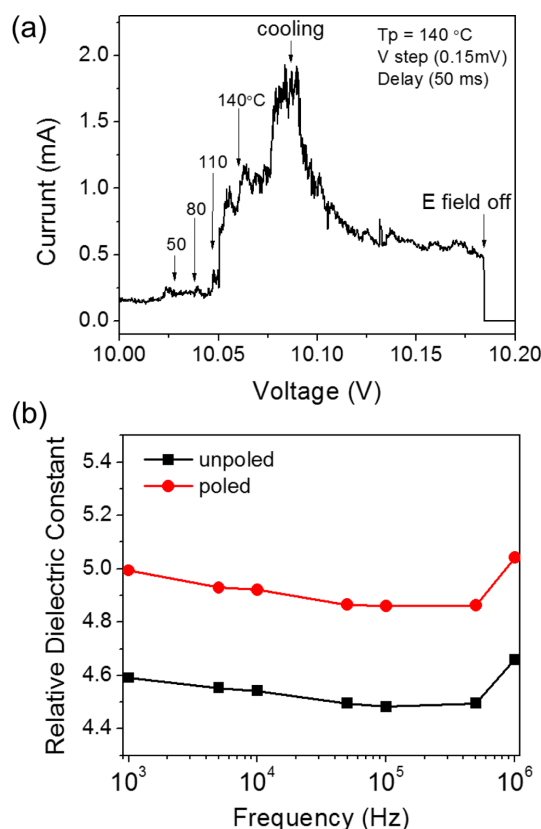


Figure 5. (a) The thermally stimulated current of BHJ films; (b) dielectric permittivity with respect to frequency for poled and unpoled BHJ films.

but its shape is relatively complicated owing to the heterogeneous environment of structural defects and accumulated charges near the amorphous/crystalline or lamella interfaces in the BHJ system.

The dipole alignment in poled BHJ films was quantified by measuring the dielectric permittivity of the films. We observed that the dielectric permittivity was increased from 4.65 to 5.05 at 1 MHz after poling (Figure 5(b)). Since the dielectric enhancement from BHJ films is similar to the dielectric enhancement of films comprised of only PIDTT-QxOCN, and the dipole moment of the ester group (~ 1.8 Debye)¹⁴ from PC₇₁BM is much weaker than that of the nitrile group (~ 4.0 Debye)¹⁵ from PIDTT-QxOCN, we believe that the poling induced orientational polarization of PIDTT-QxOCN plays a major role in controlling dielectric properties of its BHJ films.

We have fabricated BHJ SCs as described above with the and tested under simulated AM 1.5G illumination at 100 mW/cm² in nitrogen filled glove box. Figure 6 shows the J-V characteristics of poled and unpoled devices.

The photovoltaic parameters are summarized in Table 1.

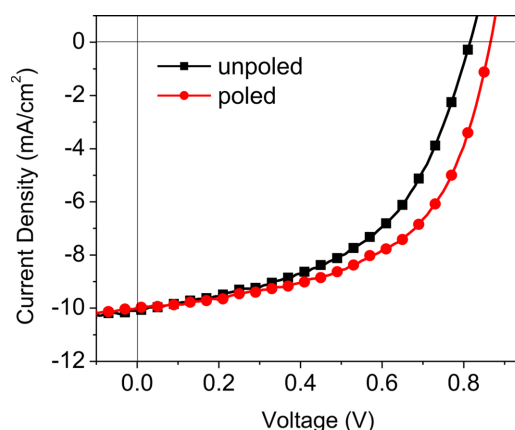


Figure 6. J-V characteristics of poled and unpoled BHJ SCs.

Table 1. Summary of Device Performance for Poled and Unpoled BHJ SCs

Device	ϵ_r	V_{OC} (V)	J_{SC} (mA/cm ²)	FF	PCE (%)
Unpoled	4.65	0.82 (± 0.01)	10.1 (± 0.07)	0.51 (± 0.02)	4.18 (± 0.08)
Poled	5.05	0.87 (± 0.01)	10.0 (± 0.09)	0.56 (± 0.03)	4.82 (± 0.09)

Poled devices show superior device performance with improved V_{OC} and fill factor (FF), leading to an increased power conversion efficiency (PCE) from 4.18 to 4.82%. The V_{OC} observed from poled devices is 50 mV larger than that of the unpoled devices. Since we previously reported that the charge transfer (CT) state energy is identical for alkyl side-chain polymer/C₆₀ and nitrile side-chain polymer/C₆₀ devices, we hypothesize that the increase in V_{OC} for poled devices arises from higher carrier densities the larger intermolecular CT state energy formed at the D/A interface after poling. Transient photovoltage (TPV) and charge extraction (CE) measurements to evaluate the rate of non-geminate recombination near V_{OC} .

We found that the voltage decay time for devices with nitrile functionalized polymer are in the range of microseconds time scale. Note that this microsecond timescales correlated with non-geminate recombination of carriers are in the range where we observed the dielectric enhancement (KHz – MHz) from poled BHJ devices. Thus, we have concluded that the increase in decay lifetime and charge carrier density could be due to suppressed recombination¹⁶ because of an increase in macroscopic dielectric permittivity of the films. In this regard, we also expect that the longer decay lifetimes and reduced recom-

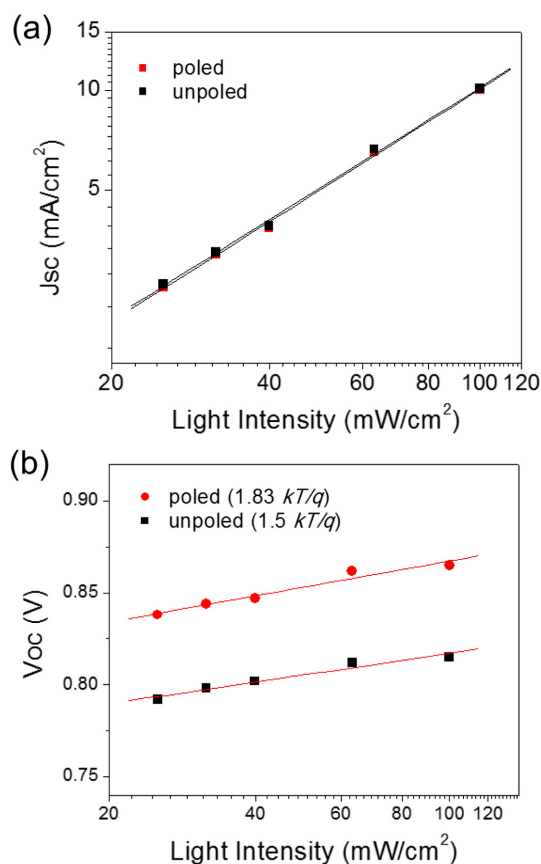


Figure 7. (a) Light intensity dependence of J_{sc} ; (b) V_{oc} of poled and unpoled BHJ devices.

bination losses for poled devices which could result in the larger V_{oc} and FF.

To prove this hypothesis, we performed light intensity dependent J_{sc} and V_{oc} measurements for poled and unpoled devices (Figure 7(a) and (b)). Note that the poled devices show a steeper slope of 1.83 kT/q than the 1.50 kT/q slope of the unpoled devices, suggesting that geminate recombination which generally caused by large amount of traps is dominant in poled devices.^{5,17-20} However, we find that there is no discernible difference in the slope of light intensity dependent J_{sc} between poled and unpoled devices (Figure 7(a)). From this result we speculate that the poling effect on geminate recombination and/or trap assisted recombination is negligible in our BHJ devices. By considering the fact that geminate and non-geminate recombination are competing in BHJ SCs^{21,22} and also assuming that the poling effect is negligible on trap densities and geminate recombination, the steeper slope of V_{oc} in poled devices presumably indicates that there is less bimolecular recombination in poled devices.

Conclusions

In conclusion, we have demonstrated the viability of electric field assisted poling of the donor polymer possessing conformationally labile nitrile groups to increase dipolar polarization and dielectric permittivity. We show that electric field assisted poling of the donor polymer enhances dielectric permittivity and reduces non-geminate recombination losses in BHJ SCs, resulting in increased V_{oc} compared with unpoled devices. This result reveals the importance of dielectric permittivity of polymers and also signifies the promising applicability of electric field assisted poling for high dielectric polymers in BHJ SCs.

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