

Modulating the Mixing Gibbs Free Energy to Enhance Solid–Liquid Phase Separation for High-Performance Organic Solar Cells

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Organic solar cells (OSC) feature a hierarchical structure with the electron donor/acceptor layer sandwiched by anode and cathode, which raises the importance of controlling the molecular crystal orientation, domain size, and vertical distribution to facilitate the charge collection at electrodes. However, the similar conjugated backbone of donor/acceptor material and fast film-formation kinetics have led to spinodal-decomposition-orientated phase separation that result in the film presenting an intimately mixed morphology and random molecular orientation. To solve the issue, the mixing Gibbs free energy-triggered solid–liquid phase separation during the film formation process is enhanced by solidifying one component and solvating the other based on a liquid additive. Following the liquid evaporation process, a favorable vertical distribution is obtained. Meanwhile, the prolonged solvation process enlarges the domain size and assists the molecules to diffuse and orient properly, enabling better exciton/charge dynamics during the power conversion processes. As a result, the fabricated devices exhibit a fill factor over 80% and an efficiency of 18.72%, which is one of the top efficiencies for binary OSCs. Insights and a methodology is provided here to manipulate the organic donor/acceptor phase separation in terms of mixing Gibbs free energy.

donor and acceptor in OSCs. There have been suggestions that a domain size of around 20 nm shall be achieved to balance the exciton diffusion and charge transportation due to limited exciton diffusion length in donor and acceptor domains (≈ 10 nm).^[4] However, the state-of-the-art nonfullerene acceptors (NFAs) can achieve exciton diffusion length over 30 nm and it is over 20 nm for some donors such as D18-Cl,^[5,6] indicating bigger domain sizes are more favorable and beneficial for the device performance. Unfortunately, most of high-performance organic active layers especially bulk-heterojunction blend layers are made from spin-coating process with chloroform (CF) as solvent, the phase separation is limited at very early stage due to the fast kinetic of spin-coating and low boiling point of chloroform.^[7,8] In addition, the high-efficiency donors and acceptors have similar large conjugated backbone, which endows them a strong molecular interaction and therefore they

tend to phase separate via spinodal decomposition. As a consequence, the donor and acceptor intimately intermixed with each other at random orientation, leading to charge recombination and poorer performance.

Encouragingly, various approaches such as additive, sequential deposition, solvent vapor annealing, and thermal annealing have been successfully demonstrated to tune the morphology.^[9–14] Among them, additive that incorporates small

1. Introduction

Organic solar cells (OSCs) as an emerging photovoltaic technology arouse wide interest due to the colorfulness, light weight, unique mechanical properties, solution processability, etc.^[1–3] With electron donor and acceptor domains in active layer serve together to convert solar energy to electrical output, it is of critical importance to control the positions and sizes of

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amount of solid or liquid materials have been proven simple, controllable, and powerful to ameliorate the phase separation in active layer. Recently, solid additive that will volatilize after thermal annealing have attracted marvelous attention to tune the molecular stacking, crystallization, and other properties.^[14–16] Compared to that, liquid additive features the unique advantage of solvent-assisted donor/acceptor demixing, which certainly is more efficient for the molecules to diffuse or orient and also prolongs the phase separation process. For example, our group has previously shown that liquid additive 1-chloronaphthalene will further assist the acceptor to diffuse even after the main solvent is vaporized.^[17] Since OSCs are sandwich-structured with the active layer encapped by the anode and cathode (buffer layer), it is more favorable for donors and acceptors to enrich near anode and cathode, respectively, to facilitate charge collection. Liquid additives offer an exceptional chance to achieve the above target because it is feasible to selectively solvate one component to promote its further diffusion and orientation, i.e., solid–liquid (S-L) phase separation. Therefore, it is deduced that, by tuning S-L phase separation during the film formation, a suitable vertical distribution can be obtained.

General criteria for liquid additive such as high boiling point and selectively stronger interaction with donor/acceptor have been proposed in both fullerene and nonfullerene OSCs.^[18–20] During solvent vaporization, the high boiling point additive will remain and become more concentrated, combined with the selective solvation, it can promote phase separation and molecular crystallization. For example, Chen et al. reported that diiodomethane liquid additive can selectively solvate the NFA, leading to much better microstructure and improved efficiency.^[20] However, the additive selection is still tedious and normally result-oriented. Ternary phase diagram have been applied to calculate the phase separation behavior in fullerene-based OSCs in terms of Gibbs free energy.^[7,8,21,22] Upon mixing the components (polymer/fullerene/solvent) with different ratios, the free energy in the system is likely to change (endothermic or exothermic). The system will evolve toward the lowest mixing energy state, which is normally donor/acceptor-separated morphology. Donor/acceptor phase separation will happen in this process. For example, Schoot's group has forecasted the phase separation behavior of systems contain different fullerenes, polymers, and solvents.^[8] Since this tool can calculate the thermodynamically stable state of the mixed organic solids and solvent liquid, it is therefore very powerful to evaluate the S-L phase separation of a system and thus guide the additive selection.

In this work, the mixing Gibbs free energy-triggered phase separation behavior is revisited and employed to direct the S-L demixing in a representative nonfullerene binary OSC system, D18-Cl:N3 (full names in the experimental section). At first, we experimentally probe the exciton diffusion length of D18-Cl and N3 to be 27.3 and 43.2 nm, respectively. However, the strong donor/acceptor interaction and fast film-formation kinetics has enabled the bulk-heterojunction film with small phase/domain size (<20 nm) and polycrystalline feature, which intensively mismatches with such long exciton diffusion length and leads to strong charge recombination. To solve the issues, we propose to alter the phase separation behavior from original L-L demixing to S-L demixing during the film formation process

to prolong the phase separation and assist the molecules to further orient. Through analyzing the ternary mixing energy diagram of liquid/D18-Cl/N3, we identify a liquid additive to enable a pronounced and unique S-L phase separation. The direct results of such S-L phase separation are the enlarged phase domains, favorable vertical distribution and significantly ordered crystal orientation, which contributes to a high fill factor (FF) of >80%. The corresponding device power conversion efficiency (PCE) reaches 18.72% with a short-circuit current density (J_{sc}) of 27.30 mA cm⁻² and open-circuit voltage (V_{oc}) of 0.854 V. Importantly, the better light stability is also captured in the more phase-separated device. This work optimizes donor/acceptor vertical distribution and orientation by enhancing the S-L phase separation via a predictable method for realizing high-performance and stable OSCs.

2. Result and Discussion

As mentioned, donor/acceptor phase separation plays an essential role in the device performance. Since it is closely related to the exciton diffusion length (L_D) of the employed materials, we first measure the L_D of singlet excitons in a high-performance donor/NFA system, D18-Cl:N3, as an example. L_D can be determined by $L_D = (D\tau)^{1/2}$, where D and τ represent the diffusion constant and intrinsic exciton lifetime, respectively.^[6] The detailed measurement and calculation are provided in the Supporting Information.^[6,23,24] Due to the high diffusion constant and long exciton lifetime (Table S1, Supporting Information), a long L_D of 27.3 and 43.2 nm for D18-Cl and N3 are characterized (Figure 1a,b), suggesting a rather big phase separation shall be achieved in the blend. However, the D18-Cl:N3 blend presents an intimately mixed morphology with phase/domain size <20 nm (Figures 1c and 3a) when spin-coated from chloroform solution because of the strong donor/acceptor interaction and fast kinetic of chloroform spin-coating process, which counters the measured long L_D and leads to charge recombination.

To monitor the phase separation during the film formation, we then calculate the mixing Gibbs free energy of D18-Cl, N3, and chloroform system, the detailed calculation is stated in the Supporting Information. Figure 1d shows the mixing energy of D18-Cl, N3, and chloroform with different ratios (in the form of $\Delta G/RT$). The corresponding tie line figure is shown in Figure S3 in the Supporting Information. It is clear that blending D18-Cl, N3, and chloroform is an endothermic process, suggesting the dissolution of D18-Cl and N3 in chloroform is thermodynamically favorable. When the volume ratio of chloroform resides between 0.2 and 0.5, there is more heat released. The yellowish dashed line in Figure 1d shows the mixing energy with different chloroform ratios under a fixed donor/acceptor volume proportion of 1:1.33, which is set to monitor the evolution of solvent evaporation process. The pink tie line connects the compositions with equal chemical potential. The crossing point of yellow and pink lines presents at the composition of (0.302, 0.398, 0.300), correlates to the (solvent, acceptor, donor) volume ratio. Since the mixing energy at this point is higher than the total energy of the coexisting phases at the two ends of the pink tie line, the system will evolve toward the coexisting phases as directed by the grey arrows.

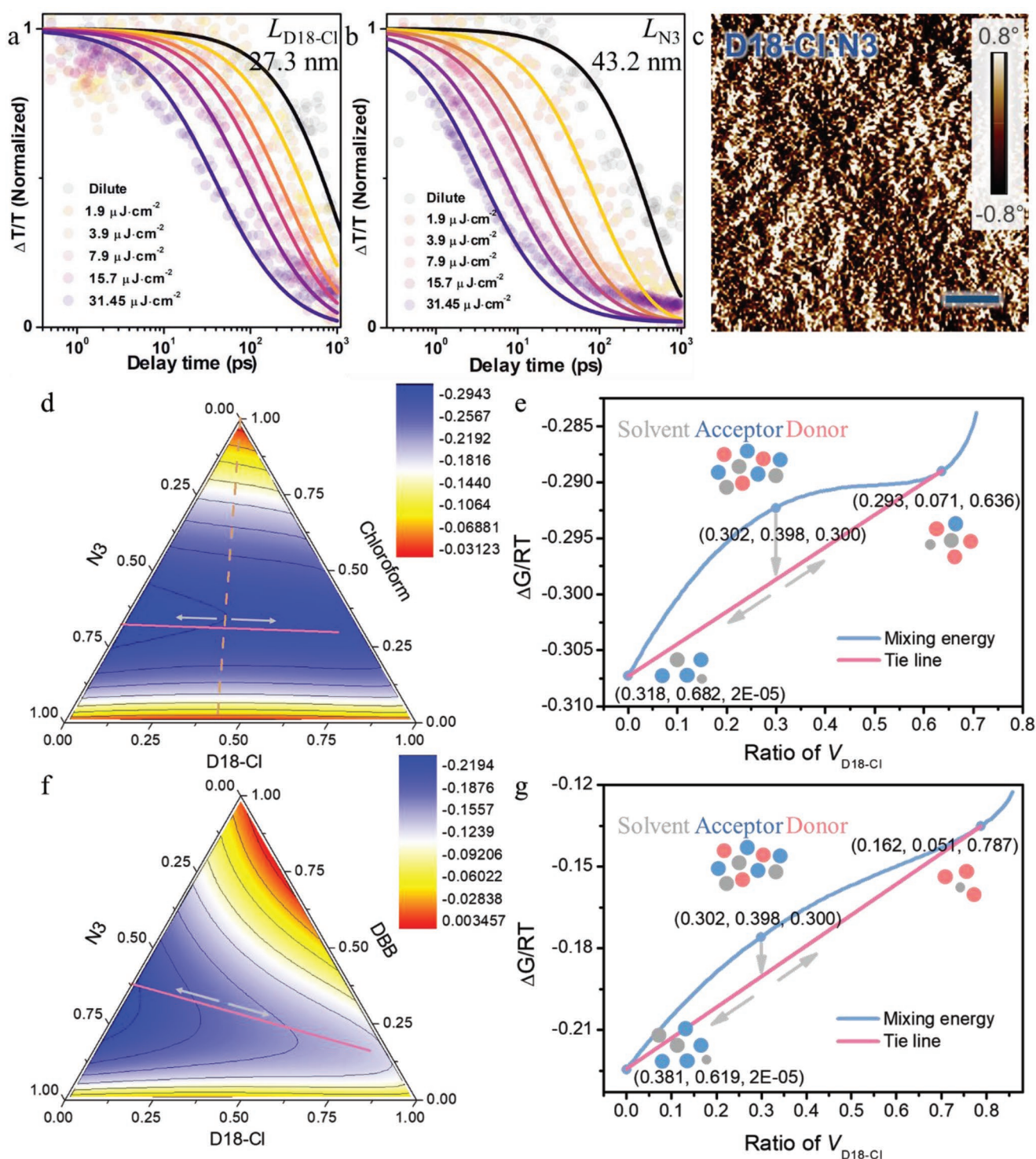


Figure 1. Normalized transient absorption kinetics at different excitation fluences a) D18-Cl and b) N3. The dilute curves are obtained from the corresponding polystyrene blended films. c) The AFM phase image of D18-Cl:N3 blend film processed from chloroform by spin-coating process. The mixing Gibbs free energy of different components d) D18-Cl:N3:CF and f) D18-Cl:N3:DBB. The Gibbs free energy along the pink tie lines in the ternary diagram projected on the $V_{\text{D18-Cl}}$ scale e) D18-Cl:N3:CF and g) D18-Cl:N3:DBB.

To better demonstrate this process, Figure 1e exhibits the mixing energy along the pink tie line that projected on $V_{\text{D18-Cl}}$ scale (mixing energy vs $V_{\text{D18-Cl}}$). When we mix chloroform,

N3 and D18-Cl at a volume ratio of $1^*(0.302, 0.398, 0.300)$, the mixing energy is high. Assuming chloroform do not vaporize, the system tends to separate into two equilibrium phases with

approximate volume ratio of $0.515 \times (0.318, 0.682, 2 \times 10^{-5})$ and $0.472 \times (0.293, 0.071, 0.636)$ based on the law of conservation of mass. Energy will be further released during the phase separation process to a more stable state. It is apparent that one of the phases is acceptor-rich phase while the other is donor-rich phase. The first phase has a V_{CF} of 0.318 and V_{N3} of 0.682, while the second phase has a V_{CF} of 0.293 and V_{D18-Cl} of 0.636. The solvent CF has a similar volume ratio in the two phases (0.318 vs 0.293), which means it will fairly solvate the donor and acceptor. They will phase separate via two liquids model, Liquid (acceptor)–Liquid (donor). L-L demixing may hinder the phase separation particularly donor/acceptor vertical separation under fast film-formation kinetics endowed by the spin-coating deposition and low-boiling solvent. Therefore, it is necessary to trigger S-L demixing in current OSC system to promote more liquid resides in one of the components and subsequently better vertical distribution.

In a conventional structured device with the cathode on top and anode on substrate side, we need the liquid that has stronger interaction with the acceptor to facilitate the acceptor enriching at the top cathode region. From Flory–Huggins theory, the interaction parameters between a nonpolar solvent and nonpolar polymer could be estimated by the following equation^[25,26]

$$\chi_{12} = \frac{V}{RT}(\delta_1 - \delta_2)^2 + \chi_s \quad (1)$$

A lower χ value suggests a stronger interaction. The first and second term in the right of the equation are enthalpic and entropic component, respectively. 0.34 is normally adopted for the entropic term, χ_s .^[7,26] V represents the molar volume of one solvent molecule. R , T , and δ stands for ideal gas constant, Kelvin temperature, and solubility parameters, respectively. The δ value for D18-Cl and N3 are 17.94 and 19.48 MPa^{1/2}, which are evaluated from experimentally determined surface tension value, details are exhibited in Figure S1 and Tables S2 and S3 in the Supporting Information. δ value for chloroform is 18.95, which is located in between D18-Cl and N3. Therefore, it is rather difficult to reserve much more chloroform in N3. After evaluating different low-polar liquids from the solubility point of view, we pay our attention to 1,2-dibromobenzene (DBB). In details, it shows a δ of 22.33 MPa^{1/2}, which is far away from δ_{D18-Cl} and close to δ_{N3} . Notably, the solubility parameter is tightly related to dispersion (δ_D), polarity (δ_P), and hydrogen bonding (δ_H) properties of a liquid, the corresponding values of the additive should be similar to the main solvent to ensure proper miscibility with the main solvent. DBB presents a suitable δ_D , δ_P , and δ_H of 20.7, 6.5, and 5.3 MPa^{1/2}, respectively, which is close to that of chloroform (17.8, 3.1, and 5.7 MPa^{1/2}). Therefore, we identify DBB to conduct the following demonstration.

The mixing energy ternary diagram of DBB, N3, and D18-Cl is plotted in Figure 1f. Compared to chloroform, the overall mixing energy of DBB plot is higher because DBB is less miscible with the donor/acceptor. Now if we mix DBB, N3, and D18-Cl at the same volume ratio of $1 \times (0.302, 0.398, 0.300)$, the system tends to separate into two equilibrium phases with volume ratio of $0.630 \times (0.381, 0.619, 2 \times 10^{-5})$ and $0.381 \times (0.162,$

$0.051, 0.787)$. Apparently, there is more liquid goes to the acceptor-rich phase, and the donor phase is closer to pure solid donor, which fits the S-L phase separation feature.

To verify the S-L separation and experimentally monitor the donor/acceptor phase separation during spin-coating process, we have conducted time-resolved in situ ultraviolet visible (UV-vis) absorption spectroscopy. Additionally, to better understand that it is the liquidity of the additive triggers the S-L phase separation, we select a volatile solid additive, 1,2,3-trichlorobenzene (TCB), that has similar physical properties to the liquid DBB including boiling point, dipole moment, accessible molecular area and volume to conduct parallel experiments. More details about the additive properties including volatility are provided in Figures S4 and S5 and Table S4 in the Supporting Information. As shown in the in situ UV-vis spectra (Figure 2a–c), all samples experienced a sharp transformation from solution to solid film within 2 s and finally exhibit two broad peaks at around 450–600 and 650–850, corresponding to donor and acceptor absorption peak, respectively. The spectrum of the sample without additive (no additive, NA) shows almost no change with the prolonging of spinning time. Similarly, the solid TCB case presents a very slight intensity weakening in the early spinning stage (3–5 s) at the absorption onset of acceptor peak (≈ 850 nm), which is ascribed to be the volatilization of solid TCB. Differently, in the liquid DBB sample, a much more pronounced and prolonged intensity weakening of the absorption onset is captured as indicated by the orange arrow. Intuitively, the peak becomes sharper with less absorption tail while the peak position remains unchanged. Such peak sharpening appears when the solution evolves toward solid film (Figure S6, Supporting Information) and is induced by the more ordered molecular stacking during the liquid evaporation. We further track the sample after spin-coating process for 300 min at D18-Cl (500–550 nm) and N3 (830–880) absorption edge in Figure 2d. The full spectrum is provided in Figure S7 in the Supporting Information. As expected, the absorption edge in NA and solid TCB samples remain overlapped for both donor and acceptor in different times. Interestingly, in liquid DBB case, the absorption edge keeps shrinking toward the peak center, and the acceptor absorption evolves more than the donor (5 nm over 3 nm at the half maximum) as indicated by the arrow, which supplements that more liquid additive goes to the acceptor domain. To further verify it, we carry out in situ absorption of the film for spinning about 3 s where the main solvent is vaporized (Figure 2a) and more liquid additive exists compared to that of 30 s. The donor peak of 3 s sample shows almost no change with time goes by while the acceptor absorption edge presents a more significant evolution (≈ 7 nm at the half maximum), which indicates the DBB mostly solvates the acceptor and leave the donor unchanged as solid. Overall, the results affirm that the liquid additive DBB successfully promotes the S-L phase separation in the organic layer formation process, which is unique compared to the NA and solid TCB samples. Further to the S-L phase separation, Figure 3e shows the atomic force microscopy (AFM) phase image of films with different additive ratios, which confirms the wide tunability of phase domain sizes by the liquid additive. The corresponding AFM height images are provided in Figure S8 in the Supporting Information.

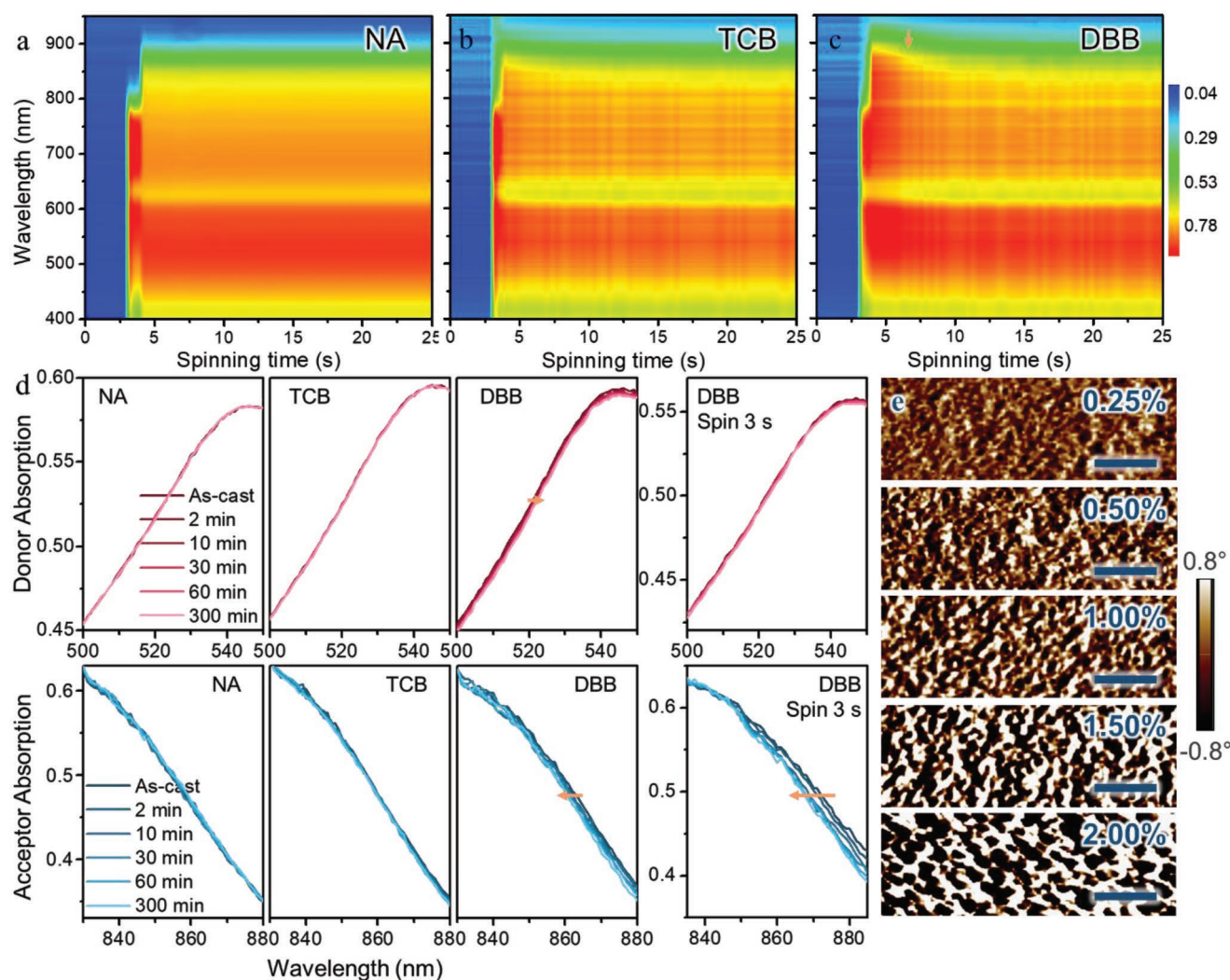


Figure 2. The in situ UV-vis absorption spectra of a) NA, b) TCB, and c) DBB. They share the same time scale and wavelength scale. d) The edge evolution of the donor/acceptor absorption peak after spin coating. Unless specified, all the other spin-coating conditions are 2200 rpm and 30 s. e) The AFM phase images of the active layer with different liquid additive (DBB) ratios. The scale bar is 1 μm.

Next step is to investigate the consequences brought by the S-L phase separation, which will be interpreted in terms of crystallization behavior, vertical distribution, and device physics study. As shown in Figure 3a–c, the transmission electron microscopy (TEM) images of all films show fibril morphology with NA film presenting an intimately mixed morphology. However, bigger domains with high contrast in the DBB film are clearly captured. The morphology is also probed by AFM. NA and TCB film exhibit small root mean square roughness (R_{RMS}) of 0.950 and 0.949 nm, respectively, while the liquid-additive film displays sharper contrast and slightly higher roughness of 1.189, which is similar to the TEM images. The corresponding phase images are displayed Figure S9 in the Supporting Information, of which the histogram information is extracted and plotted in Figure 3d. The AFM phase images provide the phase shift information, which could be used to discriminate different materials by the phase contrast. In Figure 3d, NA and TCB samples present a broad peak at 0° while the DBB sample shows almost two peaks located in about $\pm 0.15^\circ$, suggesting the

existence of two separated phases in the DBB sample. To make detailed comparison, we have extracted the line profiles from the AFM phase images of the samples with higher resolution.^[6] The full-width half-maximum of the peaks are shown in Figure S10 in the Supporting Information. The calculated average values are 17.27, 21.00, and 28.79 nm for NA, TCB, and DBB samples, respectively, confirming that DBB liquid additive enables bigger phase domain size. We also probe the molecular stacking information by grazing-incidence wide-angle X-ray scattering measurement (GIWAXS). All samples show pronounced (010) π - π diffraction and (100) lamellar stacking peaks at out-of-plane ((OOP), $1.727 \text{ \AA}^{-1}$) and in-plane ((IP), $0.297 \text{ \AA}^{-1}$) direction, respectively, suggesting the preferred “face-on” orientation.^[27–29] However, the NA film shows three rings in the 2D image at the Q of around 1.98, 1.75, and $1.55 \text{ \AA}^{-1}$ as directed by the yellow arrows, indicating randomly oriented molecules.^[30] The polycrystalline feature is also seen in some other blends and NFAs,^[31,32] which is ascribed to small molecule crystals (here is the NFA, N3). The results coincide with the observed spinodal decomposition at

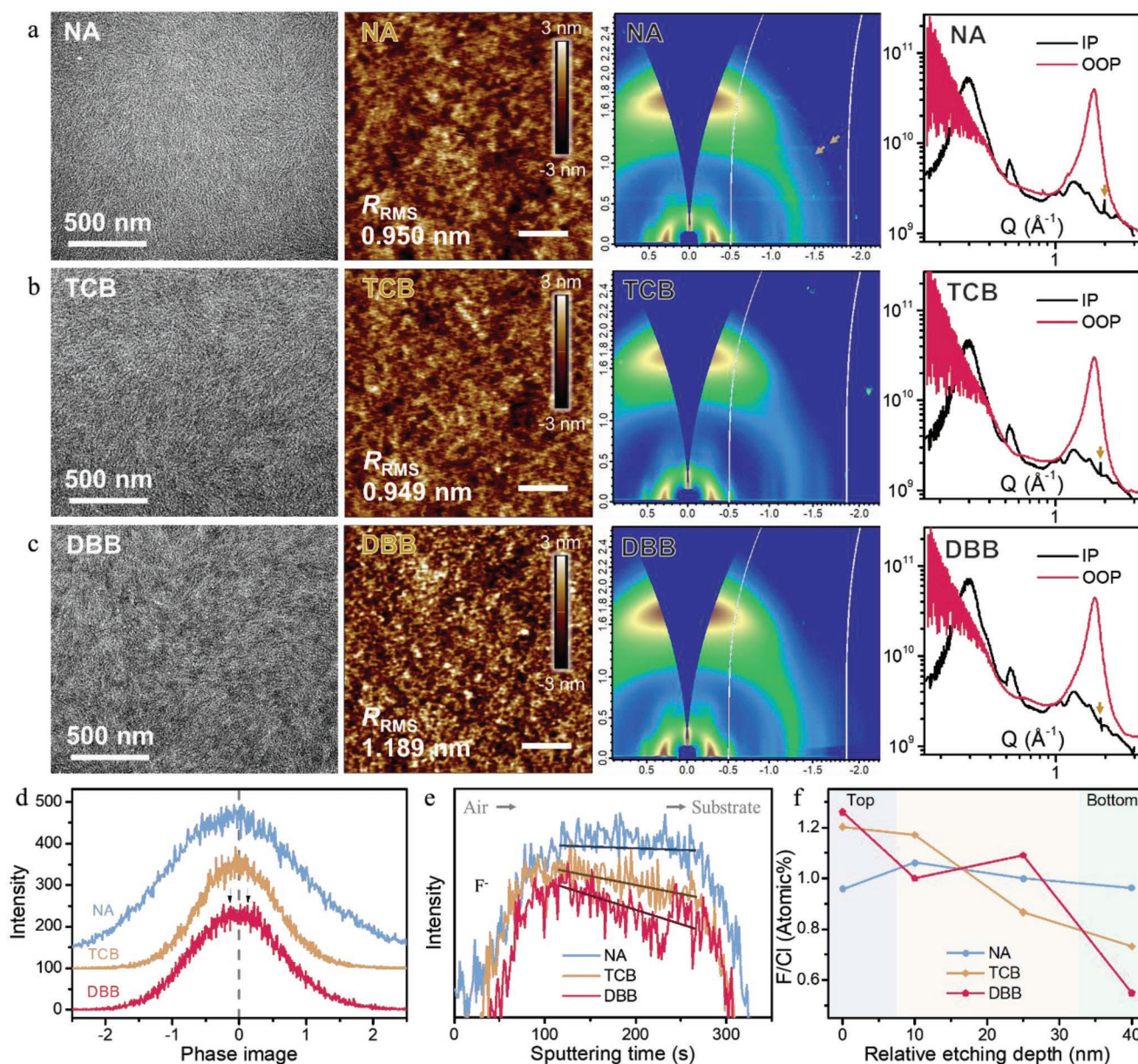


Figure 3. The TEM, AFM height, GIWAXS, and 1D line-cut figures (from left to right) of a) NA, b) TCB, and c) DBB. d) The extracted histogram profiles from the AFM phase images of different films. e) The F^- ion ToF-SIMS profile of different samples. f) F/Cl atomic% in different etching depths from depth-profile XPS measurement. The etching depth is calibrated by Ta_2O_5 and the depth is relative to Ta_2O_5 etching depth, 0.25 nm s^{-1} . The results here are obtained from films with optimized additive ratios (TCB, 52.9 wt% to acceptor; DBB, 0.5 vol% to main solvent).

early stage for NA sample, as the molecules have not fully orientated during the fast spin-coating process. Such polycrystalline feature is not detectable in the 2D images of solid and liquid additive sample. In the 1D line-cut profile, the most conspicuous difference comes from the diffraction peak at $1.981 \text{ \AA}^{-1}$ for NA sample (the polycrystalline ring in 2D image). In TCB sample, the peak shifts to $1.879 \text{ \AA}^{-1}$, while it significantly vanishes in the DBB samples. The possible reason could be that this is an intermediate scattering feature induced by the fast film-formation kinetics. The less volatile additive helps the small molecules to further diffuse, and the small acceptor crystals are redissolved and merged into the main domains, leading to the weakening

of this scattering feature. Further characterizations and analysis are needed to uncover the reasons behind. Importantly, the disappearance of polycrystalline feature clearly shows that the liquid additive promotes the crystal orientation during the S-L phase separation process.

To supplement the crystallization profile and horizontal phase separation, we characterize the donor/acceptor vertical separation by time-of-flight secondary ion mass spectrometry (ToF-SIMS). Figure S11 in the Supporting Information plots the ion intensity versus sputtering time of the NA sample with the configuration of glass/indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS)/Active

layer. F^- and Cl^- are characteristic ions that belong to acceptor (N3) and donor (D18-Cl), respectively. It shows a hierarchical structure with the F^- (Cl^-), $^{34}S^-$ and InO^- indexed to the active layer, PEDOT:PSS and ITO, respectively. In the NA film (Figure S11a, Supporting Information), F^- and Cl^- exhibit stable signal in the bulk region and suggest a uniform distribution in the vertical direction. The F^- signal (acceptor) of the three samples are extracted and compared together in Figure 3e. The straight lines connect the two points at around 116 and 265 s by averaging ten data points at corresponding regions to indicate the element vertical evolution in the bulk area. From top surface to the bottom, F^- evenly spreads in the NA samples, and a significant declining trend is formed in the DBB sample, which affirms a prominent vertical phase separation with more acceptor at the top surface. Notably, the Cl^- profile of all samples shows a relatively flat trend from top surface to bottom (Figure S11d, Supporting Information), which could be ascribed to that the additive mostly solvate the acceptor (N3) and the polymer D18-Cl is too bulky to be moved. To further support the conclusion about donor/acceptor vertical distribution, we have conducted depth-profile X-ray photoelectron spectroscopy (XPS) on the films. The samples are probed on surfaces after etching different thicknesses (relative etching depth). The atomic ratio (atomic%) of F and Cl in different depths are listed in Table S5 in the Supporting Information. F/Cl atomic% is extracted and plotted in Figure 3f to indicate the acceptor/donor

ratio change in different depths, the corresponding XPS survey spectra are shown in Figure S12 in the Supporting Information. In Figure 3f, the F/Cl ratio in NA sample is similar at different depths, suggesting a uniform distribution of donor and acceptor. In DBB sample, the F/Cl ratio decreases from 1.26 at 0 nm to 0.55 at 40 nm relative depth, supporting that acceptor/donor ratio is decreasing from top to bottom of the film, which is in consistent with the ToF-SIMS measurement. To sum up, we have shown that the active layer without additive tend to phase separate via L-L demixing to form uniformly distributed, randomly orientated and well-intermixed morphology. A proper liquid additive triggers pronounced S-L phase separation during solution casting process, which will promote the horizontal and vertical donor/acceptor separation and facilitate their crystal orientation in the bulk film.

Next step is to monitor the photo and electrical properties of the films and devices correlating to the morphological evolution. Transient absorption (TA) is performed for all samples to investigate the exciton and carrier transfer dynamic in the active layers. Figure 4a shows the TA spectra of DBB sample and Figure S13 in the Supporting Information displays the TA contour plots of neat D18-Cl, N3 and blend films at different wavelengths after different delay times. Upon excitation of the films at 750 nm (exciting the acceptor), the TA spectra present a positive ground state bleach (GSB) band and negative excited state absorption (ESA) band at around 850 and 930 nm,

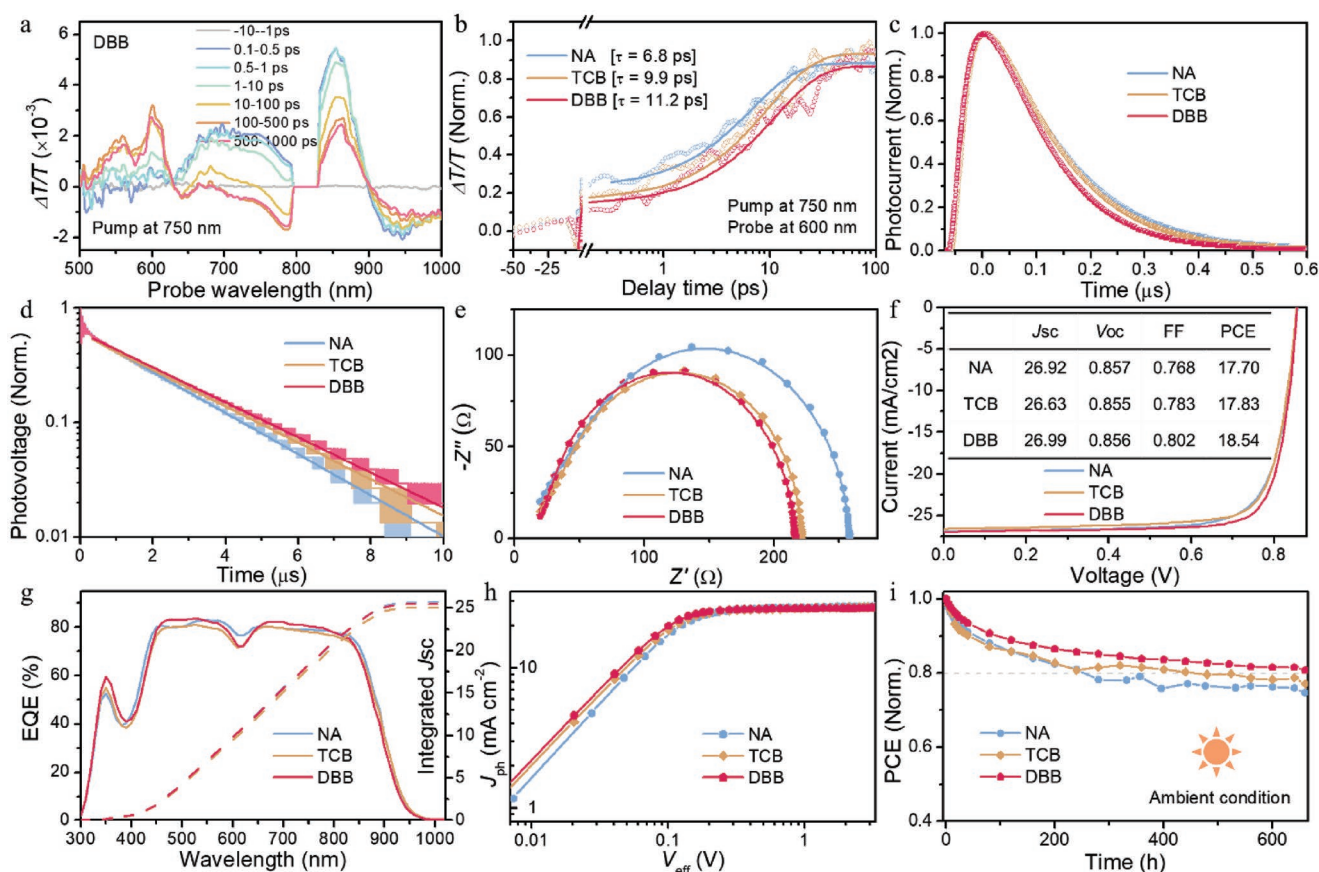


Figure 4. a) TA spectra of DBB sample at different delay times. The b) TA kinetics, c) TPC, d) TPV, e) EIS, f) J - V curves, g) EQE spectra, h) photocurrent verse effective voltage curve, and i) stability test under continuous light illumination at ambient condition of NA, solid TCB, and liquid DBB samples.

respectively, which starts to decay with the increasing delay time. In the blended samples, following the decay of N3 (GSB and ESA signal), a positive peak ascribed to the GSB of D18-Cl at ≈ 600 nm emerges within several picosecond and persists up to 1000 ps, which affirms the hole transfer from acceptor to donor phase.^[33,34] Figure 4b shows the TA traces pumped at 750 nm (into the acceptor) and probed at 600 nm of all blends. A lifetime of 6.8, 9.9, and 11.2 ps of NA, TCB, and DBB blend film are fitted, respectively. The longer rise time in DBB film is ascribed to the bigger acceptor domain, which takes longer time for the exciton diffusion toward interface. The electron transfer is measured by pumping at 530 nm and probing at 850 nm. The corresponding lifetimes for three samples do not show large deviation (around 0.29 ps, Figure S14, Supporting Information), which is much shorter than the hole transfer, suggesting the very efficient electron transfer in all samples.

Following the exciton generation, diffusion and charge transfer, we then fabricate devices to characterize the charge transportation/collection and overall photovoltaic performances. The device configuration is ITO/PEDOT:PSS/Active layer/N,N'-bis[3-(dimethylamino)propyl]perylene-3,4,9,10-tetracarboxylic diimide/Ag. Figure 4c,d displays the transient photocurrent (TPC) and photovoltage (TPV) results of the devices. The DBB device presents the fastest TPC lifetime of 0.11 μ s and longest TPV lifetime of 2.84 μ s, suggesting very fast charge extraction and suppressed recombination. To further confirm it, electrochemical impedance spectra (EIS) of the samples are measured in dark with 0.8 V bias and Nyquist plots are recorded in Figure 4e. The NA and TCB spectra present two arcs in the high frequency and low frequency region, corresponding to recombination resistance (R_{rec}) and transporting resistance (R_{tran}), respectively.^[35,36] In contrast, the DBB spectrum displays almost one semicircle with negligible arc in the low frequency region (Figure S15a, Supporting Information). Then, we fit the spectra with the equivalent circuit in Figure S15b in the Supporting Information and the fitting results are shown in Table S6 in the Supporting Information. NA, TCB, and DBB devices exhibit an R_{tran} of 29.79, 19.71, and 8.60 Ω , respectively, whereas the R_{rec} are around 200 Ω for all samples. Such a small R_{tran} for DBB device contributes to the fast charge extraction. The hole and electron mobility is probed based on space-charge-limited current method (Figure S16a,b and Table S7, Supporting Information). The device with liquid DBB additive shows the highest and more balanced hole/electron mobility of $7.17 \times 10^{-4}/4.76 \times 10^{-4}$ $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, which is in accordance with the improved horizontal and vertical phase separation.

We then characterize the photovoltaic performances of the devices and the J - V curves of NA, TCB, and DBB devices are shown in Figure 4f. The curve parameters of devices with different additives and concentrations are concluded in Table S8 in the Supporting Information. Without any additive, the device presents a high PCE of 17.70% with a J_{sc} of 26.92 mA cm^{-2} , V_{oc} of 0.857 V and FF of 0.768. Adding solid additive TCB has slightly improved the efficiency to 17.83% mainly ascribed the improved FF of 0.783. In comparison, the liquid DBB device shows a highest efficiency of 18.54% with vastly improved FF of 0.802. Such a high FF suggests the very efficient exciton and carrier dynamics in the device triggered by the S-L phase separation. Figure 4g plots the external quantum efficiency

(EQE) at different wavelengths with two broad peaks over 80% at 450–800 nm. The accumulated current density of 25.66, 25.05, and 25.46 mA cm^{-2} are obtained for NA, TCB, and DBB devices, respectively. To achieve better performance, we deposit a ZnO nanoparticle antireflection (AR) layer at the back of the glass to reduce light reflection of the substrate, the illustration and detailed description are provided in Figure S17 in the Supporting Information. The optimized AR/glass/ITO exhibits 1–3% higher transmittance than the glass/ITO substrate at the wavelength longer than 470 nm. Consequently, the AR-DBB device achieves a highest PCE of 18.72% with J_{sc} of 27.30 mA cm^{-2} , V_{oc} of 0.854 V, and FF of 0.803 (Figure S17c, Supporting Information), the improved J_{sc} is mainly ascribed to the improved quantum efficiency at wavelength >470 nm (Figure S17d, Supporting Information). Importantly, this is one of the top efficiencies for binary OSCs (Table S9, Supporting Information). To further support the significantly higher FF, we conduct more photovoltaic tests under different illumination conditions to uncover the charge dynamic and device recombination behavior. The detailed discussion and description are provided in the supporting information. As determined from Figure 4h and Figure S16c,d in the Supporting Information, the DBB devices shows the most efficient charge dissociation/collection probability of 99.85%/93.74%, and suppressed bimolecular and trap-assisted recombination due to enhanced phase separation and molecular orientation. Except for conventional devices, it is also critical to investigate the device with inverted structure to verify the importance of donor/acceptor vertical distribution. Inverted devices with the configuration of ITO/zinc oxide (ZnO)/active layer/molybdenum oxide (MoO_3)/Ag have been fabricated. The device performances are concluded in Figure S19 and Table S10 in the Supporting Information. Compared to conventional NA devices, the inverted NA devices present lower J_{sc} , FF, and PCE, which may be from the surficial traps of ZnO. The highest efficiency of 16.30% is achieved for inverted NA sample, which is similar to reported values.^[37] Notably, the inverted DBB devices show an average J_{sc} of 24.09 mA cm^{-2} , which is much lower than that of inverted NA device (25.39 mA cm^{-2}), indicating the vertical distribution plays a critical role in the carrier transportation and device performance.

Finally, the device stability is of great importance for the evaluation of OSCs. We monitor the conventional-structured device stability under continuous 1 sun light illumination (light-emitting diode, LED, white light array) in ambient condition. As shown in Figure 4i, the DBB device retains 80% of its original efficiency after 660 h whereas the NA and TCB suffer more loss. It is reported that dithienothiophen [3,2-b]-pyrrolobenzothiadiazole (BTP)-based NFAs have low glass transition temperature, which endows them high diffusion coefficient.^[38] After film formation, they tend to further aggregate and crystallize to form kinetically and/or thermodynamically stable phase.^[31] Since the NA film present polycrystalline feature and intimately mixed morphology with little phase separation, there would be a strong thermodynamic driving force for the mixed phase toward over purity, leading to efficiency degradation.^[38,39] For the DBB device, the liquid additive helps the donor/acceptor to further phase separate, the as-cast film present enlarged donor–acceptor segregation, which may contribute to the improved stability.

3. Conclusion

In summary, we successfully promote S-L phase separation in D18-Cl:N3 binary OSC system directed by mixing Gibbs free energy. The exciton diffusion length of D18-Cl and N3 are first probed to be 27.3 and 43.2 nm, respectively. However, because of the strong donor/acceptor interaction and fast film-formation kinetics, the bulk-heterojunction film presents very small phase/domain size (<20 nm) and random molecular orientation, which conceals such excellent exciton property of the materials and deteriorate device performance. Through introducing the mixing Gibbs free energy ternary phase diagram and analyzing the thermodynamically steady-state phase separation in OSC, we identify a liquid additive to enhance the S-L phase separation that is solidifying the polymer donor and solvating the nonfullerene acceptor. The improved S-L phase separation leads to three major improvements. 1) Due to the prolonged solvation process, a bigger phase domain size is obtained, which is more suitable for the OSC system. 2) The liquid assists the molecules further diffuse and orient to form significantly ordered morphology. 3) The acceptor will follow the evaporation of liquid additive to form a favorable vertical distribution. Various characterizations have been conducted on both film and device to probe the exciton dynamics. The enlarged domain size, ordered molecular orientation and proper vertical distribution features suppressed charge recombination and improved charge transportation/collection. Consequently, the device achieves a fill factor of >80% and an efficiency of 18.72%. This work emphasizes the free energy triggered S-L phase separation for the fabrication of efficient OSCs.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

liquid additives, mixing Gibbs free energy, morphology control, organic solar cells, solid-liquid phase separation

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