Ultrafast formation of air-processable and high-quality polymer films on an aqueous substrate

Jonghyeon Noh1,*, Seonju Jeong1,* & Jung-Yong Lee1

Polymer solar cells are attracting attention as next-generation energy sources. Scalable deposition techniques of high-quality organic films should be guaranteed to realize highly efficient polymer solar cells in large areas for commercial viability. Herein, we introduce an ultrafast, scalable, and versatile process for forming high-quality organic films on an aqueous substrate by utilizing the spontaneous spreading phenomenon. This approach provides easy control over the thickness of the films by tuning the spreading conditions, and the films can be transferred to a variety of secondary substrates. Moreover, the controlled Marangoni flow and ultrafast removal of solvent during the process cause the films to have a uniform, high-quality nanomorphology with finely separated phase domains. Polymer solar cells were fabricated from a mixture of polymer and fullerene derivatives on an aqueous substrate by using the proposed technique, and the device exhibited an excellent power conversion efficiency of 8.44%. Furthermore, a roll-to-roll production system was proposed as an air-processable and scalable commercial process for fabricating organic devices.
Control of the nanomorphology in polymer solar cells (PSCs) is a key factor for maximizing the module power conversion efficiency (PCE) and enhancing the electrical properties related to exciton dissociation at the interfaces between donors and acceptors\textsuperscript{1-3}, diffusion of charge carriers\textsuperscript{4,5}, and charge collection at each electrode\textsuperscript{6-8}. The nanomorphology of the blended film can be engineered via thermal and solvent annealing\textsuperscript{9,10} or the use of processing additives and so on, to achieve selective solubility\textsuperscript{11}. Effective manipulations may favorably influence the crystallization and orientation of the polymers\textsuperscript{12}.

Although spin-coating is the most appropriate laboratory-scale film formation process, scale-up of this process does not ensure uniformity, even within a device. This makes the spin-coating process incompatible with roll-to-roll (R2R) production under ambient conditions, where the latter is desirable for successful commercialization.

Furthermore, air processability of PSCs is a critical issue given that an inert environment is currently required for the entire process unless the devices are stable under ambient conditions. Although poly(3-hexylthiophene) (P3HT)-based devices exhibit good air processability due to reversible degradation by oxygen, highly efficient polymers containing the benzodithiophene (BDT) group, such as poly[[4,8-bis-(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl][3-fluoro-2-(2-ethylhexyl) carbonyl]thieno[3,4-b]thiophenediyl] (PTB7) and 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] (PTB7-Th), tend to undergo significant degradation on exposure to oxygen and light\textsuperscript{13-16}.

Here we propose a new approach to form high-quality organic films on an aqueous (water based) substrate under ambient conditions. A drop of organic material blended into a solvent, when dropped onto an aqueous surface, spreads spontaneously and rapidly by the Marangoni effect\textsuperscript{17,18}, leading to the rapid and uniform formation of an organic layer that can be functionalized on various substrates once transferred. Interestingly, the nanomorphology of blended films can be efficiently managed in seconds during the process of spreading on the aqueous substrate. We verify that the ultrafast solvent removal by the spontaneous spreading process can impede the infiltration of oxygen into the film via the remaining solvent effectively.

The utility of the films in functional devices is demonstrated by applying the new film formation technique to the fabrication of highly efficient PSCs. PTB7-based PSCs are successfully fabricated by exploiting the high-quality nanomorphology within the bulk heterojunction (BHJ) films. Last, we demonstrate the potential of our method as a scalable process by transferring the spontaneously spreading (SS) film from water surface to a large plastic substrate using a custom-made R2R process.

**Results**

Spontaneously spreading process of polymer solutions. When chemical agents with low surface energy (for example, hydrocarbon solvents or detergents) are dropped into high-surface-energy media (for example, water), local surface tension gradients occur on the boundary between the surrounding materials, leading to surficial flow toward regions of higher surface tension. This spontaneous spreading is called Marangoni flow\textsuperscript{17,18}. The spreading coefficient (S) dictates the speed of the spreading flow and is defined by the surface tensions at the three-phase contact line between a liquid droplet and liquid substrates\textsuperscript{19}, where $S = \gamma_{1} - \gamma_{2} - \gamma_{12}$ (\(\gamma_{1}\) and \(\gamma_{2}\) are the surface tensions of the base and polymer solutions, respectively, and \(\gamma_{12}\) is the interfacial surface tension of the two solutions). Figure 1a illustrates the different behaviours of the polymer solution depending on S when a drop of polymer solution is dropped on the base solution. The flow of the solution is determined by the net force direction of the surface tensions. If S is positive, that is, the surface tension of the base solution, \(\gamma_{1}\) (red arrow), is larger than the sum of \(\gamma_{2}\) (green arrow) and \(\gamma_{12}\) (blue arrow), the polymer solution will spread over the aqueous substrate surface and form a uniform polymer film. Otherwise, the polymer solution will ball on the aqueous substrate without dispersion.

The proportion $S^{1/2}$ describes the spreading speed of the solution\textsuperscript{20,21}, and the solution is unlikely to spread if S is negative. The spreading coefficients of 1,2-dichlorobenzene (o-DCB) and chlorobenzene (CB) are $-4.25$ and $2.35$ dyne cm\textsuperscript{-1}, respectively\textsuperscript{21,22}; thus only CB would exhibit spontaneous spreading flow on water. Dissolution of the solvent in water further accelerates drying and formation of the polymer films on aqueous substrates. Figure 1b illustrates the formation of a SS film on an aqueous substrate (here water is used as the aqueous substrate). (I) The polymer solution is dropped onto the aqueous substrate; (II) the solution quickly spreads (if S>0) over the aqueous surface within a few seconds; (III) because the solvents evaporate and dissolve into the liquid simultaneously, the drying process occurs instantaneously to form a thin solid polymer layer (the SS film) on the liquid; (IV) this thin film can readily be transferred to a variety of target substrates, for example, by stamping the substrates on the SS film gently (see Supplementary Movie 1, Supplementary Note 1 and Supplementary Fig. 1).

Because the photoactive films of polymer solar cells have dimensions below the wavelengths of visible light ($< \sim 200$ nm), control of the thickness within tens of nanometers is very important for achieving optimized performance\textsuperscript{23}. Herein, the SS film formation method is shown to be extremely reliable for controlling the thickness of polymer films over a wide range (tens to hundreds of nanometers). The ultimate thickness of organic films forming on water depends on the volume and concentration of the polymer solution, the size of the water bath, and the number of layers transferred (see Supplementary Note 2 and Supplementary Fig. 2a-d). PTB7:PC\textsubscript{70}BM solution was used for the thickness experiments.

Uniform and conformal transfer on various substrates. The SS films formed in the water bath exhibited controllable thickness and high uniformity over large areas. The SS-PTB7:PC\textsubscript{70}BM film was deposited in a square PET Petri dish ($12 \times 12$ cm$^2$), leading to a thickness of 43.9 $\pm$ 1.4 nm (see Supplementary Note 3 with Supplementary Figs 3 and 4) as determined from 16 positions on the substrate.

The SS films were also successfully transferred to various secondary substrates including polydimethylsiloxane (PDMS), polyethylene terephthalate (PET), paper, and the curved surface of a vial by the stamping method (Fig. 1c-f). An interference pattern was still apparent on the polyurethane (PU) substrate with sinusoidal gratings (period: 556 nm) after transfer of the SS film to the substrate (Supplementary Note 4; Supplementary Fig. 3b). Scanning electron microscope (SEM) images also confirmed successful formation of the SS films.

**Nanomorphology within BHJ films.** The universality of SS film formation was demonstrated by generating the SS films using several types of common polymers. AFM images (Supplementary Note 5 and Supplementary Fig. 6) show that poly(3-hexylthiophene-2,5-diyl) (P3HT), poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV), PTB7, and PTB7-Th formed uniform and smooth SS films. The SS phenomenon

*ARTICLE NATURE COMMUNICATIONS | DOI: 10.1038/ncomms12374 | www.nature.com/naturecommunications*
appeared to be uninfluenced by the presence of PC71BM and an additive such as DIO.

High-resolution transmission electron microscope analysis of the BHJ films was performed under the same defocused imaging conditions (10 μm) to compare the domain sizes of PTB7 (refs 24,25). To fabricate top--down transmission electron microscope (TEM) samples, the SS-PTB7:PC71BM film was directly transferred to 300 mesh copper TEM grids, while the spin-coated (SC-)PTB7:PC71BM films (air and N2) were floated on deionized water and transferred. To highlight the PC71BM cluster domains (dark regions) and PTB7 crystallite domains (bright regions), the bright regions are coloured red (Supplementary Note 5; dark regions) and PTB7 crystallite domains (bright regions), the spreading coefficient, S. Positive S results in a uniform polymer film; otherwise, polymer drops aggregate; (b) Schematic illustrations of formation of an SS BHJ film on water and transfer to target substrates. Actual processing images are shown. (c-f) Transferred SS-PTB7:PC71BM films on various substrates: PDMS (c), PET (d), copy paper (e) and a curved surface of a vial (f).

Figure 1 | Principle and formation process of spontaneous spreading. (a) Spreading of polymer solution dropped onto the base solution is determined by the spreading coefficient, S. Positive S results in a uniform polymer film; otherwise, polymer drops aggregate; (b) Schematic illustrations of formation of an SS BHJ film on water and transfer to target substrates. Actual processing images are shown. (c-f) Transferred SS-PTB7:PC71BM films on various substrates: PDMS (c), PET (d), copy paper (e) and a curved surface of a vial (f).
three samples prepared at different times to exclude sample-to-sample variation and measurement error. The Raman peaks of the SS-PTB7:PC71BM film at 1,435 cm$^{-1}$ (C–C intra-ring stretch mode) and at 1,490 cm$^{-1}$ (symmetric C¼C stretch mode) were almost identical to those of the SC-films. The ratio of the intensity of the peaks of the C–C and C¼C modes ($I_{C–C}/I_{C¼C}$ of the SS film) increased from 0.46 to 0.49, and the full width at half maximum (FWHM) of the C¼C mode became narrower, reflecting the enhanced degree of molecular order of the PTB7 chains in the SS film.

Grazing-incidence wide-angle X-ray scattering (GIWAXS) was also used to verify enhanced crystallization and orientation of the molecules during the spontaneous spreading process. The intensity of the (010) scattering peak at 1.6 Å$^{-1}$ for the SS-PTB7:PC71BM film increased markedly compared with that of the SC-PTB7:PC71BM film (Fig. 2j–l), indicating enhanced face-on orientation of the PTB7 chains in relation to the substrate in the SS-PTB7:PC71BM film processed in air. The enhanced face-on orientation of the SS-PTB7 film is most likely due to the interplay of Van der Waals interaction from alkyl side chains and the attractive interactions occurring between the less hydrophobic backbone of PTB7 and the water surface38,39. The intensity ratio ($I_{out}/I_{in}$) of the out-of-plane to in-plane PTB7 lamellar peaks (100) at around 0.35 Å$^{-1}$ was also calculated for quantitative
analysis of the edge-on PTB7 lamellar to face-on crystallite ratio. The \( I_{\text{out}} / I_{\text{in}} \) ratio of the SS-PTB7:PC\(_{71}\)BM film was 3.96, whereas that of the SC-PTB7:PC\(_{71}\)BM film was 29.1, indicating a significantly lower degree of edge-on orientation.

Enhanced crystallization and orientation of the molecules in the SS-PTB7:PC\(_{71}\)BM film can affect the air stability of the film. The mass density of an organic thin film, which is determined by the degree of crystallinity, can alter the ability of chemical reactants to permeate to the reaction site of molecules. Enhanced molecular packing can also strengthen chemical bonds in the film due to more rigid and planar backbones, extending the regions of delocalization, leading to a chemically more robust film.

Air processability. The air stability of the films formed by various processes was evaluated based on the Raman spectra of the SC- and SS-PTB7:PC\(_{71}\)BM films obtained under 514 nm excitation. Raman peaks corresponding to phenylene-alkoxy (–R–O–) stretching (\(~1,250\) and \(~1,350\) cm\(^{-1}\)) and \(\text{C}–\text{C}\) stretching mode of the BDT group (\(~1,500\), \(~1,550\) cm\(^{-1}\) and \(~1,580\) cm\(^{-1}\)) were observed for the air-processed SC-PTB7:PC\(_{71}\)BM film (Supplementary Note 8; Supplementary Fig. 9). The intensity of these peaks was significantly lower than that of the peaks of the N\(_2\)-processed SC-PTB7:PC\(_{71}\)BM film. This suggests that oxygen that infiltrated into the film during the spin-coating and drying processes contributes to cleavage of the alkoxy groups and insertion of oxygen into the \(\text{C}–\text{C}\) bonds in the backbone, resulting in disruption of the \(\pi\)-conjugation. This is consistent with the decreased and slightly blue-shifted absorption and photoluminescence of the air-processed SC-PTB7:PC\(_{71}\)BM film (Fig. 2h,e).

A survey scan using X-ray photoelectron spectroscopy (XPS) was also performed to confirm the air stability of the SS films. Figure 2i shows a considerable shift and peak broadening of the S2p peak for the air-processed SC-PTB7:PC\(_{71}\)BM film, which can be ascribed to chain scissions in the polymer backbone, or to loss of the side chains. The Cls spectrum of the air-processed SC-PTB7:PC\(_{71}\)BM film shows the emergence of a peak at 287 eV, derived from oxygenated carbon species, including a carboxyl group. In contrast, no detectable S2p peak broadening or Cls peak from oxygenated carbon species was observed for the SS-PTB7 and N\(_2\)-processed SC-PTB7 films (Fig. 2i). Surprisingly, no indication of degradation was observed for the SS-PTB7:PC\(_{71}\)BM films based on the XPS and Raman spectra (Fig. 2i; Supplementary Fig. 9) although the film was formed on water in air. For the air-processed SC-BHJ films, CB remaining between the polymer chains before complete drying may work as effective percolation pathways for diffusion of oxygen to the PTB7 molecules because of the significantly higher oxygen diffusivity of CB (1.16 \(\times\) 10\(^{-5}\) cm\(^2\) s\(^{-1}\)) than that of PTB7 (1.2 \(\times\) 10\(^{-8}\) cm\(^2\) s\(^{-1}\))

To examine the aftermath effects of remaining solvent on degradation of the BHJ films, the atomic ratio of oxygen to sulfur in the polymer films exposed to ambient conditions versus the drying time was probed by using XPS. Briefly, the BHJ films were spin-coated under N\(_2\) and subsequently exposed to air for different periods; finally, the films were completely dried in a N\(_2\)-filled glove box (Supplementary Note 9; Supplementary Fig. 10a). The films exposed to air for a longer time exhibited greater oxygen permeation with a broad distribution of oxygen in the films, implying that the CB molecules could provide pathways for oxygen diffusion into the BHJ film, as presented in Fig. 3a. In contrast, the O/S ratio and the atomic distribution of oxygen in SS-PTB7:PC\(_{71}\)BM film were comparable to that of the N\(_2\)-processed SC-PTB7:PC\(_{71}\)BM film, suggesting excellent air processability by the spontaneous spreading process (Supplementary Note 9; Supplementary Fig. 10b).

The effect of solvent (here, CB) on oxidation of polymer films was evaluated. DIO additive as a co-solvent was not considered because DIO molecules are steadily removed from films during the SS process due to greater specific gravity of DIO than water, as previously mentioned. The experiments, PTB7 only (that is, without fullerenes) films were prepared using different post-treatments. PTB7 films spun in nitrogen were treated under different conditions (Fig. 3a) before exposure to air for 3 h, that is, (i) as-spun without removal of solvent, (ii) thermally treated at 70 °C for 20 min. After exposure to air for 3 h, the intensity of the absorption peaks of the as-spun PTB7 film with excess solvent were considerably reduced (Fig. 3b), indicating degradation of the PTB7 polymer chains due to air exposure, as compared with the thermally treated PTB7 films. Moreover, the Raman peaks of the as-spun PTB7 film obtained under excitation at 514 nm were also significantly diminished relative to those of the other films, suggesting cleavage of the alkoxy groups and insertion of oxygen into the \(\text{C}–\text{C}\) bonds in the backbone (Fig. 3c). Oxygen within the three PTB7 films was tracked using time-of-flight secondary ion mass spectrometry (TOF-SIMS), as shown in the depth profile in Fig. 3d. Figure 3e–g shows the 3D iso-surface overlay of the intensity of the oxygen ion peaks (\(^{16}\)O and \(^{18}\)O). The intensity of oxygen near the surface of the as-spun PTB7 film was considerably higher than that of the thermally-treated PTB7 film (Fig. 3e–f), confirming that oxygen molecules penetrated the PTB7 film via the excess solvent between the PTB7 chains as explained above. In contrast, the oxygen intensity near the surface region of the SS-PTB7 film was comparable to that of the thermally treated film (Fig. 3f,g). In addition, performed studies on the effect of solvent on exposure to light and air on the oxidation of PTB7 films also suggest that oxygen adsorbed through the solvent path in the film during illumination in air contributes to accelerated disruption of the backbone conjugation of BDT group in PTB7 molecules.

It can be inferred that the spontaneous spreading process can induce rapid formation of a condensed and well-packed thin film due to the ultrafast solvent removal, which can prevent the intrusion of oxygen via the CB solvent, impeding oxidation and redistribution of the polymer and PC\(_{71}\)BM molecules in the BHJ film.

Photovoltaic performances. Polymer solar cells (hereafter, SS-PSCs) were fabricated to evaluate the applicability of the SS films to high-efficiency functional devices fabricated in air. For comparison with the SS-PSCs, SC-PSCs were fabricated under two different sets of environmental conditions, that is, in a N\(_2\) filled glove box (hereafter, SC-PSCs (N\(_2\))) and under ambient atmosphere (hereafter, SC-PSCs (air)). The air exposure time of the SC-PSCs (air) and SS-PSCs during the coating process in air was set to under 10 min. The post-drying process for the SC-PSCs (air and N\(_2\)) was performed in a N\(_2\) filled glove box (see Methods section). The device structure (Fig. 4a,e) was ITO/CBA (or ZnO)/PTB7 (or PTB7-Th):PC\(_{71}\)BM/Al (or MoO\(_3\)/Ag).

Figure 4b,f show the representative current density–voltage (\(J–V\)) characteristics of the SS-PSCs, SC-PSCs (N\(_2\)) and SC-PSCs (air) based on a mixture of PTB7:PC\(_{71}\)BM and PTB7-Th:PC\(_{71}\)BM. The SC-PSCs (air) exhibited much lower performance than the SS-PSCs and SC-PSCs (N\(_2\)), attributed to degradation of the air-processed BHJ films by oxidation as explained in relation to Fig. 2f.
The PCE of the PTB7-based SS-PSC was 6.27% (Table 1, Supplementary Note 12 and Supplementary Table 2), which is comparable to that of the SC-PSC (N₂; 6.21%). However, the PCE of the SC-PSCs (air) was significantly reduced (3.74%). The PCE of the PTB7-Th-based SS-PSC reached 8.44%, and this is the highest PCE reported for air-processed organic solar cells to date to the best of our knowledge. Details of the device performance are summarized in Table 1.

Both polymer-based SS-PSCs exhibited performance comparable to that of the SC-PSCs (N₂) with an almost identical spectral response in the external quantum efficiency (EQE) data (Fig. 4c,g). To evaluate the reliability of the SS-PSCs processed in air, statistical data for the PCEs of 30 PTB7 and PTB7-Th devices are presented in Fig. 4d,h and Supplementary Figs 13 and 14 with Supplementary Note 13, respectively.

We demonstrated the potential of our method as a scalable process by transferring the SS film to a large PET substrate using an R2R process. Figure 4i shows a SS-PTB7:PC71BM film on the water bath (30 cm × 120 cm² size), made by dropping only 200 μl of the polymer solution as a point source for spontaneous spreading (Supplementary Movie 2). After the solution spread, a 1 m long SS film was obtained in a few seconds. A custom-made R2R system was used to transfer the large SS film to the PET substrate (Fig. 4j). The SS-film was transferred successfully from the water surface to the PET substrate (Supplementary Movie 3). Figure 4k shows a PET film coated with a PTB7:PC71BM layer 60 nm thick. We anticipate that this new polymer film formation method will have great potential as a new process for R2R-processed modules with low material consumption and drying time, and consequently lower fabrication cost.

In summary, we developed an air-processable technique to form polymer films on an aqueous surface within a few seconds, using the spontaneous spreading phenomenon. Ultrafast removal of solvent during the process causes the films to have uniform and high-quality nanomorphology because oxygen diffuses into the polymer films rapidly through the remaining solvent between the polymer chains. Furthermore, the polymer films were successfully transferred onto various substrates. Finally, we demonstrated high performance of PSCs prepared using the proposed process, comparable to that of PSCs prepared by spin coating. We expect that this approach can be extended by roll-to-roll production to achieve high-quality films.

Methods
Preparation of the polymer solution. For the SC films, PTB7:PC71BM (1-Materials Nano-C) and PTB7-Th:PC71BM (1-Materials Nano-C) at a weight ratio of 1:1.5 were dissolved in chlorobenzene (CB):1,8-diiodooctane (DIO) (97:3 v/v) at 50°C. This mixture was stirred for 12 h under N₂. For the SS-films, PTB7:PC71BM
and PTB7-Th:PC71BM at a weight ratio of 1:1.5 were dissolved in 10 vol% of DIO in CB (CB:DIO = 90:10 v/v).

Solar cell fabrication for PTB7:PC71BM. PTB7:PC71BM PSCs were fabricated on ITO-deposited glass substrates ($R_{th}$ 22 ohm sq$^{-1}$). A layer of 4-chlorobenzoic acid (CBA, Sigma-Aldrich) as a hole transfer layer (HTL) was spun onto the substrates at 3,000 r.p.m. for 30 s; the substrates were then annealed at 70 °C for 5 min (ref. 50). Surplus molecules of CBA on the substrates were removed by spin coating with methanol at 6,000 r.p.m. for 30 s. Two layers of SS-PTB7:PC71BM films were transferred sequentially onto the substrates and dried at 70 °C for 10 min under N$_2$. SC-PTB7:PC71BM films were spun at 2,500 r.p.m. for 30 s and then dried at 70 °C for 10 min under N$_2$. Subsequently, bathocuproine (BCP, 8 nm) and Al (150 nm) were deposited through a shadow mask by thermal evaporation onto the devices$^{51}$.

Solar cell fabrication for PTB7-Th:PC71BM. PTB7-Th:PC71BM PSCs were fabricated on the same ITO glass substrates with PTB7:PC71BM PSCs. A layer of ZnO for electron transfer layer (ETL) was spun onto the substrates at 6,000 r.p.m. for 30 s, and the substrates were then annealed at 200 °C for 20 min (ref. 25). Two layers of SS-PTB7:PC71BM films were transferred sequentially onto the substrates. The SC-PTB7:PC71BM films were spun at 2,000 r.p.m. for 30 s. There was no additional drying process or annealing. Subsequently, MoO$_3$ (9 nm) and Ag (150 nm) were deposited through a shadow mask by thermal evaporation onto the devices$^{52}$.

### Table 1 | Representative photovoltaic performance parameters for SC- and SS-PSCs.

| PSCs    | Performance | SC-PSC (N$_2$) | SC-PSC (air) | SS-PSC (air) |
|---------|-------------|----------------|--------------|--------------|
| PTB7:PC71BM | PCE (%)     | 5.90 ± 0.27 (6.34) | 3.23 ± 0.25 (3.74) | 5.84 ± 0.25 (6.24) |
|         | $J_{sc}$ (mA cm$^{-2}$) | 14.22 ± 0.83 (15.71) | 12.27 ± 0.67 (13.28) | 14.71 ± 0.57 (15.45) |
|         | $V_{oc}$ (V)    | 0.74 ± 0.03 (0.77)    | 0.65 ± 0.03 (0.69)    | 0.74 ± 0.01 (0.76)    |
|         | FF            | 0.56 ± 0.03 (0.60)     | 0.42 ± 0.02 (0.46)     | 0.54 ± 0.02 (0.57)     |
| PTB7-Th:PC71BM | PCE (%)     | 8.41 ± 0.24 (8.86) | 5.89 ± 0.46 (6.29) | 7.95 ± 0.28 (8.44) |
|         | $J_{sc}$ (mA cm$^{-2}$) | 16.80 ± 0.27 (16.72) | 14.71 ± 0.84 (15.85) | 16.66 ± 0.34 (16.80) |
|         | $V_{oc}$ (V)    | 0.80 ± 0.01 (0.79)    | 0.78 ± 0.01 (0.79)    | 0.79 ± 0.01 (0.79)    |
|         | FF            | 0.63 ± 0.02 (0.67)     | 0.51 ± 0.03 (0.50)     | 0.60 ± 0.02 (0.64)     |

PSCs, polymer solar cells; PTB7, poly[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b’]dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl]]; SS, spontaneously spreading. Mean and s.d. are obtained from 30 devices. The values in brackets illustrate the best cell performance for each device.

**Figure 4** Fabrication of organic solar cells using SS films and potential for scalable process. (a,b) Device structure of n-PSC (PTB7:PC71BM) and i-PSC (PTB7-Th:PC71BM); (c–f) J–V characteristics and EQE spectra of PTB7-based (c,e) and PTB7-based PSCs (d,f) under AM 1.5G 100 mW cm$^{-2}$ illumination. (g,h) statistics for PCEs of 30 samples. (i) Formation of a single SS film on a large water bath (30 × 120 cm$^2$). (j) Homemade R2R coating system for large-scale transfer on flexible substrates. (k) 25 × 100 cm$^2$ PET film coated with a SS-PTB7:PC71BM film.
measurement system. The integrated response \( I_{p(\omega)} \) under the standard reference spectrum was compared with the \( I_{p(\omega)} \) value measured under the simulator, and they showed an \( \sim 2\% \) difference.

**Film analysis.** The surface morphology of the BHJ films was observed using atomic force microscopy in tapping mode under ambient conditions (AFM, Nanoman, Veeco) using a field emission scanning electron microscope (FE-SEM, FEI Sirion) and a field emission transmission electron microscope (FE-TEM, FEI Tecnai G2 30 S-Twin, 300 KeV). Photoluminescence quenching was evaluated for the SC- and SS-PTB7-PC71BM films with metal without metal electrodes using a Horiba Jobin Yvon NanoLog spectrophotometer. We performed the measurement with at least three samples to reduce the sample-to-sample variation and measurement error. The XPS and ultraviolet photoelectron spectroscopy spectra were recorded with a Sigma Probe (Thermo VG Scientific) instrument, using a micro-focused monochromatic Al X-ray source with a beam energy of 1486.74 eV and a takeoff angle of 45°. Raman spectra were obtained using a 2.4 μm-solid Raman system (LabRam HR spectrometer, JY Horiba). A 514 nm solid-state laser and a 633 nm He–Ne laser were used as the excitation light sources and were kept to less than 0.5 mW to prevent photo-degradation of the BHJ films. The laser was focused to a beam diameter of \( \sim 5\mu m \) on the sample using a \( \times 50 \) objective microscope lens. The Raman spectra were background corrected and obtained by averaging the spectra obtained from three different regions of each sample. The spectra from the different regions were almost the same, demonstrating the reliability of the results. We also confirmed the outcomes by measuring three samples prepared at different times. The spectral resolutions are within 0.2 cm\(^{-1}\) for the 514 and 633 nm excitations, respectively. GIWAXS measurements were performed using X-rays with a wavelength of \( \lambda = 1.54 \) Å at the 8C1 beam line of the Pohang Accelerator Laboratory. The 3D profiles of oxygen distribution in the PTB7 films were obtained using a TOF-SIMS 5 system (ION-TOF GmbH, Münster, Germany) equipped with a 30 KeV liquid metal ion gun and a time-of-flight mass spectrometer. To sputter the PTB7 film, a 1 KeV beam of 

**References**

1. Yang, X. N. *et al.* Nanoscale morphology of high-performance polymer solar cells. *Nano Lett.* 5, 579–583 (2005).
2. Bredas, J. L., Norton, J. E., Cornil, J. & Coropceanu, V. Molecular understanding of organic solar cells: the challenges. *Acc. Chem. Res.* 42, 1691–1699 (2009).
3. Lee, S.-H., Seo, J.-W. & Lee, J.-Y. Stable inverted small molecular organic solar cells using a p-doped optical spacer. *Adv. Funct. Mater.* 15, 2773–2782 (2015).
4. Dibb, G. F. P. *et al.* Influence of doping on charge carrier collection in normal and inverted geometry polymer: fullerene solar cells. *Sci. Rep.* 3, 3335 (2013).
5. Jeong, S. *et al.* Nanoprinting-induced nanomorphological transition in polymer solar cells: enhanced electrical and optical performance. *ACS Nano* 9, 2773–2782 (2015).
6. Lee, S.-H., Lee, J.-W. & Lee, J.-Y. Stable inverted small molecular organic solar cells using a p-doped optical spacer. *Nano Letters* 7, 157–165 (2015).
7. Capmany-Quiles, M. *et al.* Morphology evolution via self-organization and lateral and vertical diffusion in polymer: fullerene solar cell blends. *Nat. Mater.* 7, 158–164 (2008).
8. Li, G. *et al.* ‘Solvent annealing’ effect in polymer solar cells based on poly(3-alkylthiophene) and methanofullerenes. *Adv. Funct. Mater.* 17, 1636–1644 (2007).
9. Li, G. *et al.* Efficiency enhancement in low-bandgap polymer solar cells by processing with alkane dithiols. *Nat. Mater.* 6, 497–500 (2007).
10. Hammond, M. R. *et al.* Molecular order in high-efficiency polymer:fullerene Bulk heterojunction solar cells. *ACS Nano* 5, 8245–8257 (2011).
11. Norrman, K., Madsen, M. V., Vegygorov, S. A. & Krebs, F. C. Degradation patterns in water and oxygen of an inverted polymer solar cell. *J. Am. Chem. Soc.* 132, 1683–1690 (2010).
12. Alam, S. *et al.* Degradation mechanism of benzothiadiazole-based conjugated polymers when exposed to light in air. *ACS Appl. Mater. Inter.* 4, 2993–2998 (2012).
45. Kim, J. et al. Efficient charge extraction in thick bulk heterojunction solar cells through infiltrated diffusion doping. Adv. Energy Mater. 4, 1301502 (2014).
46. Eckenfelder, W. W., Bowers, A. R. & Roth, J. A. Chemical Oxidation: Technologies for the Nineties. 1–334 (Technomic, 1997).
47. Shoaei, S. & Durrant, J. R. Oxygen diffusion dynamics in organic semiconductor films. J. Mater. Chem. C 3, 10079–10084 (2015).
48. Jorgensen, M., Norrman, K. & Krebs, F. C. Stability/degradation of polymer solar cells. Sol. Energy Mater. Sol. Cells 92, 686–714 (2008).
49. Seemann, A., Egelhaaf, H.-J., Brabec, C. J. & Hauch, J. A. Influence of oxygen on semitransparent organic solar cells with gas permeable electrodes. Org. Electron. 10, 1424–1428 (2009).
50. Choi, H., Kim, H.-B., Ko, S.-J., Kim, J. Y. & Heeger, A. J. An organic surface modifier to produce a high work function transparent electrode for high performance polymer solar cells. Adv. Mater. 27, 892–896 (2015).
51. Chu, T.-Y. et al. Morphology control in polycarbazole based bulk heterojunction solar cells and its impact on device performance. Appl. Phys. Lett. 98, 253301 (2011).
52. Chang, Y.-M. & Leu, C.-Y. Conjugated polyelectrolyte and zinc oxide stacked structure as an interlayer in highly efficient and stable organic photovoltaic cells. J. Mater. Chem. A 1, 6446–6451 (2013).

Acknowledgements
This work was supported by a National Research Foundation of Korea (NRF) grant funded by the Korean Government (MSIP; no. NRF-2015R1A2A2001006689 and no. NRF-2015M1A2A2057509). We gratefully acknowledge support from the EEWS Research Project of the office of the KAIST EEWS Initiative (EEWS-2016-N11160015). We thank Changyeon Lee for GIWAXS measurement.

Author contributions
J.N., S.J. and J.L. conceived and designed the experiments and prepared the manuscript. J.N. and S.J. fabricated the spontaneous spreading films and solar cells, and performed PCE and QE measurements. S.J. analysed organic films using SEM, TEM, ToF-SIMS and XPS. J.N. designed the R2R machine and performed the large-scale transfers of the organic thin films. All authors discussed the results and commented on the manuscript.

Additional Information
Supplementary Information accompanies this paper at http://www.nature.com/naturecommunications

Competing financial interests: The authors declare no competing financial interests.

Reprints and permission information is available online at http://npg.nature.com/reprintsandpermissions/

How to cite this article: Noh, J. et al. Ultrafast formation of air-processable and high-quality polymer films on an aqueous substrate. Nat. Commun. 7:12374 doi: 10.1038/ncomms12374 (2016).

This work is licensed under a Creative Commons Attribution 4.0 International License. The images or other third party material in this article are included in the article's Creative Commons license, unless indicated otherwise in the credit line; if the material is not included under the Creative Commons license, users will need to obtain permission from the license holder to reproduce the material. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/

© The Author(s) 2016