# Two-step crystallization modulated through acenaphthene enabling 21% binary organic solar cells and 83.2% fill factor

Jiehao Fu[1,#], Hongxiang Li[2,#], Heng Liu[3,#], Peihao Huang[4], Haiyan Chen[4], Patrick W. K. Fong[1], Top Archie Dela Peña[5], Mingjie Li[6], Xinhui Lu[3], Pei Cheng[2], Zeyun Xiao[4], Shirong Lu[7], and Gang Li[1*]

[1]Department of Electrical and Electronic Engineering, Research Institute for Smart Energy (RISE), Photonic Research Institute (PRI), The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong 999077, China.

[2]College of Polymer Science and Engineering, State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu, 610065, China.

[3]Department of Physics, The Chinese University of Hong Kong, Shatin, Hong Kong 999077, China.

[4]Thin-film Solar Cell Technology Research Center, Chongqing Institute of Green and Intelligent Technology, Chongqing School, University of Chinese Academy of Sciences (UCAS Chongqing), Chinese Academy of Sciences, Chongqing 400714, China.

[5]Advanced Materials Thrust, Function Hub, The Hong Kong University of Science and Technology, Nansha, Guangzhou, 511400 China

[6]Department of Applied Physics, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong 999077, China.

[7]Zhejiang Key Laboratory for Island Green Energy and New Materials, School of Materials Science and Engineering, Taizhou University, Taizhou 318000, China.

[#] These authors contributed equally

*E-mail: G. L. (gang.w.li@polyu.edu.hk)

## Abstract

The crystallization dynamics of non-fullerene acceptors influence the morphology and charge dynamics of the organic solar cells (OSCs), ultimately determining device performance. However, the optimization of the molecular arrangement of donor and acceptor materials within active layer remains challenging. Herein, we control the crystallization kinetics of non-fullerene acceptors with a crystallization regulating agent, acenaphthene. Acenaphthene changes the self-organization of acceptor molecules by inducing a two-step crystallization: it first fixes the packing motif of the acceptor and then refines the crystallized framework, leading to highly oriented acceptors in the active layer. This forms multiple charge transport pathways that improve the charge transport properties of the device. As a result, efficiencies of 20.9% (20.4% certified) and 21% (20.5% certified) are achieved in D18/L8-BO and PM1/L8-BO-X binary organic solar cells, respectively, with a maximum fill factor of 83.2% (82.2% certified). The result is a step forward in the development of OSCs.

## Introduction

Organic solar cells (OSCs) have broken new ground due to the evolution of light-absorbing materials[1-7], especially of non-fullerene acceptors (NFAs)[1-3]. Because the as-cast organic active layer normally suffers from insufficient exciton dissociation, serious geminate recombination, and poor charge transport, morphology optimization techniques like additive engineering and thermal annealing are widely applied to NFA OSCs[8-12]. While progress in new materials and device engineering has led to encouraging OSC efficiency improvements[12-17], there is still a large efficiency gap between OSC and other mainstream photovoltaic technologies, thus new strategies are urgently needed to improve the morphology quality of OSCs.

The quality of the active layer is mainly determined by two parts. One is the phase separation of donor and acceptor (D:A), also known as the nanoscale morphology of D:A blend[18]. To ensure efficient exciton diffusion and provide enough D:A interfaces for exciton dissociation, an interpenetrating network structure with continuous donor and acceptor phase is required[18,19]. Aiming at purer and improved connectivity of D:A phases, quasi bulk-heterojunction blend fabricated by subsequently depositing donor and acceptor through two steps has attracted more and more attentions, because the blend film is more likely to form ideal vertical phase separation structure than traditional bulk-heterojunction film in which donor and acceptor are mixed in the same solvent and deposited in one step[20-24].

Another important part is the packing motif of photoactive molecules, which is tightly linked to charge transfer and transport process[25-27]. The relatively weak interactions between organic molecules normally lead to lower degree of crystallinity, poorer carrier transport than inorganic materials. Taking the representative NFA, Y6, as an example, neat Y6 film normally shows face-on orientation with a prominent π-π stacking diffraction in out-of-plane (OOP) direction and two distinguishable diffractions in in-plane (IP) direction[3]. Compared to the crystalline inorganic absorbing film with well-defined Bragg spots, the broadened polar angle spread of diffraction peaks of Y6 film indicates the poor crystalline orientation, which limits the intermolecular charge transfer and increases the risk of non-geminate recombination. Therefore, it is imperative to develop new methods that can make the packing motif of NFAs more conducive to charge carrier transport in OSCs. It is reported that the electron mobility of Y6-based field effect transistor could increase nearly four orders of magnitude via manipulating the crystalline phase of Y6 by high-temperature (210 °C) thermal annealing[28]. Although such a high temperature tends to induce excessive aggregation and is incompatible with OSC fabrication process[29], it is demonstrated that achieving better charge transport properties via controlling the crystallization kinetics of NFA is possible.

Herein, we employed a crystallization regulating agent, acenaphthene (AP), to manipulate the crystallization dynamics of NFAs on the top of donor polymer film under common OSC preparation conditions (below 100 °C). The non-covalent interactions between AP and acceptor molecules significantly changes the original packing motif of NFA and induces a new and favorable crystalline transition, contributing to highly oriented NFAs in OSC active layer indicated by well-defined Bragg spots. To be specific, carefully monitored by *in situ* GIWAXS measurement, the crystalline transition is shown to undergo two steps. The first step is to fix the packing motif of NFAs during the evaporation of host solvent chloroform (CF), and the next step is to refine the crystallized framework with the emergence of new molecular packing in a two-step crystallization manner, leading to active layer with unprecedented highly oriented NFAs showing well-defined Bragg spots. Consequently, more efficient charge extraction and transport as well as suppressed charge carrier recombination are achieved. For the mainstream OSC systems, all the AP-treated devices show much-improved efficiency with fill factors (FFs) over 80%. Especially, the D18/L8-BO and PM1/L8-BO-X OSC show significantly enhanced PCEs of 20.9% (20.4% certified) and 21% (20.5% certified), respectively, with a high FF of 83.2% (82.2% certified), which represent the top performances for OSCs so far. Even more encouraging, it is achieved in binary OSCs and thus with great potential forward. Besides, AP-treated devices exhibit improved operational stability due to tighter and more ordered molecular stacking.

## Results

### The impact of AP on device performance

The molecular structures of materials used in this work are presented in **Fig. 1a** to **c**. Here, PM6 and BTP-eC9 are employed as the donor and acceptor material, respectively[4,30]. The detailed device fabrication process can be found in the **Methods** section. We first investigated the role of AP in device performance by fabricating layer-by-layer OSCs with conventional structure, the optimization process is summarized in **Supplementary Table 1**. As shown in **Fig. 1d**, **Fig. 1e** and **Table 1**, the control devices show a champion PCE of 18.5%, with an open circuit voltage ($V_{OC}$) of 0.87 V, a current density ($J_{SC}$) of 28.0 mA/cm$^2$ and a FF of 76.4%. After the introduction of AP, although the $V_{OC}$ slightly drops to 0.86 V, the $J_{SC}$ and FF significantly increase to 29.2 mA cm$^{-2}$ and 81.3%, respectively. As a result, the champion device reached a PCE of 20.4%, certified as 20.0% by an ISO/IEC 17025:2017 accredited Calibration Lab - Enli Tech Optoelectronic Calibration Lab, Taiwan (Aug. 2023, **Table 1** and **Supplementary Figure 1**) The around 0.4% efficiency discrepancy is from device degradation caused by encapsulation and transportation time. The $J_{SC}$ values were reconfirmed by external quantum efficiency (EQE) measurements (**Fig. 1f**). The integrated $J_{SCs}$ of the control and AP device are 27.0 mA cm$^{-2}$ and 28.0 mA cm$^{-2}$, respectively, matching well with the data from current density-voltage ($J$-$V$) curves. In addition, we measured the transmittance of ITO substrate and the IQE of the AP-treated device (**Supplementary Figure 2**), which reconfirmed the reliability of our EQE tests. Moreover, we scaled up the AP-treated devices, as shown in **Supplementary Table 2** and **Supplementary Figure 3**. The AP device can work well with FF over 78% when the device area is scaled up to 0.26 cm$^2$. However, due to the leakage current caused by the aggregation of 2PACz, 1 cm$^2$ device shows unsatisfactory performance, with FF dropping to 67%. To tackle this problem, we added 1-hydroxybenzotriazole (HOBT) in 2PACz, which effectively restricts the aggregation of 2PACz[31]. As a result, we achieved nearly 19% binary OSC with active area over 1 cm$^2$, representing the top performance of 1 cm$^2$ OSC devices.

The impact of AP on device's operational stability was further investigated by maximum power point (MPP) tracking method under simulated 1-sun white light illumination. As displayed in **Supplementary Figure 4**, after 800-hour illumination, the AP-treated OSC remains 81% of initial efficiency, while its control counterpart suffers from a 28% efficiency decay. We ascribe the better light stability of AP device to the high-quality NFA crystallization formed in the active layer (will be discussed later), which could suppress the formation of morphological defects induced by light illumination[12,32,33]. Area amplification has a slight impact on device's photostability, the 1 cm$^2$ OSC shows comparable light lifetime with its small-area counterpart, especially under the first 500-hour light illumination.

## Charge carrier dynamics

As the high efficiency of the AP-processed OSC directly derives from the largely improved $J_{SC}$ and FF, both tightly linked to charge carrier dynamics, we systematically investigated the difference in charge transport, recombination, and extraction processes between the devices with and without AP processing. **Fig. 2a** and **Supplementary Table 3** present devices' charge mobilities measured by space charge limited current (SCLC) method (**Supplementary Figure 5**). The AP-processed device shows a slightly higher hole mobility ($8.3\times10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$) than the control counterpart ($6.9\times10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$), but a much-improved electron mobility ($9.0\times10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ in the AP sample versus $3.8\times10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ in the control one) due to the formation of high-quality NFA crystals (will be discussed later). The faster and more balanced charge transport is beneficial to reduce bimolecular and trap-assisted recombination, which was reconfirmed by the transient photovoltage measurement (TPV, **Supplementary Figure 6**) and the fitted slope of $V_{OC}$ versus logarithmic light intensity (**Supplementary Figure 7**). In addition, we quantitively measured the bimolecular recombination rate ($k_\beta$) and trap density ($N_t$). The relationship between $k_\beta$ and time-resolved charge density ($n$) could be expressed by the equation $\partial n/\partial t = -k_\beta n^2$, therefore we can derive the $k_\beta$ value by fitting the time-resolved data[34,35]. As plotted in **Fig. 2b**, the control device shows a higher $k_\beta$ of $5.3\times10^{-13}$ cm$^3$s$^{-1}$ than the AP counterpart ($k_\beta$= $4.8\times10^{-13}$ cm$^3$s$^{-1}$), demonstrating that AP processing could suppress device's bimolecular recombination behavior. As for the detailed trap state of our device at different levels, we conducted trap density of state (t-DOS) tests[35,36]. **Fig. 2c** presents the t-DOS distribution of our devices, it is clear that the AP device shows similar distribution of shallow traps with the control one, but obviously lower deep trap DOS distribution, which should benefit from the highly crystallized NFA stacking induced by AP processing (will be discussed in the GIWAXS part).

To get more details about charge carrier dynamics, we performed femtosecond transient absorption (fs-TAS) spectroscopy tests. The representative spectral line cuts of the control and AP samples are presented in **Fig. 2d** and **2e**, respectively, with the insertion of the two-dimensional (2D) color plots. The kinetics probed at 730-750 nm (**Fig. 2f**, the up one) and 580-600 nm (**Fig. 2f**, the bottom one) are used for the dynamics of singlet excitons ground state bleach (GSB) and hole polarons, respectively. The singlet excitons GSB appears to decay slower for the AP sample, which should be ascribed to the larger domain size in the AP-treated film (will be discussed in the morphology section), because the singlet excitons take longer diffusion time to reach D/A interface in active layer with large domain size[37,38]. Turning into polarons sub-ns recombination dynamics, the recombination of free charges in the AP-treated film is evidently slower than that in the control film. The slower polarons recombination rate will impart better photocurrent generation at maximum power point, wherein there is less effect of built-in potential drifting the free charges, therefore causing better FF value[38]. Based on the above evidence, we conclude that the evident increase in $J_{SC}$ and FF results from the more efficient carrier transport and charge extraction process, as well as the suppressed charge carrier recombination.

## Statical morphology characterization

We then studied the morphology and the structural order of the blend films by scanning electron microscopy (SEM), atomic force microscopy (AFM), transmission electron microscopy (TEM), grazing incidence small-angle X-ray scattering (GIWAXS) and grazing incidence wide-angle X-ray scattering (GIWAXS), which help clarify the origin of performance enhancements in the AP devices. Considering the sequential deposition method we used, donor and acceptor are distributed as a form of quasi-planar heterojunction, as reflected by the layered morphology in SEM images (**Supplementary Figure 8**). The AFM height images (**Supplementary Figure 9**) and TEM images (**Supplementary Figure 10**) reveal the more uniform and larger aggregations in AP-treated films. Combing the GISAXS measurements (**Supplementary Figure 11**, and **Supplementary Table 4**), we confirm the larger aggregations are related to the bigger acceptor domains, due to the high-quality acceptor crystallization induced by AP.

The 2D GIWAXS diffraction patterns and corresponding one-dimensional (1D) line cuts of these blend films are presented in **Fig. 3a**, **3b**, **3e**, and **3f**. The control film shows a typical diffraction pattern of PM6: Y-series blends, with a scattering peak at around 1.8 $Å^{-1}$ due to π-π stacking in out-of-plane (OOP) direction and a peak at around 0.3 $Å^{-1}$ due to lamellar stacking in in-plane (IP) direction[3,30]. While the AP sample exhibits a totally different diffraction pattern. First, there are four distinguishable stacking peaks in the IP direction (**Fig. 3b** and **3e**), which means the formation of high-quality crystalline domains and provides more electron hopping channels[39]. These four peaks in IP direction in **Fig. 3b** are consistent with that in **Fig. 3d**, so it's clear the highly ordered molecular stacking comes from acceptors. Second, there are discrete and well-defined Bragg diffractions in low *q* area, unlike the wide diffraction ring in the control sample. The detailed peak information is summarized in **Supplementary Table 5**, here we take the most prominent diffraction, π-π stacking peak, as an example. For the control sample, its π-π peak locates at $q_z$= 1.79 Å$^{-1}$, with crystallite coherence length (CCL) of 24.2 Å. Upon AP processing, the location of π-π peak shifts to larger *q* area ($q_z$= 1.86 Å$^{-1}$) and the corresponding CCL significantly increases to 34.5 Å, consistent with the sharper scattering peak. More interestingly, AP processing leads to the emergence of a new π-π scattering peak at $q_z$= 1.53 Å$^{-1}$ (marked with a blue star in **Fig. 3f**). According to the single crystal analysis of BTP-eC9[25,40,41], the commonly observed π-π diffraction at $q_z$= ~1.8 Å$^{-1}$ mainly origins from the terminal/terminal-butterfly (TT-butterfly, **Supplementary Figure 12**) and terminal/terminal-zig-zag (TT-zig-zag, **Supplementary Figure 12**) acceptor configurations. The new π-π diffraction is related to other configuration with wider stacking distance like core/terminal-zig-zag (CT-zig-zag, **Supplementary Figure 12**) or the packing of different dimers in the amorphous phase, both could serve as effective charge transport pathways[41-43]. Overall, AP processing induces highly ordered molecular packing in the blend film, thus facilitating charge transport and suppressing charge recombination.

Since both donor and acceptor contribute to the scattering signals of the active film, we then measured the crystalline packing structure of neat donor and acceptor films with and without AP processing. Neat PM6 (**Supplementary Figure 13**) and BTP-eC9 film (**Fig. 3c** and **3g**) exhibit obvious lamellar stacking signals in IP direction, but the π-π staking signal of PM6 film is much weaker than that of BTP-eC9 film. After AP processing, the diffraction pattern of PM6 film (**Supplementary Figure 13**) is nearly unchanged, while the acceptor film experienced a significant diffraction transition (**Fig. 3d** and **3h**). In addition to the newly appeared π-π shoulder peak ($q_z$= 1.51 Å$^{-1}$) along OOP direction, there are clear Bragg spots located at low *q* area. As presented in **Fig. 3d**, these scattering spots at ($q_r$, $q_z$) = (0.21, 0), (0.42, 0), (0.29, 0.07), (0.55, 0.14), (0.26, 0.53), (0.21, 0.47) and (0.43, 0.41) Å$^{-1}$ could be well indexed with a monoclinic unit cell with lattice parameters of a = 30 Å, b = 15 Å, c = 30 Å, $\boldsymbol{\alpha}$ = 90°,

***β*** = 90°, ***γ*** = 125°. Correspondingly, we labeled the corresponding Miller indices next to each peak for clarity and presented the schematic image of the crystal structure in **Supplementary Figure 14**. The appearance of high-order diffraction spots indicates that more long-range ordered structures are formed in the AP-processed NFA film, which is significantly distinctive from the previously known so-called "semi-crystalline" NFA films[39]. The diffraction transition occurred in the pure acceptor films is very similar to what we observed in the blend samples, demonstrating that the AP assisted NFA regulation is well preserved in the blend film. This will lead to higher carrier mobility, consistent with the SCLC results.

Based on the above information, we believe the π-π diffractions of the active layer are mainly contributed by acceptors and the distinctive diffraction pattern observed in the AP-processed blend film stems from the formation of high-quality BTP-eC9 crystals.

## ***In situ*** **crystallization kinetics of NFAs – the power of two-step crystal growth**

The interesting crystalline packing motifs inspired our curiosity for the film formation process and crystallization dynamics of the layer-by-layer blends. We carefully performed *in situ* UV-Vis (the schematic diagram is presented in **Supplementary Figure 15**) and *in situ* GIWAXS measurements to monitor the whole process of film formation from spin coating to thermal annealing in real time.

The time-resolved absorption spectra of samples without and with AP during spin coating process are plotted in **Fig. 4a** and **Fig. 4b** (reflection mode), respectively. Before dropping acceptor solution, we deposited the donor film on the substrate first. Thus, the last moment we observed neat PM6 absorption spectrum is regarded as the starting time (t=0). As evidenced by the large redshift of absorption edge, also reflected by the change in absorption at 825 nm (**Supplementary Figure 16**), both samples show quick liquid-solid transition within 1s due to the fast evaporation of chloroform. After the quick transition, the absorption spectra of the control sample get stable and no change (**Fig. 4a** and **Supplementary Figure 16**), meaning molecular self-organization finished very quickly[12]. But the absorption spectra of the AP sample experience a continuous red shift (**Fig. 4b** and **Supplementary Figure 16**) during the whole ~40s spin coating process, implying an extended self-organization process. Then, time-resolved absorption spectra of the blend films under thermal annealing are presented in **Fig. 4c** and **4d** (transmission mode), as well as **Supplementary Figure 17** (reflection mode). Although thermal annealing tends to induce the movement of molecular chains and improve the crystallinity of molecules, the control sample does not show obvious absorption change due to the relatively low processing temperature (100 °C) and short processing time (1min). It is interesting that the absorption edge of the AP film continuously redshifts again, with the redshift of acceptor's characteristic peak, especially in the first 20 seconds. The significant absorption edge and peak shifts should correspond to the removal of AP (**Supplementary Figures 18-19**) and the reorganization of acceptor molecules.

*In situ* GIWAXS results give us deeper insights into the morphology evolution and molecular self-organization process. The time-resolved 2D GIWAXS patterns of the control and AP samples during spin coating (0.5 second per frame) and thermal annealing (1 second per frame) are presented in **Supplementary Videos 1-4**. We monitored the spin coating process first, some representative 2D GIWAXS patterns are presented in **Supplementary Figure 20** and **Supplementary Figure 21**. **Figs. 5a-d** are the 1D GIWAXS line cuts at some representative time points. Here we would like to exclude the diffraction peaks at $q_z$= 0.9 Å$^{-1}$ and $q_z$= 1.4 Å$^{-1}$ (as indicated in **Fig. 5a** and **5c**), because they are the characteristic peaks of polyimide used for the protection film. After the exclusion, the control sample shows similar diffraction patterns with the diffractions of the control film from ex situ GIWAXS measurement, with a lamellar peak in IP direction (**Fig. 5a**) and a $\pi$-$\pi$ stacking peak in OOP direction (**Fig. 5b**). But the lamellar peaks at $q_r$= ~0.3 Å$^{-1}$ seem to merge to a boarder peak during the spin coating process, meaning the distance of lamellar stackings has a slight change from wet film to dry film. The nearly unchanged diffraction patterns indicate that the crystalline packing motif of the control sample is fixed due to very limited time window for molecular self-organization after the evaporation of host solvent chloroform, which is consistent with the conclusion from *in situ* UV-vis measurements. While for the AP sample, there are different phenomena. i) The diffraction patterns are from both the blend film and AP, as indicated by the newly emerging diffraction rings at different $q_r$ positions (**Supplementary Figure 21)**. ii) The stable diffraction patterns are observed from the third frame, which means that it takes more time to fix the packing motif. iii) The diffraction rings at $q_r$= ~0.9 Å$^{-1}$, ~1.3 Å$^{-1}$ and ~1.8 Å$^{-1}$ from polar angle at 10° to 60° gradually become weak and even disappear, we conclude that AP is partially removed during the spin coating process because these diffraction rings ascribe to AP (**Supplementary Figure 22 and Supplementary Figure 23**). Then, we monitored the thermal annealing process by *in situ* GIWAXS measurements. Some representative 2D GIWAXS patterns and 1D intensity profiles are presented in **Supplementary Figure 24**, **Supplementary Figure 25**, and **Fig. 5e-h**. Like the tendency observed from the spin coating process, the control film shows nearly unchanged packing motifs (**Fig. 5e**, **5f** and **Supplementary Figure 24**). In contrast, the AP film exhibits an interesting crystalline transition. In IP direction, we can observe a new diffraction peak ($q_r$= 0.52 Å$^{-1}$, indicated by the diamonds in **Fig. 5g**) that slowly appears as the heating time increases. Since the newly appearing diffraction is consistent with the characteristic peak of neat acceptor film with AP processing, we conclude that the crystalline transition mainly stems from the rearrangement of NFAs.

### Working mechanisms behind crystallization engineering

To understand the underlying mechanisms behind AP-induced crystalline transition, we conducted molecular-level explorations. **Figs. 6a-c** are the 2D $^1$H-$^1$H nuclear magnetic resonance (NMR) spectra using nuclear Overhauser effect spectroscopy (NOESY) mode, which can provide information about the spatial coupling of protons and reflect molecular interactions[44]. The NOESY cross-peaks between proton resonances are highlighted with rectangular boxes (dashed for BTP-eC9 and solid for AP) and the corresponding groups that the protons belong to are labeled beside the boxes. For example, in **Fig. 6a**, the cross-peaks circled with the box in the upper right corner are assigned to the spatial coupling of protons from alkyl chains. It is reasonable that the spectrum of the BTP-eC9:AP sample consists of crossover resonance signals of pure BTP-eC9 intermolecular interactions and AP intermolecular interactions. But there are unexpected cross-peaks found, as indicated by the red circle in **Fig. 6c**. Because these signals indicate the coupling of protons from AP and the long alkyl chains of the acceptor, we infer the interaction site lies in between the end group and benzothiadiazole (BT) of BTP-eC9. This proposal was then verified by density functional theory (DFT) simulations[45,46]. After comparing and optimizing 500 BTP-eC9:AP conformers, we obtained the optimal BTP-eC9:AP conformer with the lowest binding energy ($\Delta G_b$) of -13.81 kcal mol$^{-1}$. As presented in **Supplementary Figure 26, b**, due to non-covalent interactions such as hydrogen bond (-H…O-) and π-π interaction, AP tends to interact with the junction of the end group and the bithiophene moiety, which is consistent with the result from NOESY NMR measurements. We then studied the influence of AP on BTP-eC9 dimer via DFT simulations. By comparing the optimal configurations of BTP-eC9 dimer without (**Supplementary Figure 26**) and with AP (**Supplementary Figure 26**), we found that AP can not only change the configuration of acceptors but also induce tighter acceptor stacking. To illustrate the role of AP in acceptors' stacking clearer, we have further conducted molecular dynamics simulations (**Supplementary Figure 27**). After the introduction of AP, it is obvious that the highest g(r) peak shifts to smaller r position, meaning tighter BTP-eC9 stacking induced by AP. And after the removal of AP, the edges of main g(r) peaks are nearly unchanged, consistent with the conclusion that AP first fixes the packing motif of acceptors and then refines the crystallized framework.

Combining with the above evidence, we proposed the schematic diagram of AP-induced two-step crystallization engineering. As shown in **Fig. 6d** the non-covalent interactions between AP and acceptor serve as the driving force for the rearrangement of acceptor molecules when the host solvent CF evaporates, and the crystallized framework of NFAs is fixed at that time. Due to the good volatility of AP, some of the AP is removed after spin coating. Then during the thermal annealing process, the refinement of NFA packings starts with the complete removal of AP. Finally, the active layer with unprecedented highly ordered packing motif forms, with well-defined Bragg spots and tighter molecular stacking in the OSCs.

## Generality of two-step crystallization strategy

The generality of our two-step crystallization strategy was further confirmed in more state-of-the-art high-performance polymer/NFA OSC systems, including PM6/Y6, PM6/BO-4Cl, PM6/L8-BO, D18/L8-BO and PM1/L8-BO-X [3,4,6,47-50]. As shown in **Supplementary Figure 28** and **Supplementary Figure 29**, we have further investigated the impact of AP on the stacking of other NFA molecules, like Y6, BO-4Cl, and L8-BO. All AP-treated NFA films show obviously higher crystallinity than their counterparts, as reflected by the Bragg spots in small $q$ area, demonstrating AP can significantly increase the molecular ordering of mainstream NFAs. The detailed photovoltaic performance of various OSC systems without and with AP processing is summarized in **Table 2** and **Supplementary Figure 30**. Like the trend we observed in PM6/BTP-eC9 system, the AP processed devices show significantly improved efficiency with higher $J_{SC}$ and more remarkable FF values than the control counterparts. Because of the much higher crystallinity induced by AP, compared to the control counterpart, the AP-treated device shows slightly narrower bandgap and weaker electroluminescence quantum efficiency ($EQE_{EL}$) (**Supplementary Figure 31** and **Supplementary Table 6**), thus lower $V_{OC}$. But it is worth noting that all AP treated OSCs exhibit over 80% FF values and represent the best performance in their corresponding binary systems (19.0% for PM6/Y6, 19.5% for PM6/BO-4Cl, 19.8% for PM6/L8-BO). Excitingly, the D18/L8-BO based binary OSC achieved 20.9% PCE with a fill factor of 83.2% and a steady-state output PCE of 20.4% (**Fig. 6e** and **Supplementary Figure 32**), certified as 20.4% efficiency with fill factor of 82.2% (**Supplementary Figure 33**). Moreover, the efficiency of PM1/L8-BO-X based OSC was further boosted to 21.0% (**Fig. 6f**), certified as 20.5%, (**Supplementary Figure 34**), representing the top performance of binary OSCs (**Fig. 6g**).

## Conclusions

In summary, we developed a two-step crystallization strategy that can effectively rearrange the packing motif of NFA in OSC and induce the formation of very high-quality NFA crystals exhibiting obvious Bragg diffraction spots. The long-range ordered crystalline packing is well-reserved in the OSC active layer, ensuring high-speed charge transport channels. In addition, *in situ* characterization techniques detailly revealed the underlying crystallization dynamics. First, the non-covalent interactions between AP and acceptor induce the rearrangement of NFAs within just several seconds after the evaporation of host solvent. Second, another crystalline transition occurs during the thermal annealing process with the removal of AP, which fine tunes the crystalline packing motif. Consequently, a champion PCE of 21% (20.5% certified) was achieved in AP processed PM1/L8-BO-X binary OSC, representing the new frontier efficiency of OSCs. This two-step crystallization strategy demonstrated the importance of molecular packing and would inspire further development of OSCs.

## Methods

**Materials.** All materials are provided by commercial suppliers: PM6 (Solarmer Energy Inc.), D18 (Solarmer Energy Inc.), BTP-eC9 (Solarmer Energy Inc.), Y6 (Solarmer Energy Inc.), BO-4Cl (Solarmer Energy Inc.), L8-BO (Solarmer Energy Inc.), PM1 (Solarmer Energy Inc.), L8-BO-X (Solarmer Energy Inc.), PFN-Br (Solarmer Energy Inc.), AP (Adamas-beta Co., Ltd.), Chloroform (Sigma-Aldrich, Ltd.), and methanol (Sigma-Aldrich, Ltd.). All reagents and solvents are used directly without further purification.

**Device fabrication and testing.** The OSCs were fabricated with a conventional structure of ITO/2PACz/active layer/PFN-Br/Ag. At first, the ITO-coated glass substrates were cleaned sequentially with detergent, de-ionized water, acetone, and isopropyl alcohol (IPA) for 15 min under sonication. Then the substrates were dried in nitrogen flow and treated with UV ozone for 30 min. After that, 2PACz in ethanol solution was dripped on ITO substrates and spin-coated at 3000 rpm for 30 s, followed by thermal annealing on a hot plate at 100 °C for 10 min. Then, the substrates were transferred into a glovebox filled with nitrogen ($O_2$< 10 ppm; $H_2O$ < 10 ppm). The active layer was fabricated by subsequentially depositing ~60 nm-thick donor and ~60 nm-thick acceptor with and without AP. Except for D18 (dissolved in chlorobenzene), all photoactive materials were dissolved in chloroform. For the optimized device, the weight ratio of acceptor: AP is 1:0.2. Then the active layer experienced a process of thermal annealing at 100°C for 5 min. The next stage is to coat electron transport material, about 5nm PFN-Br (from methanol solution) was coated on the top of the active layer. Finally, these semi-finished cells were transferred into a thermal evaporation chamber with a base pressure of approximately $2\times10^{-4}$ Pa, where 100 nm Ag was deposited through a shadow mask with the active area of 4 $mm^2$. The *J–V* curves of OSCs were tested by a Keithley 2400 source meter and an AAA grade solar simulator (SS-F7-3A, Enli Tech. Co., Ltd., Taiwan) along with AM 1.5 G spectra whose intensity was corrected by a standard silicon solar cell at 1000 $W/m^2$. The *J-V* curves are measured in the forward direction from -0.2 to 1.2 V. The external quantum efficiency (EQE) was measured by a certified incident photon to electron conversion (IPCE) equipment (QE-R) from Enli Technology Co., Ltd.

**AFM and GIWAXS**. The atomic force microscopic (AFM) images were acquired using a Bruker Dimension EDGE in tapping mode. *Ex situ* GIWAXS measurements were carried out with a Xeuss 2.0 SAXS/WAXS laboratory beamline using a Cu X-ray source (8.05 keV, 1.54 Å) and Pilatus3R 300K detector. All samples with silicon substrates were prepared according to device fabrication process, the incidence angle is 0.2°. *In situ* GIWAXS measurements were conducted at beamline BL02U2, Shanghai Synchrotron Radiation Facility (SSRF). The 10 keV X-ray beam was incident at a grazing angle of 0.2° with the exposure of 0.5 s (for spin coating process) and 1 s (for thermal annealing process). The scattered x-ray was detected using a Dectris Pilatus 2M photon counting detector. *In situ* spin-coating GIWAXS experiments are conducted using Synchrotron *in situ* micro-controlled temperature spin coater, which was jointly developed by Sichuan University, Beijing Synchrotron Radiation Facility, and Beijing Zhongke Wanyuan Technology Co., Ltd. It allows remote solution dripping, remote speed adjustment, and remote temperature control, it can be used in different types of atmospheres with adjustable gas flow, enabling *in situ* GIWAXS monitoring.

**SCLC mobility measurements.** Electron-only devices with the structure of ITO/ZnO/PFN-Br/active layer/PFN-Br/Ag and hole-only devices with the structure of ITO/$MoO_3$/active layer/$MoO_3$/Ag are used to conduct SCLC measurements. The mobilities were determined by fitting the dark-field current density voltage curves using the Mott-Gurney relationship, which is described in the following equation,

$$\mathrm{J(V)} = \frac{9}{8}\varepsilon_0\varepsilon_r\mu_0\frac{V^2}{L^3} \quad (1)$$

where J is the current density, $\varepsilon_0$ is the permittivity of free space, $\varepsilon_r$ is the relative permittivity of the material, $\mu_0$ is the zero-field mobility, V is the effective voltage and L is the thickness of the active layer. From the plot of *J* versus *V*, the hole and electron mobilities can be obtained by fitting with the Mott-Gurney equation.

**Transient photovoltage (TPV) measurements.** TPV is tested under the open-circuit and 1 sun intensity background light condition to explore the photovoltage decay. The subsequent voltage decay is then recorded by the digital storage oscilloscope to directly monitor charge carrier recombination. The intensity of light is 230 μW/cm$^2$ and the wavelength of light is 520 nm. The light pulse is 10 ns. The normalized curves are easier to compare the decay time and the slower decline one is the one with a longer lifetime. The photovoltage decay kinetics of all devices follow a mono-exponential decay: $\delta V = A\exp(-t/\tau)$ where t is the time, and τ is the decay time. The fitted decay time would not be affected by the A value, thus the TPV curves are normalized.

**Femtosecond transient absorption spectroscopy (fs-TAS).** Fs-TAS was measured with an amplified Ti:sapphire femtosecond laser (800 nm wavelength, 50 fs, 1 kHz repetition; Coherent Libra) and a Helios pump/probe setup (Ultrafast Systems). The 400 nm pump pulses with a pump fluence of 0.5 or < 3 μJ/cm2 were obtained by frequency doubling the 800 nm fundamental regenerative amplifier output. The white-light continuum probe pulses were generated by focusing a small portion of the regenerative amplifier's fundamental 800 nm laser pulses into a 2 mm sapphire crystal.

**t-DoS calculation.** The density of the state of trap distributions was performed through measurement of capacitance spectroscopy in a dark environment. In which, we applied capacitance-voltage (C-V) measurements under a frequency of 100 kHz at a different applied voltage from -1V to 1.2V, and in the capacitance-frequency (C-f) measurement a varied frequency from 10 MHz to 10 Hz were used. The demarcation energy $E_\omega$ and modulation frequency ω are described as:

$$\omega = \omega_0\, exp\left(-\frac{\Delta E}{\mathrm{k_B} T}\right) \tag{2}$$

with the solution of:

$$E_{\omega} = k_B T \, ln\left(\frac{\omega_0}{\omega}\right) \tag{3}$$

The trap density at energy DoS can be acquired as:

$$DoS = \frac{V_{bi}}{qW}\frac{dC}{d\omega}\frac{\omega}{k_B T} \tag{4}$$

where $\omega_0 = 2\pi\nu_0$ ($\nu_0 = 10^{12}$ s$^{-1}$) is called the attempt-to-escape frequency, W is the depletion width, $dC/d\omega$ is the derivative of each point in the capacitance with respect of AC frequency.

**Density Functional Theory Computation.** The molecular geometry optimizations of BTP-eC9 and AP are performed by Gaussian 16 at B3LYP/6-31G* level, where the long alkyl side chains are simplified to methyl groups to save computational cost. Conformational searches of the complex are performed to find the low-energy conformers. 500 conformers are generated and optimized by semi-empirical extended tight-binding method GFN2-xTB as implemented in xtb program. The conformers with the lowest energy are further optimized by Gaussian 16. The 6-311G** basis set in conjunction with the D3BJ dispersion correction is used to calculate Gibbs free energy. The binding energy is determined by $\Delta G_b = G_{com} - (G_{M1} + G_{M2})$, where $G_{M1}$, $G_{M2}$ and $G_{com}$ are the Gibbs free energy of molecule 1, molecule 2 and their complex.

## Data availability

The data that support the findings of this study are available within the Article and its Supplementary Information. Source data are provided with this paper.

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## Author contributions

J.F. and G.L. conceived the study. J.F. fabricated the devices and performed most characterizations and analysis. Ho.L. and P.C. performed *in situ* GIWAXS measurements and analysis. He.L. and X.L. performed *ex situ* GISAXS measurements and analysis. P.H. performed the DFT calculations. H.C., Z.X., and S.L. assisted NMR measurements and analysis. P.F. conducted *in situ* UV-vis characterization. G. L. guided the study and supervised the execution. The manuscript is prepared, revised, and finalized by J.F., Ho.L., He.L., and G.L. All authors discussed the results and commented on the manuscript.

## Competing interests

The authors declare no competing interests.

**Table 1** Photovoltaic parameters of PM6/BTP-eC9 OSCs with and without AP treatment.

| Treatment | $V_{OC}$ (V) | $J_{SC}$ (mA cm$^{-2}$) | $J_{SC}^{cal}$ (mA cm$^{-2}$) | FF (%) | PCE[a] (%) |
|---|---|---|---|---|---|
| Control | 0.87 | 28.0 | 27.0 | 76.4 | 18.5 (18.3±0.1) |
| AP | 0.86 | 29.2 | 28.0 | 81.3 | 20.4 (20.1±0.1) |
| AP[b] | 0.85 | 29.2 | / | 80.2 | 20.0 |

[a]The average PCEs with standard deviation calculated from 33 devices in each case.
[cal]Integrated $J_{SC}$ values from EQE measurements.
[b]The certified photovoltaic parameters from Enli Tech Optoelectronic Calibration Lab, Accreditation Criteria: ISO/IEC 17025:2017.

**Table 2** Summary of photovoltaic parameters for 5 NFA OSC systems without and with AP treatment.

| Condition | $V_{OC}$ (V) | $J_{SC}$ (mA cm$^{-2}$) | $J_{SC}^{cal}$ (mA cm$^{-2}$) | FF (%) | PCE[a] (%) |
|---|---|---|---|---|---|
| PM6/Y6, Control | 0.86 | 27.2 | 26.4 | 75.1 | 17.5 (17.2±0.1) |
| PM6/Y6, AP | 0.84 | 28.1 | 27.3 | 80.2 | 19.0 (18.6±0.2) |
| PM6/BO-4Cl, Control | 0.87 | 27.7 | 26.7 | 75.3 | 18.1 (17.7±0.2) |
| PM6/BO-4Cl, AP | 0.85 | 28.5 | 27.6 | 80.4 | 19.5 (19.1±0.2) |
| PM6/L8-BO, Control | 0.90 | 26.5 | 25.6 | 77.0 | 18.4 (18.2±0.1) |
| PM6/L8-BO, AP | 0.89 | 27.3 | 26.3 | 81.4 | 19.8 (19.5±0.1) |
| D18/L8-BO, Control | 0.93 | 26.4 | 25.6 | 77.5 | 19.0 (18.7±0.2) |
| D18/L8-BO, AP | 0.92 | 27.4 | 26.5 | 83.2 | 20.9 (20.5±0.1) |
| D18/L8-BO, AP[b] | 0.91 | 27.2 | / | 82.2 | 20.4 |
| PM1/ L8-BO-X, Control | 0.92 | 26.9 | 25.9 | 77.1 | 19.2 (18.8±0.1) |
| PM1/ L8-BO-X, AP | 0.91 | 27.9 | 27.0 | 82.3 | 21.0 (20.7±0.2) |
| PM1/ L8-BO-X, AP[b] | 0.91 | 27.8 | / | 80.9 | 20.5 |

[a] The average PCEs with standard deviation calculated from 20 devices. All devices were tested with a metal mask. [cal]Integrated $J_{SC}$ values from EQE measurements. [b]The certified photovoltaic parameters from Enli Tech Optoelectronic Calibration Lab, Accreditation Criteria: ISO/IEC 17025:2017.

**Fig. 1 Chemical structures and device performance**. Chemical structure of PM6 (**a**), AP (**b**) and BTP-eC9 (**c**). *J-V* curves (**d**), PCE histograms (**e**), and EQE spectra (**f**) of PM6/BTP-eC9 OSCs with and without AP treatment.

**Fig. 2 Charge carrier dynamics**. **a** Charge mobilities of PM6/BTP-eC9 devices calculated by SCLC methods. **b** Charge carrier density of PM6/BTP-eC9 devices as a function of delay time and the bimolecular recombination fits (solid lines). **c** t-DOS of PM6/BTP-eC9 devices without and with AP treatment. 2D color plots of fs-TA spectra of PM6/BTP-eC9 films without (**d**) and with (**e**) AP treatment. Representative fs-TA spectra of PM6/BTP-eC9 films without (**f**) and with (**g**) AP treatment at indicated delay times. **h** The corresponding single-state exciton recombination (the up one) as well as hole polaron generation and recombination dynamics (the bottom one).

**Fig. 3 Crystalline packing motifs.** 2D GIWAXS diffraction patterns of PM6/BTP-eC9 films without (**a**) and with (**b**) AP treatment. 2D GIWAXS diffraction patterns of pure BTP-eC9 films without (**c**) and with (**d**) AP treatment. The corresponding 1D GIWAXS line cuts (**e-h**), the π-π shoulder peaks are indicated with blue stars and the location of π-π main peaks are labelled with blue numbers.

**Fig. 4 *In situ* UV-vis characterizations.** *In situ* UV-vis spectra as a function of spin-coating time (**a**, **b**) and as a function of thermal annealing time (**c**, **d**) for PM6/BTP-eC9 samples without and with AP processing.

**Fig. 5 *In situ* GIWAXS characterizations. a-d** 1D GIWAXS line cuts of the PM6/BTP-eC9 samples without and with AP at some representative spin coating time points. **e-h** 1D GIWAXS line cuts of the PM6/BTP-eC9 samples without and with AP at some representative thermal annealing time points.

**Fig. 6 The interactions between AP and NFA molecules as well as the best device performance.** 2D $^1$H-$^1$H NOESY NMR spectra of neat BTP-eC9 (**a**), neat AP (**b**), and the mixture of BTP-eC9 and AP (**c**). **d**, The schematic diagram of AP-induced two-step crystallization engineering. To present the packing motif of NFAs more clearly, AP, the core and the end group of NFA are marked in dark blue, pink and green, respectively. *J–V* curves of D18/L8-BO (**e**) and PM1/L8-BO-X (**f**) OSCs without and with AP processing. **g**, Comparison of certified PCEs versus certified fill factor values in reported OSCs with certified efficiency of 19.5% and above[7,16,17,51-57].

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