Solvent-Resistant Organic Transistors and Thermally Stable Organic Photovoltaics Based on Cross-linkable Conjugated Polymers

Hyeong Jun Kim,[†] A-Reum Han,[‡] Chul-Hee Cho,[†] Hyunbum Kang,[†] Han-Hee Cho,[†] Moo Yeol Lee,[‡] Jean M. J. Fréchet,[§,‖] Joon Hak Oh,*[,‡] and Bumjoon J. Kim*[,†]

[†]Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 305-701, Korea

[‡]School of Nano-Bioscience & Chemical Engineering and KIER-UNIST Advanced Center for Energy, Ulsan National Institute of Science and Technology (UNIST), Ulsan 689-798, Korea

[§]Department of Chemistry, and Department of Chemical Engineering, University of California Berkeley, California 94720-1460, United States

[‖]King Abdullah University of Science and Technology, Thuwal 23955-6900, Saudi Arabia

S *Supporting Information*

ABSTRACT: Conjugated polymers, in general, are unstable when exposed to air, solvent, or thermal treatment, and these challenges limit their practical applications. Therefore, it is of great importance to develop new materials or methodologies that can enable organic electronics with air stability, solvent resistance, and thermal stability. Herein, we have developed a simple but powerful approach to achieve solvent-resistant and thermally stable organic electronic devices with a remarkably improved air stability, by introducing an azide cross-linkable group into a conjugated polymer. To demonstrate this concept, we have synthesized polythiophene with azide groups attached

to end of the alkyl chain (P3HT-azide). Photo-cross-linking of P3HT-azide copolymers dramatically improves the solvent resistance of the active layer without disrupting the molecular ordering and charge transport. This is the first demonstration of solvent-resistant organic transistors. Furthermore, the bulk-heterojunction organic photovoltaics (BHJ OPVs) containing P3HT-azide copolymers show an average efficiency higher than 3.3% after 40 h annealing at an elevated temperature of 150 °C, which represents one of the most thermally stable OPV devices reported to date. This enhanced stability is due to an in situ compatibilizer that forms at the P3HT/PCBM interface and suppresses macrophase separation. Our approach paves a way toward organic electronics with robust and stable operations.

KEYWORDS: solvent-resistant OTFTs, thermally stable OPVs, in-situ compatibilizer, cross-linkable conjugated polymers
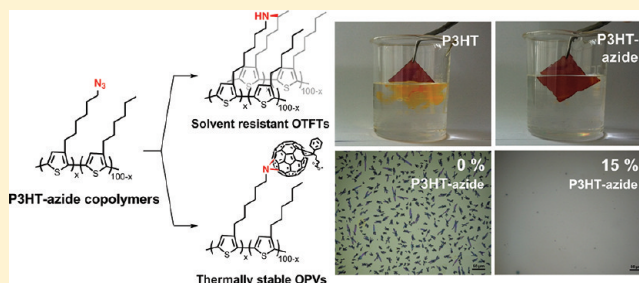
■ INTRODUCTION

Conjugated polymer-based organic electronics, such as organic photovoltaics (OPVs), light-emitting diodes (OLEDs), and thin-film transistors (OTFTs), have attracted a great deal of attention due to the potential for low-cost solution fabrication, mechanically flexible devices, and lightweight constructions.[1−5] Furthermore, the ability to chemically manipulate the properties of conjugated polymers has provided numerous opportunities for further improvements and fundamental studies.[6−9] Currently, OTFTs based on conjugated polymers exhibit high mobility comparable to that of amorphous silicon,[10,11] and the power conversion efficiency (PCE) of the OPVs has exceeded 6−8%.[12−15] However, conjugated polymers are unstable when exposed to air, solvent, or thermal treatment, and these challenges limit their practical applications. Therefore, it is of great importance to develop new polymers toward stable organic electronics.

A significant drawback of commonly used conjugated polymers is poor solvent resistance. In particular, OTFTs are key building blocks for thin-film electronics such as flexible displays and sensors. However, their poor solvent resistance limits the availability of polymeric semiconductor materials for the active layer. Furthermore, most chemical and biological sensors reported to date can only operate under aqueous conditions.[16] The development of organic active materials with organic solvent resistance will expand the range of applications.

In addition to solvent resistance, thermal stability is also an important property. Efficient bulk-heterojunction (BHJ) solar cells require the formation of an interpenetrating network of electron donor and acceptor materials with a large interfacial area. Heating induced by solar irradiation is detrimental to their

Scheme 1. Synthesis of P3HT-azide Copolymers and Their Functions as a Hole Transporting Material for Solvent-Resistant OTFTs and in Situ Compatibilizer for Thermally Stable OPVs
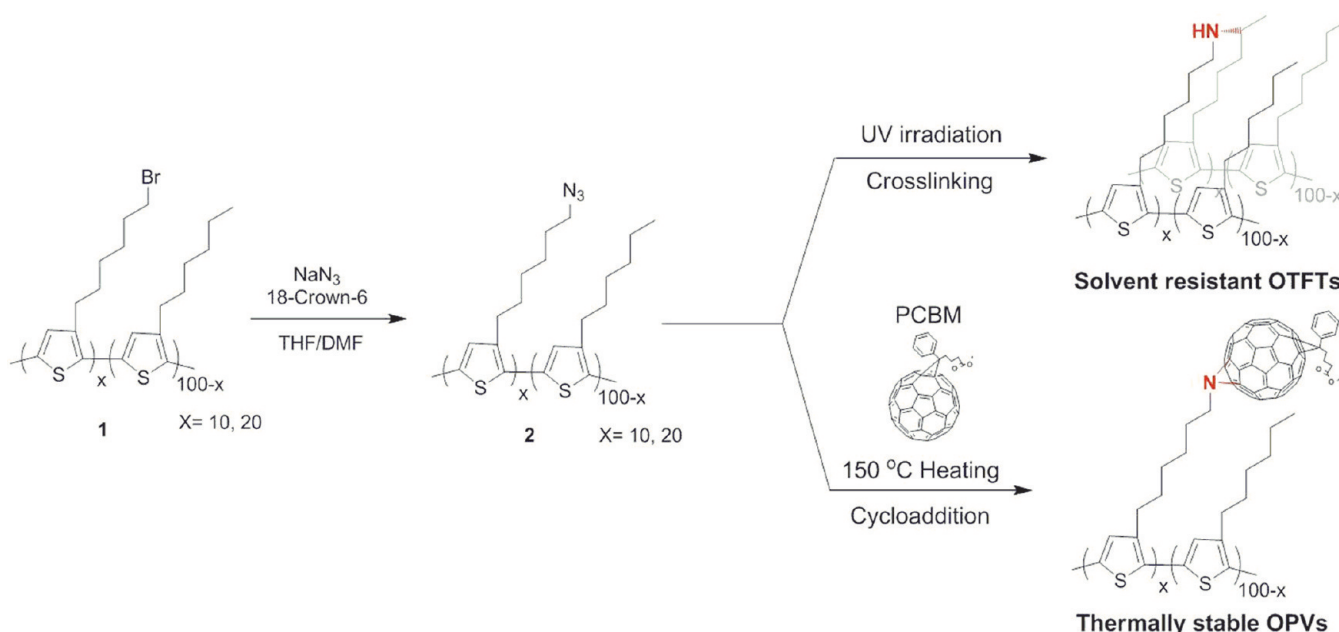
performance because of the relatively low glass transition temperature (T_g) of the polymers and the possible macro-phase separation driven by the strong immiscibility between the active components. Although compatibilizer approaches have been effective at enhancing the thermal stability,[17−20] the synthesis of a compatibilizer often requires multiple post-polymerization steps and suffers from the low solubility of fullerenes. Furthermore, the formation of undesired micelles could reduce the PCE by disturbing the continuous pathway for charge transport. The ideal method is to lock-in the morphology by in situ compatibilization of donors and acceptors formed at the blend interface.

A cross-linking strategy could be a powerful solution for achieving both solvent resistance and thermal stability.[21−25] However, the introduction of cross-linking bridges in conjugated polymers often disturbs their molecular packing, significantly reducing their performance.[26] Therefore, although the cross-linking concept is simple and powerful, the development of cross-linkable materials with high performance remains a challenge.

In this study, we successfully developed a simple and powerful approach to introduce an azide cross-linkable group into conjugated polymers. This *on-demand* cross-linking mechanism enables production of a solvent-resistant hole-transporting material for OTFTs and an in situ compatibilizer in OPVs. Our target is to develop efficient cross-linking materials that resist solvent molecules and prevent phase separation in BHJs but that can be activated under very mild conditions to ensure high mobility and efficiency in the devices. Among various types of conjugated polymers, we have carefully chosen poly(3-hexylthiophene) (P3HT) as a model system to introduce azide cross-linkable units. Regioregular P3HT is the most widely investigated polymer semiconductor for organic electronics, and it exhibits great performance in both OTFTs (mobility: $10^{-1} \sim 10^{-2}$ cm^2 V^{-1} s^{-1})[27] and BHJ solar cells blended with a fullerene derivative, [6,6]-phenyl-C$_{61}$-butyric acid (PCBM) (PCE $\sim$ 4−5%).[28,29]

Azide groups attached to the end of the alkyl chain in P3HT (P3HT-azide) were cross-linked in a few minutes upon exposure to UV light, and the OTFT devices based on the cross-linked P3HT maintained their transistor properties even after washing with chlorobenzene (CB), whereas pristine P3HT devices were completely destroyed. In addition, P3HT-azide polymers formed fullerene-attached diblock copolymers. These copolymers act as in situ compatibilizers in P3HT/PCBM BHJs, thereby enabling the production of highly efficient and thermally stable OPVs.

■ RESULTS AND DISCUSSION

Two P3HT-azide copolymers were synthesized to obtain two compositions of 10 and 20 mol % 3-(azidohexyl)thiophene monomer (P3HT-azide10 and P3HT-azide20), respectively (Scheme 1). Bromine-functionalized copolymers (P3HT-Br) **1** were synthesized according to a previously reported method.[30] After the polymerization of the P3HT-Br copolymers, the bromine groups were replaced with azide units (N$_3$) by adding NaN$_3$ and 18-crown-6 as a phase transfer catalyst in a THF/ DMF mixed solution. Then, residual NaN$_3$ was removed by Soxhlet purification using methanol. The introduction of the azide unit (N$_3$) was confirmed by ^{1}H NMR and FT-IR (Fourier transform infrared) measurements. After azidation, a strong N$_3$ peak (2100 cm^{-1}) was found from FT-IR measurement, while P3HT-Br did not show the peak (Figure S1 in the Supporting Information). Compositions of azide unit in P3HT-azide10 and -20 were confirmed by NMR (Figure S2 in the Supporting Information). Details on the synthesis and characterization of the P3HT-azide copolymers are included in the Supporting Information.

To elucidate the relationship between the molecular structure of P3HT-azide copolymers and the function of solar cell devices, BHJ-type photovoltaic cells (ITO/PEDOT:PSS/ P3HT-azide:PCBM/LiF/Al) were fabricated using blends of these azide copolymers with PCBM. In addition, OTFTs based on P3HT-azide copolymers were prepared, and their electrical
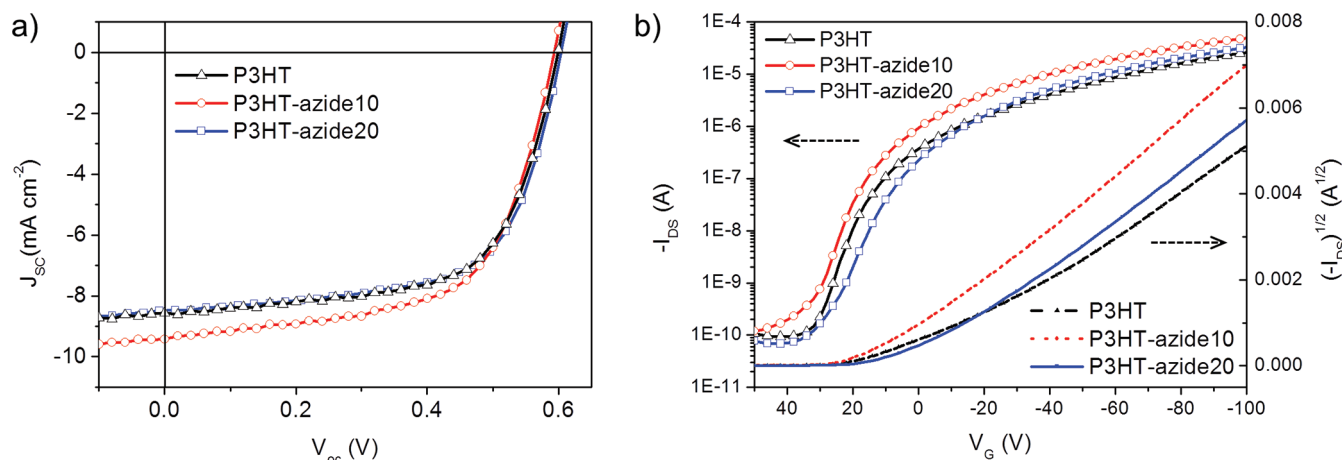
Figure 1. (a) Current density−voltage characteristics of BHJ solar cells; P3HT/PCBM (△), P3HT-azide10/PCBM (○), and P3HT-azide20/PCBM (□). All copolymers blended with PCBM at 60:40 weight ratio showed similar performances under AM 1.5 G illumination (100 mW cm^{-2}). (b) Transfer characteristics of three different P3HT copolymers field effect transistors with $V_{DS} = -100$ V. Bottom-gated, top-contact geometry with OTS treated SiO$_2$/Si wafer. P3HT (△), P3HT-azide10 (○), and P3HT-azide20 (□).

properties were measured. High quality P3HT was purchased from Rieke Metals, Inc. and used as a control sample.

Figure 1a shows the current density−voltage curve of the BHJ solar cells consisting of PCBM mixed with P3HT, P3HT-azide10, and P3HT-azide20, under AM 1.5G with an intensity of 100 mW cm^{-2}. Three devices were prepared under the same conditions, including the blend ratio of polymer to PCBM (60:40, w/w) and solvent concentration. A solvent annealing method was used to develop optimal morphology.[29] The device characteristics of the BHJ solar cells are summarized in Table 1.

Table 1. Device Characteristics of Solar Cells Composed of PCBM Blended with P3HT, P3HT-azide10, or P3HT-azide20, under AM 1.5G-Simulated Solar Illumination (100 mW cm^{-2})

OPV	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
P3HT	0.60	8.68	63	3.28
azide10	0.59	9.44	62	3.45
azide20	0.58	8.86	64	3.29

It is noteworthy that all three devices exhibit similar performance, indicating that the incorporation of azide substituents at the end of the alkyl chain of P3HT does not affect solar cell performance. OTFT devices based on P3HT, P3HT-azide10, and P3HT-azide20 were fabricated in top-contact, bottom-gate geometry using n-doped SiO$_2$/Si wafer, which was utilized as the gate and dielectric. The SiO$_2$ dielectric surface was treated with octadecyltrimethoxysilane (OTS).[31] Table 2 and Figure 1b show the OTFT performance of the drop-cast copolymer thin films, where hole mobilities of 3.09, 4.53, and 3.84 × 10^{-2} cm^2 V^{-1} s^{-1} were obtained for P3HT, P3HT-azide10, and P3HT-azide20, respectively, with similar on/off current ratios (∼10^5). Charge transport is directly

Table 2. OTFT Characteristics of P3HT, P3HT-azide10, and P3HT-azide20

OTFT	mobility [cm^{2}V^{-1}s^{-1}]	on/off ratio	V_t [V]
P3HT	3.09 × 10^{-2}	2.8 × 10^5	−6.85
azide10	4.53 × 10^{-2}	4.1 × 10^5	7.32
azide10	3.84 × 10^{-2}	4.8 × 10^5	−4.61

affected by the molecular packing of conjugated polymers, which is frequently disrupted by functional group introduction, as a result of the disturbance of π−π interactions.[32,33] However, OTFTs based on the P3HT-azide copolymers showed even slightly higher peak mobility compared with pristine P3HT. This finding indicates that the incorporation of the small size and efficiently cross-linkable azide unit to P3HT-azide polymers truly does not disturb their molecular packing of polymers, thereby maintaining the high charge carrier mobility and enhancing the stability effectively.

Figure 2a shows the photo-cross-linking behaviors of the P3HT-azide copolymers as a function of UV exposure time. P3HT, P3HT-azide10, and P3HT-azide20 were spun cast from CB solution to produce films of approximately 50 nm thickness on Si substrates. Photo-cross-linking of the films was carried out under nitrogen atmosphere using UV light (λ = 254 nm) from a low power hand-held lamp (1.9 mW cm^{-2}), with the exposure time in the range of 0−20 min. For quantitative measurements of the degree of cross-linking in the polymer films, the films were immersed in CB for 5 min, followed by rinsing with acetone, and the film thicknesses before and after washing were compared. After 5 min of exposure to UV light, both P3HT-azide10 and P3HT-azide20 polymers became totally insoluble in CB, whereas no insoluble fraction was observed with the P3HT film regardless of the UV exposure time. These data demonstrate that azide groups were successfully photo-cross-linked to produce an insoluble film of P3HT-azide polymers. We propose that during photolysis, the azide group decomposes to generate a highly reactive nitrene by its triplet sensitization, which can undergo reaction with neighboring molecules.[34,35]

To gain a deeper insight into the possible changes in molecular packing of polymers due to azide unit introduction and cross-linking, we carried out UV/vis absorption (Figure S3 in the Supporting Information) and grazing incidence wide-angle X-ray scattering (GIWAXS) measurements (Figure S4 in the Supporting Information). First, the UV/vis spectra of P3HT-azide copolymers were identical to that of P3HT. In addition, there was no shift in UV/vis absorption spectra after cross-linking, indicating that the two-dimensional molecular packing of the P3HT-azide copolymers was almost unaffected after cross-linking. This evidence is further supported by
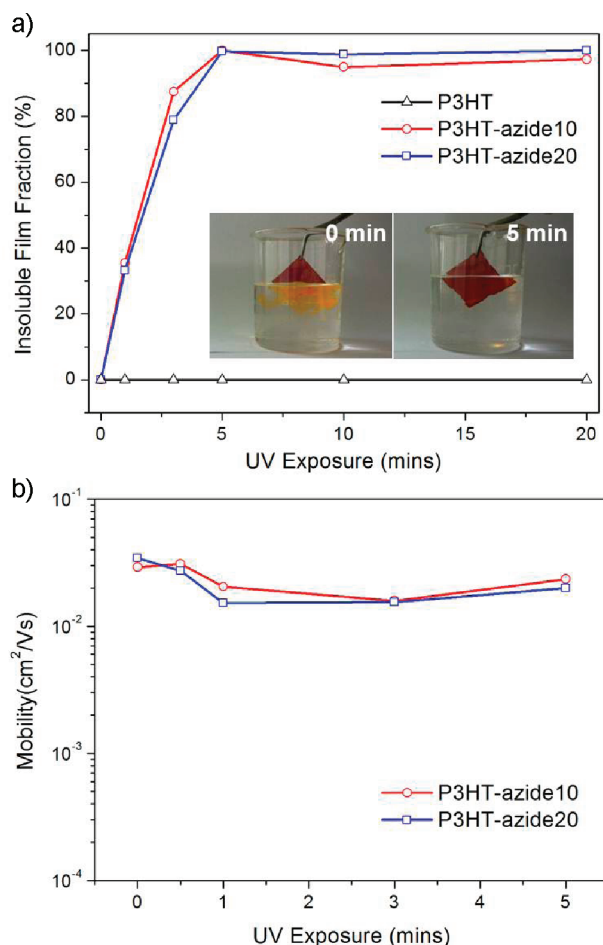
Figure 2. (a) Photo-cross-linking behavior of P3HT-azide copolymers. The insoluble fraction was measured as a function of UV exposure time. (b) OTFT mobility change of P3HT-azide10 and P3HT-azide20 as a function of UV exposure time. Mobilities of P3HT-azide10 and P3HT-azide20 were almost unchanged after the photo-cross-linking.

GIWAXS measurements. From the GIWAXS diffraction pattern, the distances between adjacent P3HT-azide chains and the $\pi-\pi$ stacking distance were found to be 1.67 and 0.38 nm, respectively, which were consistent with those from well-ordered P3HT chains.[30,36,37] After cross-linking, the distance

between adjacent P3HT-azide chains was 1.69 nm and the $\pi-\pi$ stacking distance was 0.38 nm. The increase of 0.02 nm is most likely due to the formation of a bridged structure between alkyl chains in different P3HT lamellas, but the change is very small. It should be noted that $\pi-\pi$ stacking between P3HT-azide chains, a critical factor in the charge mobility of P3HTs, was unchanged with a distance of 0.38 nm. This is consistent with the result that similar mobilities were obtained for P3HT, P3HT-azide10, and P3HT-azide20.

Figure 2b shows the OTFT mobilities of P3HT-azide copolymers as a function of UV exposure time. We changed the UV exposure time from 0 min (0% insoluble fraction) to 5 min (100% insoluble fraction) to examine the effect of the degree of cross-linking on OTFT mobility. Surprisingly, the mobilities of P3HT-azide copolymers showed very similar values above 10^{-2} cm^2 V^{-1} s^{-1} regardless of the degree of cross-linking (Table S2 in the Supporting Information). Therefore, cross-linked polymer films can be made solvent-resistant without sacrificing their charge transport properties.

Figure 3a presents a comparison of OTFT devices made from pristine P3HT and cross-linked P3HT-azide20 films before and after washing with CB. Both the P3HT and P3HT-azide20 films were exposed to UV irradiation for 5 min before washing. Figure 3b displays the optical microscope images of OTFT devices based on P3HT and P3HT-azide20 after washing. The P3HT OTFT film was completely washed out, and the electrodes were lifted off in top contact OTFT geometry. No field-effect behavior was observed from the pristine P3HT OTFT after washing. In contrast, the cross-linked P3HT-azide20 OTFT devices exhibited the same order of magnitude mobility after CB washing. (Table 3) These results clearly demonstrate that our cross-linking approach is an efficient method of achieving solvent-resistant OTFTs and stable charge transport under an organic solvent. To our knowledge, this study presents the first demonstration of the successful fabrication of OTFT devices that can operate under the good organic solvent.

This feature expands their potential applications significantly. For example, it may be possible to fabricate high performance OTFT sensors that can operate under a harsh environment such as organic solvent wastes. As a preliminary experiment to this end, we fabricated a flexible OTFT using the P3HT-azide10 copolymer as the active layer on a flexible plastic substrate, polyethylene naphthalate (PEN) film, which can potentially be used for flexible OTFT sensors. The flexible
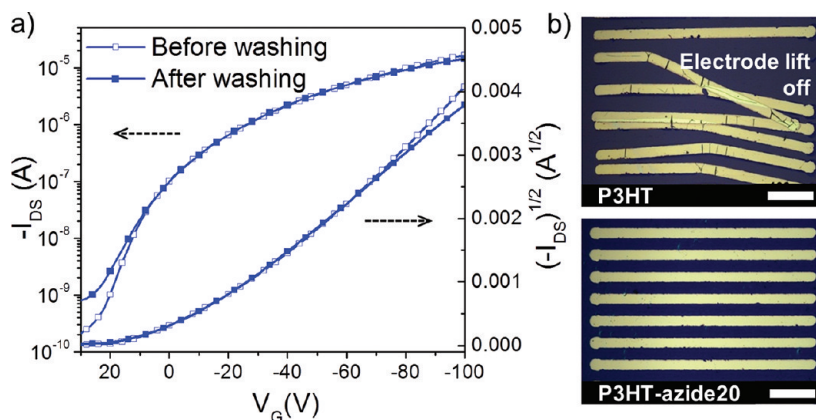

Figure 3. (a) Transfer curves of cross-linked P3HT-azide20 before and after washing with CB. The mobility of pristine P3HT could not be measured, because the pristine P3HT thin film disappeared after the wash with CB. (b) Comparison of OTFT film morphology of P3HT and P3HT-azide20 after washing with CB. Scale bar = 200 μm.

Table 3. OTFT Characteristics of P3HT and Cross-linked P3HT-azide20 before and after Washing with CB

	before washing		after washing[a]	
	mobility [cm^2/(V s)]	on/off ratio	mobility [cm^2/(V s)]	on/off ratio
P3HT	3.01×10^{-2}	3.2×10^5		
azide20	2.15×10^{-2}	1.5×10^5	1.53×10^{-2}	2.3×10^4

[a]P3HT film could not be measured due to the lift-off of the electrodes.

OTFTs based on the cross-linked P3HT-azide copolymer remained stable after washing with CB (Figure 4). Additionally, the air stability of OTFTs based on the azide copolymer was measured in air for about one month. The cross-linked P3HT-azide OTFTs were more stable in air compared with pristine P3HT OTFTs (Figure S6 in the Supporting Information). This finding indicates that our approach can improve ambient stability to some degree in addition to providing solvent resistivity. We suggest that the cross-linked top surfaces might slow down the diffusion of oxygen into the channel area.

In addition to solvent resistance and ambient stability, enhancing thermal stability in organic electronics, particularly in BHJ OPVs, is of great importance. To investigate the effect of P3HT-azide copolymers on the performance and thermal stability of the solar cells, the performance of (P3HT + P3HT-azide10)/PCBM blend (w/w = 1:1), including various proportions of P3HT-azide10, was measured as a function of annealing time at 150 °C (Figure 5). The weight ratio of P3HT-azide10 to (P3HT + P3HT-azide10) was varied from 0 to 15%. Initially, P3HT and P3HT/P3HT-azide blended devices showed almost identical peak performance. However, they showed a dramatic contrast in thermal stability after annealing at an elevated temperature of 150 °C (Table 4). Whereas the PCE of the control P3HT/PCBM device decreased rapidly upon annealing at 150 °C, the device including 15% P3HT-azide10 exhibited superior thermal stability, showing a PCE of over 3.3% for 40 h of annealing at 150 °C.

This dramatic contrast in thermal stability took place through the formation of in situ fullerene attached P3HT-azide graft copolymers at the P3HT/PCBM interface, because the azide group in P3HT-azide copolymers undergoes a cyclo-addition reaction with the sp^2 bond of PCBM under heating conditions.[34] In FT-IR measurement, the azide peak in the blend with PCBM totally disappeared after 30 min of annealing at 150 °C, indicating that fullerenes were attached to the P3HT-azide copolymer (Figure S7 in the Supporting Information). The graft copolymers formed at the P3HT/PCBM interface can reduce the interfacial tension and suppress the macrophase separation that occurs upon long-term annealing. It should be noted that the in situ compatibilizer approach using P3HT-azide copolymers has a strong advantage over other conventional approaches using premade compatibilizers.[38−40] The peak performance of the device has typically been sacrificed by the addition of premade compatibilizers, as a result of the presence of some compatibilizer units in either the electron donor or acceptor phase as undesired micelles, which reduces PCE by disturbing the continuous pathway for charge transport. In contrast, our P3HT-azide copolymers should form in situ graft compatibilizers only at the electron donor/acceptor interface. In addition, the synthesis of P3HT-azide copolymers is straightforward, and the graft copolymers formed are composed of only P3HT and PCBM, without the introduction of any electronically impure group in the compatibilizer, unlike other approaches.[41,42]

Deeper insight into the extreme contrast in thermal stability can be gleaned by examination of the morphology of the active layer via optical microscopy. Figure 6 shows optical microscopic images of (P3HT + P3HT-azide10)/PCBM blends (w/w = 1:1), including various proportions of P3HT-azide10 copolymer. The weight ratio of P3HT-azide10 to (P3HT + P3HT-azide10) was varied from 0 to 15 wt %, which is identical to the device condition. For the P3HT/PCBM sample, without P3HT-azide10, thermal annealing at 150 °C for 24 h induced the formation of many needle-like PCBM crystals, revealing that there was severe macro-phase separation driven by the crystallization of donors and
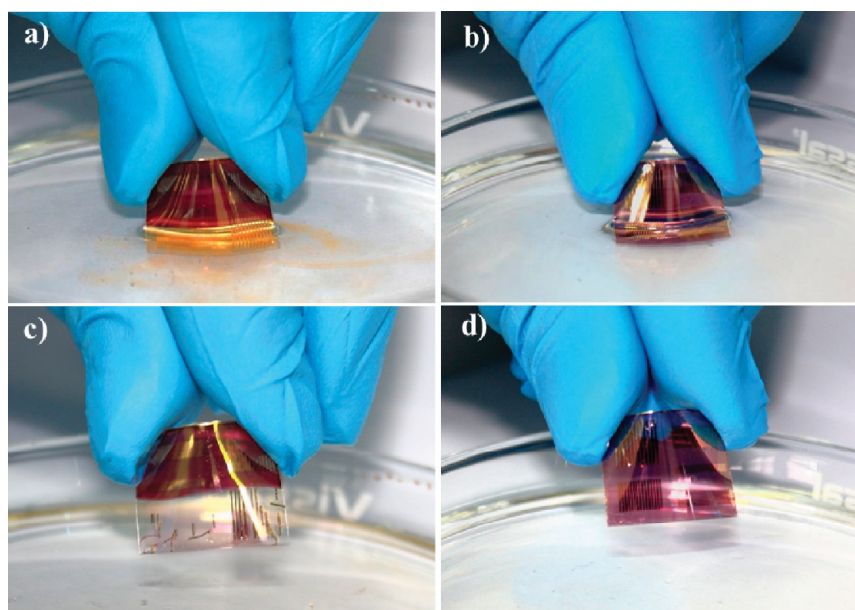

Figure 4. Photographic images of the solvent resistance test of flexible OTFTs. (a) P3HT and (b) cross-linked P3HT-azide10 were immersed into CB. (c) The P3HT film was washed out, and the electrodes were lifted off in top contact geometry, (d) whereas cross-linked P3HT-azide10 films remained stable after washing with CB.
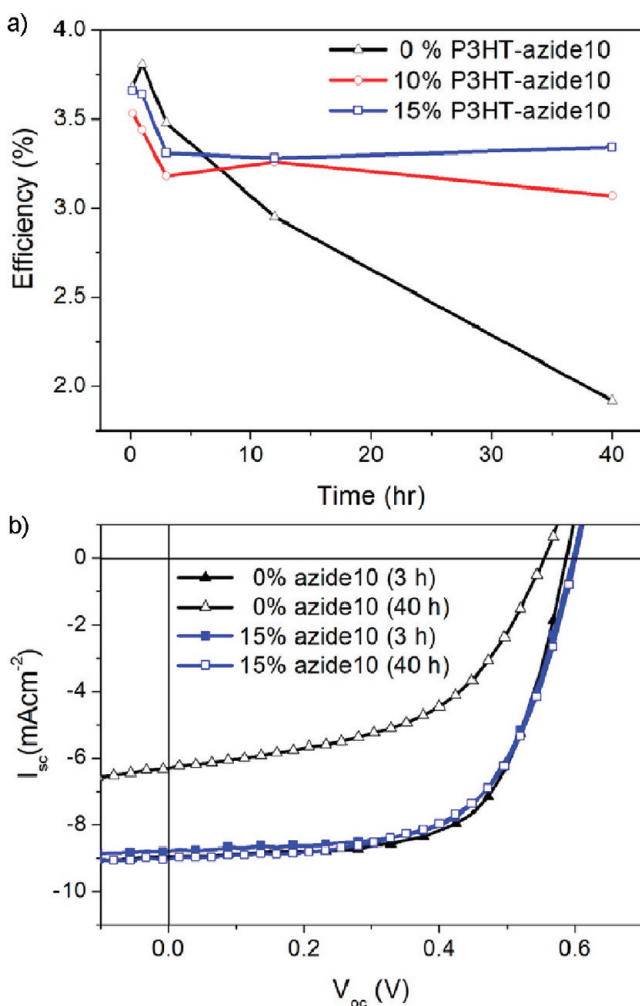
Figure 5. (a) Efficiencies of P3HT/PCBM devices containing 0, 10, or 15% of P3HT-azide10 copolymer during thermal annealing at 150 °C with PCBM as the electron accteptor. (b) Current−voltage curves of the 0% and 15% P3HT-azide10 devices with initial (full symbols, 3 h) and long-term (open symbols, 40 h) thermal annealing.

Table 4. Device Characteristics of (1) P3HT/PCBM (P3HT:PCBM = 1:1, w/w) and (2) P3HT/P3HT-azide10/PCBM ((P3HT + P3HT-azide10 (15%))/PCBM = 1:1, w/w) for Thermal Stability Test at 150 °C

	annealing time [h]	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
0% P3HT-azide10	3	0.59	8.96	65	3.44
	40	0.56	6.45	53	1.92
15% P3HT-azide10	3	0.60	8.81	63	3.32
	40	0.60	9.06	61	3.34

acceptors. In striking contrast, the blend film with 15% P3HT-azide10 showed a homogeneous film without any dark PCBM crystals. This result clearly explains the dramatic improvement of thermal stabilities and solar cell performance from the addition of P3HT-azide10 copolymer. We think that in situ chemical bonding of acceptor and donor materials in BHJ film interface is an ideal way to enhance the stability while maintaining the original efficiency.

■ CONCLUSIONS

In this study, we demonstrated a simple and powerful method to enhance the stability of organic electronic devices using cross-linkable azide functional groups. P3HT-azide copolymers show excellent electrical performance with high solvent resistance and thermal stability. Photo-cross-linking provides solvent resistance without disrupting the transistor properties, including the on/off ratio and mobility. OTFTs of P3HT-azide copolymers exhibited excellent charge mobility with stable operation after washing with the organic solvent. This is the first demonstration of solvent-resistant OTFT devices. Furthermore, thermally stable OPVs were also produced with P3HT-azide copolymers. After 40 h of thermal annealing at 150 °C, a PCE of more than 3.3% was obtained from the OPV device containing 15% of P3HT-azide10 copolymer. This enhanced stability is due to an in situ compatibilizer that forms at the P3HT/PCBM interface and suppresses macro-phase separation. This result represents one of the most thermally stable BHJ OPV devices reported to date. Our approach is envisioned to expand practical applications of conjugated polymers in electronic devices.

■ EXPERIMENTAL SECTION

OTFT Fabrication. OTFTs were fabricated on heavily n-type doped silicon (Si) wafers with a 300 nm thick thermally grown SiO$_2$ layer (C$_i$ = 10 nF cm^{-2}). Octadecyltrimethoxysilane (OTS) treated substrates were prepared as follows: SiO$_2$/Si wafers were cleaned using piranha solution (7:3 mixtures of H$_2$SO$_4$ and H$_2$O$_2$, v/v) for 30 min, rinsed with DI water, and dried under a nitrogen stream. This process provides a hydrophilic, organic contaminant-free surface. The SiO$_2$/Si pieces were treated with UV-ozone plasma. OTS in trichloroethylene (3 mM solution) was spin-coated on the cleaned wafers at 3000 rpm for 30 s with prespin wetting time (∼20 s). Then, wafers were moved into a desiccator filled with ammonia vapor, and kept overnight at room temperature. The wafers were then washed sequentially with toluene, acetone, and isopropyl alcohol and dried under a nitrogen stream. A contact angle of DI water on the OTS-treated wafer was approximately 108°.

We made 2 mg mL^{-1} solutions with chloroform, stirring to dissolve the compounds completely. Films were produced by drop casting on OTS-treated substrates and then dried in a vacuum oven at 40 °C overnight to remove solvent completely. Then, they were annealed on a hot plate at 150 °C for 30 min. Photo-cross-linking of P3HT-azide copolymers was conducted using UV light (λ = 254 nm) for 5 min in nitrogen atmosphere. Then, approximately 40 nm of Au was thermally evaporated on the substrates with 50 μm channel length (L) and 20 of W/L ratio. We used Keithley 4200 semiconductor parametric analyzer in a glovebox to record the electrical characteristics of OTFTs. The solvent resistance test of the OTFT devices was carried out through washing with CB. After drying, electrical characteristics of the solvent-washed devices were measured.

OPV Fabrication. ITO-coated glass substrates were subjected to ultrasonication in different solvent systems including acetone, 2% soap in water, deionized water, and then iso-propanol. A filtered dispersion of PEDOT:PSS in water (Baytron PH500) was spuncast at 3000 rpm for 40 s, followed by baking for 10 min at 140 °C. Afterward, all procedures were performed in an inert-atmosphere glovebox. Three different solutions of P3HT, P3HT-azide, and PCBM in CB (30 mg mL^{-1}) were prepared and stirred at 110 °C for more than 24 h. The solutions were passed through a 0.2 mm PTFE syringe filter. The weight ratio of P3HT-azide10 to (P3HT + P3HT-azide10) was varied from 0 to 15%. The (P3HT + P3HT-azide10):PCBM blend solutions (w/w = 1:1) were prepared with the polymer concentration of 15 mg mL^{-1} and spin coated at 1200 rpm for 40 s. A part of the organic layer was removed to allow contact with the ITO and 0.8 nm LiF, and a 100 nm thick Al cathode was deposited by thermal evaporation under vacuum (10^{-6} Torr).
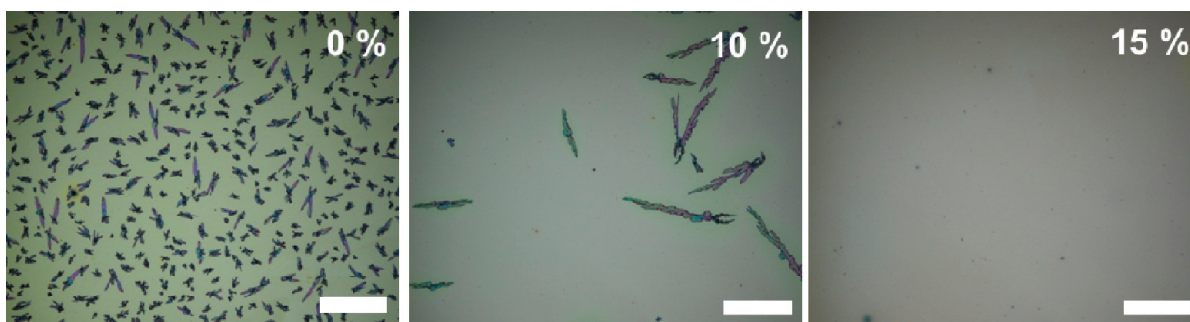
Figure 6. Optical microscopy images of the P3HT/PCBM films containing 0, 10, or 15% P3HT-azide10 copolymer after annealing at 150 °C for 24 h. Scale bar = 100 μm.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Materials and methods, detailed experimental procedures, and additional data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors
*E-mail: bumjoonkim@kaist.ac.kr.
*E-mail: joonhoh@unist.ac.kr.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Arias, A. C.; MacKenzie, J. D.; McCulloch, I.; Rivnay, J.; Salleo, A. *Chem. Rev.* **2010**, *110*, 3.

(2) Oh, J. H.; Lee, W. Y.; Noe, T.; Chen, W. C.; Konemann, M.; Bao, Z. *J. Am. Chem. Soc.* **2011**, *133*, 4204.

(3) Ku, S. Y.; Liman, C. D.; Cochran, J. E.; Toney, M. F.; Chabinyc, M. L.; Hawker, C. J. *Adv. Mater.* **2011**, *23*, 2289.

(4) Gsänger, M.; Oh, J. H.; Könemann, M.; Höffken, H. W.; Krause, A.-M.; Bao, Z.; Würthner, F. *Angew. Chem., Int. Ed.* **2010**, *122*, 752.

(5) Kang, D. J.; Kwon, T.; Kim, M. P.; Cho, C.-H.; Jung, H.; Bang, J.; Kim, B. J. *ACS Nano* **2011**, *5*, 9017.

(6) Facchetti, A. *Chem. Mater.* **2011**, *23*, 733.

(7) Cho, C.-H.; Kang, H.; Kang, T. E.; Cho, H.-H.; Yoon, S. C.; Jeon, M.-K.; Kim, B. J. *Chem. Commun.* **2011**, *47*, 3577.

(8) Cheng, Y. J.; Yang, S. H.; Hsu, C. S. *Chem. Rev.* **2009**, *109*, 5868.

(9) Kim, K.-H.; Kang, H.; Nam, S. Y.; Jung, J.; Kim, P. S.; Cho, C.-H.; Lee, C.; Yoon, S. C.; Kim, B. J. *Chem. Mater.* **2011**, *23*, 5090.

(10) Zhang, M.; Tsao, H. N.; Pisula, W.; Yang, C.; Mishra, A. K.; Müllen, K. *J. Am. Chem. Soc.* **2007**, *129*, 3472.

(11) Sonar, P.; Singh, S. P.; Li, Y.; Soh, M. S.; Dodabalapur, A. *Adv. Mater.* **2010**, *22*, 5409.

(12) Liang, Y. Y.; Xu, Z.; Xia, J. B.; Tsai, S. T.; Wu, Y.; Li, G.; Ray, C.; Yu, L. P. *Adv. Mater.* **2010**, *22*, E135.

(13) Zhou, H.; Yang, L.; Price, S. C.; Knight, K. J.; You, W. *Angew. Chem., Int. Ed.* **2010**, *49*, 7992.

(14) Piliego, C.; Holcombe, T. W.; Douglas, J. D.; Woo, C. H.; Beaujuge, P. M.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2010**, *132*, 7595.

(15) Chu, T. Y.; Lu, J. P.; Beaupre, S.; Zhang, Y. G.; Pouliot, J. R.; Wakim, S.; Zhou, J. Y.; Leclerc, M.; Li, Z.; Ding, J. F.; Tao, Y. *J. Am. Chem. Soc.* **2011**, *133*, 4250.

(16) Khan, H. U.; Roberts, M. E.; Johnson, O.; Forch, R.; Knoll, W.; Bao, Z. *Adv. Mater.* **2010**, *22*, 4452.

(17) Sivula, K.; Ball, Z. T.; Watanabe, N.; Fréchet, J. M. J. *Adv. Mater.* **2006**, *18*, 206.

(18) Miyanishi, S.; Zhang, Y.; Tajima, K.; Hashimoto, K. *Chem. Commun.* **2010**, *46*, 6723.

(19) Lee, J. U.; Jung, J. W.; Emrick, T.; Russell, T. P.; Jo, W. H. *J. Mater.Chem.* **2010**, *20*, 3287.

(20) Rajaram, S.; Armstrong, P. B.; Kim, B. J.; Fréchet, J. M. J. *Chem. Mater.* **2009**, *21*, 1775.

(21) Miyanishi, S.; Tajima, K.; Hashimoto, K. *Macromolecules* **2009**, *42*, 1610.

(22) Cheng, Y. J.; Hsieh, C. H.; Li, P. J.; Hsu, C. S. *Adv. Funct. Mater.* **2011**, *21*, 1723.

(23) Ma, B. W.; Kim, B. J.; Poulsen, D. A.; Pastine, S. J.; Fréchet, J. M. J. *Adv. Funct. Mater.* **2009**, *19*, 1024.

(24) Lim, J.; Yang, H.; Paek, K.; Cho, C.-H.; Kim, S.; Bang, J.; Kim, B. J. *J. Polym. Sci., Part A: Polym. Chem.* **2011**, *49*, 3464.

(25) Yoo, M.; Kim, S.; Lim, J.-M.; Kramer, E. J.; Hawker, C. J.; Kim, B. J.; Bang, J. *Macromolecules* **2010**, *43*, 3570.

(26) Drees, M.; Hoppe, H.; Winder, C.; Neugebauer, H.; Sariciftci, N. S.; Schwinger, W.; Schaffler, F.; Topf, C.; Scharber, M. C.; Zhu, Z. G.; Gaudiana, R. *J. Mater.Chem.* **2005**, *15*, 5158.

(27) Bao, Z.; Dodabalapur, A.; Lovinger, A. J. *Appl. Phys. Lett.* **1996**, *69*, 4108.

(28) Ma, W. L.; Yang, C. Y.; Gong, X.; Lee, K.; Heeger, A. J. *Adv. Funct. Mater.* **2005**, *15*, 1617.

(29) Li, G.; Shrotriya, V.; Huang, J. S.; Yao, Y.; Moriarty, T.; Emery, K.; Yang, Y. *Nat. Mater.* **2005**, *4*, 864.

(30) Kim, B. J.; Miyamoto, Y.; Ma, B.; Fréchet, J. M. J. *Adv. Funct. Mater.* **2009**, *19*, 2273.

(31) Ito, Y.; Virkar, A. A.; Mannsfeld, S.; Oh, J. H.; Toney, M.; Locklin, J.; Bao, Z. *J. Am. Chem. Soc.* **2009**, *131*, 9396.

(32) Salleo, A.; Kline, R. J.; DeLongchamp, D. M.; Chabinyc, M. L. *Adv. Mater.* **2010**, *22*, 3812.

(33) Wurthner, F. *Chem. Commun.* **2004**, 1564.

(34) Brase, S.; Gil, C.; Knepper, K.; Zimmermann, V. *Angew. Chem., Int. Ed.* **2005**, *44*, 5188.

(35) Klima, R. F.; Gudmundsdottir, A. D. *J. Photochem. Photobiol., A* **2004**, *162*, 239.

(36) Kang, H.; Lee, C.; Yoon, S. C.; Cho, C.-H.; Cho, J.; Kim, B. J. *Langmuir* **2010**, *26*, 17589.

(37) Woo, C. H.; Thompson, B. C.; Kim, B. J.; Toney, M. F.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2008**, *130*, 16324.

(38) Jones, T. D.; Schulze, J. S.; Macosko, C. W.; Lodge, T. P. *Macromolecules* **2003**, *36*, 7212.

(39) Jeon, H. K.; Zhang, J.; Macosko, C. W. *Polymer* **2005**, *46*, 12422.

(40) Yin, Z.; Koulic, C.; Pagnoulle, C.; Jérôme, R. *Macromolecules* **2001**, *34*, 5132.

(41) Gholamkhass, B.; Holdcroft, S. *Chem. Mater.* **2010**, *22*, 5371.

(42) Lee, J. U.; Jung, J. W.; Emrick, T.; Russell, T. P.; Jo, W. H. *Nanotechnology* **2010**, *21*, 105201.