Thermally stable, highly efficient, ultraflexible organic photovoltaics

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Flexible photovoltaics with extreme mechanical compliance present appealing possibilities to power Internet of Things (IoT) sensors and wearable electronic devices. Although improvement in thermal stability is essential, simultaneous achievement of high power conversion efficiency (PCE) and thermal stability in flexible organic photovoltaics (OPVs) remains challenging due to the difficulties in maintaining an optimal microstructure of the active layer under thermal stress. The insufficient thermal capability of a plastic substrate and the environmental influences cannot be fully expelled by ultrathin barrier coatings. Here, we have successfully fabricated ultraflexible OPVs with initial efficiencies of up to 10% that can endure temperatures of over 100 °C, maintaining 80% of the initial efficiency under accelerated testing conditions for over 500 hours in air. Particularly, we introduce a low-bandgap poly(benzothiophene-co-thieno[3,4-b]thiophene) (PBDTTT) donor polymer that forms a sturdy microstructure when blended with a fullerene acceptor. We demonstrate a feasible way to adhere ultraflexible OPVs onto textiles through a hot-melt process without causing severe performance degradation.

organic photovoltaics | thermal stability | power conversion efficiency | ultraflexibility

Power sources that are flexible enough to be attached onto curved and rough surfaces are one of the most promising solutions to supplying electrical power directly to Internet of Things sensors, wearable sensors, and electronic devices. As one of the thinnest, lightest, and most flexible photovoltaic technologies, organic photovoltaics (OPVs) are promising for extensive integration in various shapes and sizes, thus extending power sources from space-intensive to the prevailing wearable form of electronics.

The power conversion efficiency (PCE) of OPVs improved from 1 to 10% (1–4), which is considered a representative efficiency for widespread applications. A latest rational design of a single-junction binary blend brings the record value up to 13.1% (5). Such a high performance has been demonstrated using rigid glass substrates. After considerable progress was made on the development of highly efficient OPVs on rigid substrates, an outlook was presented on driving this emerging technology with the inherent stability of the active layers. OPVs having initial efficiencies of up to 10% (13), especially those with the fullerene acceptor [6,6]-phenyl-C61-butyric acid methyl ester (PC61BM), were reported to exhibit rapid degradation due to a general tendency of phase reorganization at high temperatures (14, 15). Strategies to suppress fullerene crystallization (16–18) including the use of cross-linking polymers, oligomeric fullerene derivatives, or other additives led to enhanced intrinsic stability of the OPVs. A representative system demonstrated that 80% of the initial PCE could be maintained after the devices were heated at 130 °C for 2 h in an inert atmosphere (19). The best-performing fullerene-free OPVs exhibited a $T_{50}$ lifetime (defined as the lifetime when the efficiency of a device degrades by 20% from its initial PCE) (20) of over 250 h at 100 °C when encapsulated with thermally stable, highly efficient, ultraflexible organic photovoltaics (OPV) that achieves sufficient thermal stability of up to 120 °C and a high power conversion efficiency of 10% with a total thickness of 3 μm. By combining an inherently stable donor:acceptor blend as the active layer and ultrathin substrate and barriers with excellent thermal capability, we were able to overcome the trade-offs between efficiency, stability, and device thickness. The ultraflexible and thermally stable OPV can be easily integrated into textiles through the commercially available hot-melt process without causing performance degradation, thereby presenting great potential in ubiquitous and wearable power source in daily life.

Significance

Author contributions: X.X., K.F., and T.S. designed research; X.X., K.F., S.P., H.K., H.J., N.W., S.Y., S.S., D.K., T.Y., and S.U. performed research; N.W., S.Y., S.S., and D.K. contributed new reagents/analytic tools; X.X., K.F., A.K., T.-Q.N., and T.S. analyzed data; and X.X., K.F., A.K., D.K., T.-Q.N., and T.S. wrote the paper.

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Flexible OPVs have been explored employing reduced graphene oxide (22) or epoxy resin (23) to effectively enhance the stability under multiple aging conditions. The most stable system, poly (3-hexylthiophene) blended with fullerene acceptor as the active layer, was reported with 95% retained performance after 1,000 h under 85 °C and 85% relative humidity with an initial PCE of 2.7% (23).

Until now, however, there have been no documented OPVs that achieve sufficient thermal stability (above 100 °C), high efficiency (10%), and mechanical durability (micrometer-scale bending radius) simultaneously. Indeed, removal of the glass back support and encapsulation often leads to dramatically deteriorated cell performances. Due to the high gas permeability of a thin plastic substrate and passivation layer, especially when local temperature rises, the upkeep of device efficiency over a long run in ambient conditions require an intrinsically thermally stable active layer (24). Additionally, at elevated temperatures, conventional flexible substrates having relatively low glass-transition temperatures may result in irreversible performance degradation due to the induced mechanical strains during phase change (25).

Here we report a 3-μm-thick OPV system that exhibits an initial efficiency of up to 10% and demonstrates a remarkably enhanced thermal stability. The donor polymer, poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b’]dithiophene]−2,6-diyl-alt-(4-octyl-3-fluorothieno[3,4-b]thiophene)-2-carboxylato-2,6-diy(d) (PBDTTT-OFT, Fig. 1C), exhibits a high degree of face-on orientation when blended with PC71BM, enabling a superior percolating network and maintaining a sturdy microstructure even when heated to 120 °C on an ultrathin substrate. Besides, the application of a thermally stable transparent polyimide substrate and Teflon/parylene double-barrier layers (Fig. 1B) shows high uniformity, as revealed by the cross-section scanning electron microscope (SEM) image (SI Appendix, Fig. S1A). We adopted an inverted device structure to prevent direct contact between indium tin oxide (ITO) and poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS), thus avoiding proton etching of ITO and its subsequent degradation (27).

To achieve high efficiencies for the OPVs on the basis of ultrathin plastic substrate, transparent polyimide was chosen as the substrate film due to three important features, namely, high thermal stability, transparency, and surface flatness. The ultrathin transparent polyimide film having a glass transition temperature of 265 °C was stable during the subsequent high-temperature fabrication and worked without inducing mechanical strains (25). As indicated from the transmittance spectra, the transparency of the 1.3-μm-thick polyimide is comparable to that of glass in the visible spectrum. Besides, the transparent polyimide thin film exhibits a unique UV-cutoff property at a wavelength of around 360 nm (28) (SI Appendix, Fig. S1B), and could thus potentially suppress the UV-induced photochemical degradation (29). Additionally, the transparent polyimide thin film exhibits an ultrasmooth surface with a roughness of around 0.2 nm, and thus the top layers are as uniform as those cast on glass (SI Appendix, Fig. S2).

The ultraflexible OPVs demonstrate comparable PCEs as opposed to their rigid counterpart devices (Table 1). Statistics from 20 ultraflexible cells with active areas of 0.04 cm2 show an average open-circuit voltage (VOC) of 0.79 ± 0.01 V, short-circuit current density (JSC) and fill factor (FF) of 17.2 ± 0.3 mA cm−2 and 69 ± 1%, respectively, and a PCE of 9.4 ± 0.2% under one-sun illumination. The current density–voltage (J–V) characteristic shown in Fig. 1D reveals the highest efficiency of 10% with
excellent diode characteristics (SI Appendix, Fig. S3A) and negligible hysteresis (SI Appendix, Fig. S3B). The performances of the devices on transparent polyimide were slightly better than those of the devices on glass (SI Appendix, Fig. S3C). This is attributed to a higher shunt resistance and thus an enhanced FF (SI Appendix, Fig. S3D), indicating a highly continuous and flat transparent polyimide surface with fewer defects or microscopic pinholes (27, 30) that could induce inhomogeneity in the deposited layers on top.

Starting from well-known copolymers combining benzothio- phene (BDT) and thienothiophene (TT) moieties, which have narrow bandgaps and have been widely applied in OPVs with PCEs exceeding 10% (31), we designed a BDT-TT-type donor polymer, PBDTTT-OFT, with a linear alkyl side chain attached to the ester group of the fluorene-substituted TT unit. With a more stabilized as-cast packing and transport property compared with that of the branched counterpart polymer, poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b’]dithiophene-2,6-diyl-alt-(4-(2-ethylhexyl)-3-fluorothieno[3,4-b]thiophene)-2-carboxylate-2-6-diyl] (PBDTTT-EFT) (32, 33) (SI Appendix, Fig. S4A), both enhanced PCE and improved thermal stability can be expected (34). PBDTTT-OFT retains the coplanarity of the main chain and has a similar optical bandgap (Eg,opt) of 1.57 eV with an absorption onset at 790 nm (Fig. 2A) and a highest-occupied molecular orbital of 4.95 eV (SI Appendix, Fig. S4B). The PBDTTT-OFT blend film shows a slightly higher absorption coefficient ranging from 630 to 800 nm (Fig. 2B) than that of the PBDTTT-EFT:PC71BM blend.

Grazing-incidence wide-angle X-ray scattering (GIWAXS) measurement (Fig. 2C) reveals a predominant face-on packing of the pristine PBDTTT-OFT, showing well-defined π-π and lamellar peaks at q∥ = 1.65 Å−1 (aromatic stacking spacing d1 = 3.80 Å) and q⊥ = 0.24 Å−1 (lamellar stacking spacing d2 = 26.0 Å). After blending with PC71BM (1:1.2 ratio), the sharp face-on packing peaks with high intensities were observed together with a broad reflection halo centered at q ∼ 1.37 Å−1 (d spacing = 4.59 Å), which indicate a random orientation and short-range ordering of PC71BM aggregates. Compared with the PBDTTT-EFT:PC71BM film, which showed a ring-like lamellar peak, a weak and broad π-π peak in the out-of-plane direction at q∥ = 1.60 Å−1 (d1 = 3.93 Å) (35), the stronger reflections of PBDTTT-OFT imply a higher degree of crystallinity with face-on orientation. These consequently result in enhanced charge transport and improved PCE (SI Appendix, Fig. S4C). The optimal blend microstructure was further evidenced by a confined bimolecular recombination (SI Appendix, Fig. S4D).

Thermal Stability and Lifetime

The 3-μm-thick ultraflexible OPVs based on the PBDTTT-OFT:PC71BM blend exhibited superior high-temperature durability than the well-known PBDTTT-EFT:PC71BM blend having the same device structure did. After being heated in ambient air from 20 to 130 °C for 5 min under each step, the PBDTTT-OFT:PC71BM OPVs showed continuous performance deterioration, while the PCEs of the PBDTTT-OFT:PC71BM OPVs remained unchanged even when the temperature was raised to 100 °C (Fig. 3A). The ultraflexible PBDTTT-OFT:PC71BM OPVs could endure thermal stress at 100 °C for 4 h without any change in efficiency (SI Appendix, Fig. S5A). We observed a slight PCE deterioration by 7.4 and 13.8% of the initial efficiency when the PBDTTT-OFT:PC71BM cells were kept in air at 120 and 130 °C, respectively. On the other hand, the PCEs of the PBDTTT-EFT:PC71BM OPVs severely degraded by 37.6% at 130 °C with decreased Jsc and FF (SI Appendix, Fig. S5B and C), which is mainly correlated with phase reorganization (36).

To gain insights into the intrinsic stability of the bulk heterojunctions, we performed comparative study of the two blends by subjecting the OPVs to thermal stress over a relatively long time inside a glove box. After heating at 130 °C for 4 h in N2 atmosphere, a drastic decrease in the photocurrent from 92 to 39 pA by 58% was observed in the PBDTTT-EFT:PC71BM film by mapping with photoconductive atomic force microscopy (AFM) (37) (Fig. 3C), which revealed undesired transport degradation that led to PCE loss. This is consistent with the bicontinuous topography change in dimensions (SI Appendix, Fig. S6), which indicates phase reorganization under thermal stress. In comparison, the microstructure of the PBDTTT-OFT:PC71BM film shows robustness under the same annealing condition, maintaining a photocurrent of 142 pA, which is responsible for the retention of high PCE. This optimal as-cast microstructure yields a high efficiency and excellent thermal stability simultaneously (13).

Table 1. Photovoltaic parameters of the OPV single cells

| Substrate           | Active area, cm² | Jsc, mA cm⁻² | Voc, V  | FF, %  | PCE, %  |
|---------------------|------------------|--------------|---------|--------|---------|
| Glass               | 0.04             | 17.2 ± 0.3   | 0.79 ± 0.01 | 0.68 ± 0.01 | 9.2 ± 0.3 (9.7) |
| Transparent Polyimide | 0.04             | 17.2 ± 0.3   | 0.79 ± 0.01 | 0.69 ± 0.01 | 9.4 ± 0.3 (10.0) |
|                     | 0.16             | 17.1 ± 0.3   | 0.79 ± 0.01 | 0.67 ± 0.01 | 9.0 ± 0.2 (9.3) |
|                     | 1.00             | 16.5 ± 0.5   | 0.79 ± 0.01 | 0.63 ± 0.01 | 8.2 ± 0.3 (8.8) |

The statistics were calculated from 20 devices for each case. In the parentheses are maximum values from the best-performing devices.
As shown in the photoconductive AFM results (Fig. 3B), the PBDTTT-OFT:PC71BM blend film is more thermally robust than the PBDTTT-EFT:PC71BM film. The improved thermal stability can be ascribed to the favorable packing of molecules due to the difference in the side chains of the two compounds. The side chain of PBDTTT-EFT is a branched ethylhexyl group, whereas the side chain of PBDTTT-OFT is a linear octyl. In general, linear alkyl chains lead to films with higher crystallinity and reduce the diffusion rates of water and oxygen through the film, as compared with amorphous/disordered films, which improves the thermal stability of PBDTTT-OFT:PC71BM films. Indeed, the crystallinity of PBDTTT-OFT:PC71BM is better than that of PBDTTT-EFT:PC71BM, as observed from the GIWAXS results (Fig. 2C and SI Appendix, Fig. S6C). All of these allude to the fact that compound PBDTTT-OFT is indeed responsible for an improved thermal stability.

Next, we performed an aging test following the international summit on OPV stability (ISOS) protocol (38). The ultraflexible OPVs with 1.36-μm-thick Teflon/parylene double-barrier layers were kept at 85 °C in air under controlled humidity of 30% for 500 h under continuous thermal stress (Fig. 3C).

The plastic barriers significantly prolong the device storage lifetime to >2,000 h at room temperature (ISOS-D-1 protocol) compared with the nonencapsulated devices (around 400 h, Fig. 3D) and parylene single-layer encapsulated devices (SI Appendix, Fig. S7). Since there is a trade-off between barrier thickness and device lifetime (9), the double-layer barriers demonstrated here offer a solution to maintaining the ultrathinness simultaneously with strong barrier property, and thus, excellent environmental stability of the devices.

**Scalability and Mechanical Compliance**

The scalability of the ultraflexible OPVs interpreted by the average photovoltaic parameters with different working areas is summarized in Table 1. The fabrication processes involve sequential depositions of the stacks on transparent polyimide-coated supporting glass plates, followed by a delamination process that causes no obvious deterioration of the electrical performance (SI Appendix, Fig. S8 A–C). With the aperture area increased to 0.16 and 1.0 cm², the ultraflexible devices still retain a VOC of 0.79 V and exhibit maximum PCEs of 9.3 and 8.8%, respectively (Table 1 and SI Appendix, Fig. S8D). The short-circuit currents from the I–V measurements are in good agreement with the calculated VOC obtained by integrating the external quantum efficiency (EQE, SI Appendix, Fig. S8E).

We further fabricated multiple 3-μm-thick solar modules with a substrate size of 5 × 5 cm². The module illustrated in Fig. 4A and B has a total working area of 4.4 cm², a per-area mass of 5.4 g m⁻², an overall PCE of 8.2%, and a power-per-weight of up to 16.7 g W⁻¹, generating a power output of around 36 mW under one-sun illumination (Fig. 4C). A decorative sunflower-shaped module, as depicted in SI Appendix, Fig. S8 F and G, generates 20 mW power under one-sun illumination. The excellent scalability with high efficiency is due to the great uniformity of the as-cast PBDTTT-OFT:PC71BM blend. A complete intermixing between the donor polymer and PC71BM, which is insensitive to deposition temperatures, offers viability in practical applications.

![Image](https://example.com/image.png)

**Fig. 3.** Thermal stability and lifetime of the ultraflexible OPV. (A) Short-time thermal stability comparison between OPVs with PBDTTT-OFT:PC71BM and PBDTTT-EFT:PC71BM blends, with the same device structure and heat-treated in ambient air. (B) AFM photocurrent images collected under a white-light source with a power of 30 W cm⁻² of PBDTTT-OFT:PC71BM (Top) and PBDTTT-EFT:PC71BM (Bottom) blends before (Left) and after (Right) thermal treatment at 130 °C for 4 h in a glove box. The photoactive films were deposited on transparent polyimide/ITO/ZnO substrates with glass support. The photocurrent images were collected using a chromium/platinum AFM probe with a bias applied to the substrate. (C) Aging test of the PBDTTT-OFT:PC71BM-based 3-μm-thick ultraflexible OPVs under thermal stress at 85 °C in air. (D) Storage lifetime comparison between the ultraflexible cells encapsulated with 1.36-μm Teflon/parylene double barriers (magenta hollows) and the glass-supported rigid devices without encapsulation (dark-gray squares).
roll-to-roll production of large-area flexible modules under room temperature.

The modules endure repeated rolling, folding, or crumpling without obvious cracks or performance deterioration (SI Appendix, Fig. S9). This high level of compliance suggests that the devices can be stretchable using the buckling phenomenon. To demonstrate the stretchability of the OPV cells, we transferred the 3-μm-thick OPVs on a prestretched acrylic elastomer. Releasing the elastomer applies compression strain to the closely attached ultrathin OPVs, and the resulting sinusoidal waves, as revealed by the SEM image, showed a bending radius of ~10 μm when the devices were compressed by 50%. We were able to perform a cyclic compression/stretching test with a maximum strain of 66.7% applied for 100 cycles, and observed only 12% degradation in the initial efficiency. This further suggests good mechanical property of our high-performance OPVs.

**Methods**

**Material Synthesis and Characterization.** The synthetic procedures for PDTTT-OFT were detailed in SI Appendix. All of the results are obtained from PDTTT-OFT with molecular mass (Mn) of around 40 kDa and a polydispersity index below 2.2.

**Thin-Film Characterization.** Thin-film thicknesses were determined with a stylus profilometer (DEKTAK 6M; Bruker). UV-vis absorption spectra were recorded on a JASCO V-670 spectrophotometer. Two-dimensional GIWAXS measurements were conducted at beamline BL46XU of SPring-8. The irradiation wavelength was λ = 0.10 nm (energy: 12.4 keV) and the incident angle was fixed at 0.12°. The GIWAXS patterns were recorded by a Pilatus 300K 2D image detector with a camera length of 170.3 mm. The irradiation time was fixed at 1 s for all of the samples. Polymer and bulk heterojunction samples were prepared on Si substrates by spin-coating. AFM images were obtained with a Shimadzu SPM-9700HT scanning probe microscope in the tapping mode. Photoconductive AFM measurements were done with an Asylum Research MFP-3D microscope sitting atop an inverted optical microscope (IX71; Olympus). The photoactive films were deposited on transparent polymide/ITO/zinc oxide (ZnO) substrates with glass support and scanned under inert atmosphere. A white-light source with a power of 30 W cm⁻² was used to generate photocurrent which was recorded by an internal preamplifier (Asylum Research ORCA head model). Chromium/platinum-coated silicon probes with a spring constant of 0.2 N m⁻¹ and resonant frequency of 13 kHz (Budget Sensors) were used. The light was focused on the sample through an inverted optical microscope (Olympus), and the tip was positioned at the center of the light spot, which was ~160 μm in diameter.

**Device Fabrication and Characterization.** The OPV devices were manufactured on 1.3-μm-thick transparent polyimide and then packaged with 1.36-μm barrier coatings. Finally, they were detached into a freestanding state with a total thickness of 3 μm. To fabricate the transparent polyimide substrate, a precursor (ECRIOS, Mitsui Chemicals, Inc.) was first spin-coated on a glass plate with the surface pretreated by a fluorinated polymer layer (Novec 2702; 3M Company), followed by an imidization reaction at 270 °C for 2 h in a N₂ atmosphere. After the curing treatment, the ultrathin transparent polyimide substrate forms a highly cross-linked structure, which is directly responsible for mechanical and temperature strength. Encapsulation of the finishing device was realized with ultrathin plastic barriers, including a 360-nm-thick Teflon (AF 1600; Dupont) layer spinned-coated and cured at 100 °C for 0.5 h, together with a 1-μm-thick parylene (dixi-5R; Daisan Kasei Co., Ltd.) layer formed by chemical vapor deposition. The main effective stacks adopted for the inverted OPV structure: ITO/ZnO/hole transport layer/active layer (a 100 nm-thick ITO layer formed as a transparent electrode by sputtering. The 30-nm ZnO layer, i.e., the electron transport layer (hole-blocking layer), was deposited by a sol-gel method. The ZnO precursor solution was prepared by dissolving zinc acetate dehydrate (0.5 g) and ethanolamine (0.14 mL) in 5 mL 2-methoxyethanol, and then spin-coated (MS-B100 Spin-Coater, Mikasa; 5,000 rpm for 30 s) on top of ITO, followed by baking in air at 180 °C for 30 min. The active layer, PDTTT-OFT/Pc71BM (about 110 nm), was deposited in a glove box by spin-coating a Chlorobenzene solution (with 2% 1,8-Diiodooctane additive) containing PDTTT-OFT and Pc71BM with a weight ratio of 1:1.2 (sonicate for 0.5 h to complete dissolution) at 600 rpm for 20 s (MS-B100 Spin-Coater, Mikasa). The thin film was then dried in vacuum for 0.5 h. The counterpart active layer of PDTTT-EFT:PC71BM (1:1.5, wt/wt) was spin-coated at 1,500 rpm for 60 s (MS-B100 Spin-Coater, Mikasa) from its solution in chlorobenzene/DIO (97:3 vol/vol, stir for 24 h for a complete dissolving), and dried overnight. A thin layer of PEDOT:PSS was spin-coated (MS-B100 Spin-Coater, Mikasa; 2000 rpm for 30 s) from a 2-propanol solution (15% in volume) and annealed at 80 °C on a hot plate for 5 min inside the glove box. Finally, Ag (100 nm) anode was deposited through a shadow mask in a vacuum evaporator. Large-area modules with the same device architecture were fabricated using designed masks for patterning. The OPV single cells and modules were characterized under simulated solar illumination (AM 1.5 global spectrum, 100 mW cm⁻² calibrated with a standard 1000-W xenon lamp).
silicon reference diode). The J–V characteristics were recorded using a Keithley 2400 source meter at a rate of 0.17 V s⁻¹ in ambient atmosphere. Additional gold wirings (100 nm Au deposited on 12.5-μm-thick polyimide films) were used to improve the connection between the freestanding devices and the source meter. EQE was measured with monochromatic light (SM-250F; Bunkoh-Keiki).

Stability Test. To examine the thermal stability following the ISOS-D-2 protocol, the devices were incubated in an oven (SH-242 Bench-top Type Temperature & Humidity Chamber; Espec) at a controlled temperature of 85 °C and humidity of 30% RH. The shelf life was measured following the ISOS-D-1 protocol, i.e., devices being stored in ambient conditions (in a light-shielded desiccator at a controlled temperature of 25 °C and humidity of 30%), with periodic testing under AM 1.5 illumination in ambient atmosphere. To perform the compression/stretch cyclic test, freestanding OPVs were first laminated on a prestretched acrylic elastomer (3M VHB Y-4955), whose two ends were fixed on a mechanical stage. The elastomer was prestretched by 200% at the initial state and then released in steps with a maximum compression strain of 66.7% applied to the OPVs. The actual working area of the device in the compressed strain was calculated from the optical photographs under each compressive strain, and the device PCE was calibrated by considering the change in the actual projection area.

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