Thermally stable poly(3-hexylthiophene): Nonfullerene solar cells with efficiency breaking 10%

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Abstract
Solar cells featuring polythiophenes as donors are one of the optoelectronic devices that hold notable promises for commercial application, profiting from the lowest synthetic complexity and excellent scalability. However, the complex phase behaviors of polythiophenes and their blends put constraints on modulating electrical performance and thus realizing stable performance under thermal stress. In this contribution, we present a multi-technique approach that combines calorimetry, scattering, spectroscopy, and microscopy to thoroughly probe the thermodynamic mixing, thermal properties of materials, the evolution of nanoscale domain structure, and device performance and thus realizing stable performance under thermal stress. In this contribution, we present a multi-technique approach that combines calorimetry, scattering, spectroscopy, and microscopy to thoroughly probe the thermodynamic mixing, thermal properties of materials, the evolution of nanoscale domain structure, and device performance and thus realizing stable performance under thermal stress.

KEYWORDS
multi-technique approach, organic solar cells, phase separation, polythiophene, thermal stability

1 | INTRODUCTION

Organic solar cell (OSC), taking advantage of nanostructured charge transport pathways, is one of the most promising clean-energy technologies that convert sunlight to electric power.[11–51] In recent years, tremendous efforts have been devoted to designing new materials, achieving impressive power conversion efficiencies (PCEs) that approach 19% in several systems.[6–9] To advance their commercial applications, the production cost and stability of OSCs should also be taken into account in the meantime.[10–12] The main factors that lead to degradation of device performance include intrinsic degradation, atmospheric environment (humidity, oxygen), light, and heat.[13,14] Degradation caused by the environment can be avoided by proper encapsulation, while suppressing the light and thermal-induced degradations is exceedingly arduous and lacks effective methods.[15,16] Particularly, thermal degradation is inevitable throughout the operation of OSCs since the prolonged exposure to light results in high working temperatures (50°C–80°C, even reaching 100°C) during outdoor applications.[17,18]

Many highly efficient OSCs are extremely sensitive to thermal stress,[19–20] for instance, the PM6:BTP-C3-4F binary cell can maintain 80% of the initial PCE after the storage of 600 h at room temperature, while the PCE dramatically degrades to 66% of the initial value with the continuous aging at 80°C.[21] Evidently, thermal stability is one of the important hindrances for the practical applications of
Photovoltaic performance and thermal stability of emerging polythiophene OSCs based on semi-crystalline components.

To establish structure–performance–thermal stability relationships and provide instructive optimization guides for the emerging cost-effective systems, we employ a multi-technique approach that covers calorimetry, X-ray scattering, absorption spectroscopy, and electron microscopy (Figure 1A) for thoroughly characterizing the thermal properties, molecular mixing, nanoscale packing, orientation, and phase separation of P3HT with four popular NFAs (3,9-bis(2-methylene-(3,1-dicyanomethylene)-indanone))-5, 5, 11, 11-tetrakis(4-hexyloxyphenyl)-dithieno[2,3-d:2,3'-d']-s-indaceno[1,2-b:5,6-b']dithiophene (ITIC), [52] (5Z,5′-Z,5,5′-((7,7′-4,4,9,9-tetraoctyl-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene)-2,7-diy1)bis(benzo[c][1,2,5]thiadazole-7,4-diy1)(methyleneylidene)bis(3-ethyl-2-thioxothiazolidin-4-one) (IDTBR), [53] 2,2′-(2,2′-Z)-(12,13-bis(2-ethylhexyl)-3,9-diundecyl-12,13-dihydro-1,2,5-thiadiazolo[3,4-e]thieno[2′,3′:4,5′][thieno[2′,3′:4,5′]pyrrolo[3,2-g]thieno[2′,3′:4,5′][thieno[3,2-b,j]indaceno[2,1,6-d]-1,2,5-thiadiazolo[3,4-e]thieno[3,2-b,j]indaceno[2,1-d]pyridine)] bis(methane-lidene)bis(5,6-dichloro-1H-indene-1,3(2H) dione) (ZY-4C) [55] (Figure 1B). Among these, P3HT:ZY-4C was found to display the best performance of over 10% and a prominent stability under continuous thermal annealing at 80°C with an extrapolated T_80 (80% of the initial PCE) lifetime of up to 6350 h. To the best of our knowledge, this T_80 lifetime is the highest among the reported P3HT-based OSCs and approximately five times higher than the prior record (Table S1). [53] In contrast, the coarsening of P3HT crystals and aggregation of ITIC during the thermal annealing at 80°C resulted in rapid performance degradation within an hour for P3HT:ITIC devices. Accordingly, two novel materials matching guidelines of P3HT:NFA solar cells are established: (i) hypo-miscible blend with weak vitrification effect are prerequisites for high device performance; (ii) utilizing the diffusion limiting crystallization process of NFA to restrict the chain movement of P3HT is an effective method to avoid the formation of excessive domain sizes and thus improve thermal stability. We hope that the established guidance can open an avenue for further design and optimization of thermally stable, cheap, and highly efficient OSCs based on poly(3-alkylthiophene) and their close variations (e.g., poly[bis(2-butylcoctyl) [2,2′:5′,2″-terthiophene]-4,4″-dicarboxylate-5,5″-dil vinylene] (PTVT-T), [56] 3,3′-difluoro-3″,4″-bis(2-hexyldicyclo)-5,5″-dimethyl-2,2′:5′,2″-terthiophene (P4T2F-HD) [57].

2 | RESULTS

2.1 | Photovoltaic performance and thermal stability

To gain a thorough understanding of how the performance and its degradation details of blend films under thermal stress vary with different acceptors, we first fabricated OSC devices with a conventional device architecture of

OSCs, which has drawn abundant attention. [17, 19, 21] Thermal stress during outdoor operation generally has a great impact on morphological stability, which usually does not involve chemical reactions such as decomposition and photooxidation. [16] The thermal stability of OSC active layer is associated with the thermodynamics of blend systems and the kinetics of thermal treatments. [19, 22, 23] The initial morphology of the as-cast active layer generally remains in a non-equilibrium state and lacks adequate electron transport pathways, resulting in inferior performance. However, short-time thermal annealing or solvent vapor annealing provides large thermodynamic driving forces to regulate the molecular stacking and optimize phase separation structure. [24] Further morphology evolution under long-term thermal stress will lead to the degradation of device performance. [25] Such morphology evolution is driven by two factors; [26] one is the thermodynamic relaxation of the mixed amorphous phase as moving from the quenched state to the binodal, the other is the nucleation, growth and coarsening of the semi-crystalline components. [22, 27]

Blends of poly(3-hexylthiophene) (P3HT) and organic electron acceptor (fullerene, rylene diimide, etc.) are one of the most widely studied OSC material systems [27–32] and are often used as the model systems for stability studies. [33–36] For the P3HT:[6,6]-Phenyl-C61-butyric acid methyl ester (PC61BM) device, it has been observed that fullerenes with high diffusion coefficients can easily diffuse into microcrystals upon heating the blend above 60°C, inducing the formation of large aggregates of PCBM and dramatically reduced device efficiency. [37] P3HT:fullerene system is no longer the fruit-fly in the OSC community due to the strong aggregation tendency of fullerenes and inferior thermal stability of their devices. Instead, P3HT:nonfullerene acceptor (NFA) systems are receiving growing and worldwide interest, [38–45] owing to the adjustable chemical structure of NFAs and unprecedentedly high industrial figure of merits. [44] Nevertheless, the PCE and thermal stability of P3HT:NFA OSCs [45] are still significantly lower than that of the state-of-the-art results achieved with benzodithiophene-based copolymers. [19, 21] For instance, poly [(2,6′-4,8-di(5-ethylhexylthiienyl)benzo[1,2-b:3,3-b′]dithiophene)]-3-fluoro-2(2-ethylhexyl)carbonyl[thieno[3,4-b]thiophenediyl] (PTB 7-Th); [52] (5Z,5′-Z,5,5′-((4,4,9,9-tetrakis(2-ethylthienyl)-4,9-dihydro-s-indaceno[1,2-b:5,6-b′]dithiophene)-2,7-diy1)bis(benzo [c][1,2,5]thiadiazole-7,4-diy1)(methyleneylidene)bis(3-ethyl-2-thioxothiazolidin-4-one) (EH-IDTBR) delivered the best thermal stability than P3HT:EH-IDTBR under high temperature (120°C). [22] It is noteworthy that the T_g of P3HT (~25°C) is much lower than that of the widely studied benzodithiophene-based polymer donors. [46] Additionally, there are also pure polymer crystalline phase in P3HT-based OSCs, in addition to amorphous polymer-rich mixed domains and almost pure acceptor-rich domains. [47, 48] Further complicating this quandary is the fact that the semi-crystalline behavior of NFAs varies markedly with the chemical structure. Moreover, due to the complex and poorly manageable phase separation structure of the systems with semi-crystalline donors, the morphological stability investigations of these systems are far from satisfactory. To fulfill the above gap, it is exceedingly essential to establish new materials matching guidelines to simultaneously achieve high device performance and thermal stability [49–51] for these
FIGURE 1 (A) The multi-technique approach that covers spectroscopy, calorimetry, scattering, and microscopy in this work. (B) Chemical structures of the semi-crystalline polymer poly(3-hexylthiophene) (P3HT) and four representative nonfullerene acceptors (NFAs), namely ITIC, IDTBR, Y6, and ZY-4Cl. (C) Current density–voltage (J–V) characteristics and (D) External quantum efficiency (EQE) curves of the four organic solar cells (OSCs) under the optimized conditions. (E) Normalized power conversion efficiencies (PCEs) of the four P3HT:NFA devices versus the annealing time of active layer under continuous thermal heating at 80°C and the extrapolated T80 lifetime (i.e., the time required to reach 80% of the initial PCE) of the four systems. The vertical and dashed arrows mark the T80 of the four systems. (F) The summary of T80 lifetimes of P3HT-based solar cells reported to date. The details of each point are provided in Table S1.

ITO/poly(3,4-ethylenedioxythiophene) (PEDOT):poly (styrenesulfonate) (PSS)/P3HT:NFA/PDINO/Al. To endow a fair comparison of the photovoltaic performance based on P3HT donor and ITIC, IDTBR, Y6, ZY-4Cl acceptors, the devices were fabricated at the respective optimal conditions. The detailed methods of device fabrication can be found in Section “Experimental”. The typical current density–voltage (J–V) curves and external quantum efficiency (EQE) curves of the optimized devices are shown in Figure 1C,D, respectively, and the detailed device parameters of the four devices are summarized in Table S2. The integrated JSC values by EQE tests are in accordance with those from J–V data. The optimized device based on P3HT:ZY-4Cl exhibited the highest PCE of 10.2% with an open-circuit voltage (VOC) of 0.90 V, a short-circuit current density (JSC) of 16.7 mA cm−2, and a fill factor (FF) of 68.0%. Furthermore, we continuously monitored the thermal stability of these P3HT:NFA solar cells. Figure S1 depicts the normalized photovoltaic performance parameters of the four P3HT:NFA devices versus the annealed time of the active layers. During the continuous thermal treatment at 80°C in the dark, the most stable P3HT:ZY-4Cl solar cell exhibits an extrapolated T80 lifetime of 6350 h under continuous thermal annealing (Figure 1E), which is the highest reported for P3HT-based
2.2 Molecular stacking and orientation behaviors

Grazing incidence wide-angle X-ray scattering (GIWAXS) was employed to investigate the molecular stacking and orientation of P3HT:NFA blend films at the optimized conditions. The four blends displayed the preferential face-on molecular orientation as shown in 2D diffraction patterns (Figure 2A). To gain a thorough understanding of the molecular stacking and crystalline features, we proceeded to analyze the 1D scattering profiles of the blend films (Figure 2B). The corresponding in-plane (IP) and out-of-plane (OOP) line profiles and peak fitting results are shown in Figure S2, and the detailed parameters are presented in Table S3. For all P3HT:NFA blend films, strong π–π stacking (010) diffraction peaks appear at ∼1.68 Å⁻¹ with a d-spacing of ∼3.7 Å in the OOP direction and IP (100) diffraction peaks locate at ∼0.38 Å⁻¹ were assigned to P3HT. Considering the peak width of the diffraction peaks are often affected by paracrystalline disorder and lattice parameter fluctuation, it is difficult to get accurate crystallization properties by simply using the full width at half maximum of the peaks.\[58\]

It is well established that a higher crystalline/ordered volume fraction in films often promotes the intermolecular charge transport in OSCs.\[16\] The volume fraction of crystalline or paracrystalline regions in a film can be measured by the degree of crystallinity (DoC), which generally scales with the integrated intensity of the diffraction peaks in GIWAXS.\[59–61\] To quantify and further corroborate the effects of the different blend P3HT:NFA system on polymer crystallinity and orientation, we first performed pole figures and the relative DoC (rDoC) analysis of the P3HT scattering
AGGREGATE

FIGURE 3  (A) Atomic force microscopy (AFM) height images of four poly(3-hexylthiophene) (P3HT):nonfullerene acceptor (NFA) blend films. The scanned area is 2 μM × 2 μM. (B) Transmission electron microscopy (TEM) images of four P3HT:NFA blend films. The scale bars are inserted in the TEM images. (C) Size distributions in the four P3HT:NFA blend films

peaks in the optimized conditions. We plotted the pole figures of the P3HT (010) π–π stacking peak (Figure 2C) and calculated the rDoC of four P3HT:NFA blend films by integrating the scattering intensity across all angles (ω) from 0° to 90° (Figure 2D). The detailed step by step analysis procedures are shown in Supporting Information. Obviously, the rDoC of P3HT is the highest in P3HT:ZY-4Cl system, indicating that it has highly ordered molecular packing. The rDoC values of P3HT in P3HT:IDTBR and P3HT:Y6 were modest, and that of P3HT:ITIC was the lowest. For the (100) lamellar stacking peaks of P3HT, the pole figures (Figure 2E) and the rDoC values of P3HT in the four blend films (Figure 2F) also displayed a similar trend with the results of (010) π–π stacking peak. P3HT in the P3HT:ZY-4Cl blend has high rDoC in the backbone stacking direction and side-chain stacking direction, which provides favorable conditions for effective charge transport, and thus has a higher $J_{SC}$.

2.3  |  Morphological features

Hoping to further investigate how the blend morphology affects the OSC performances, we utilized atomic force microscopy (AFM) and transmission electron microscopy (TEM) to detail the morphological characteristics of the P3HT:NFA blend films (Figure 3A,B). The film surface roughness data of ITIC, IDTBR, Y6, and ZY-4Cl blends are 2.6, 2.7, 2.2, and 4.0 nm, respectively. As illustrated in TEM images, except for P3HT:ITIC, exhibiting a spindly fibrilar feature, all the blend films show short fiber aggregates. The difference in mechanical properties (e.g., modulus) between polymer donor and NFA materials can be effectively used to separate the components in blend films (see Figure S7). To gain some quantitative information of domain spacings of the four blends, we performed a fast Fourier transform analysis to attain the power spectral density (PSD) profiles of the real-space microscopy images. As shown in Figure 3C, P3HT:ZY-4Cl shows one characteristic peak and the corresponding average feature domain spacing reaches ~50 nm, indicating that the blend has more finely dispersed and smaller phase separation with interpenetrating structures, which are beneficial for efficient charge generation and charge transport. Unlike the P3HT:ZY-4Cl film, the other three blend films have multiple characteristic size scales. For P3HT:ITIC films, the peak in the low-q region (0.01–0.1 nm$^{-1}$) corresponds to the average length (~118 nm) of the long fibers in the film and the peak in the high-q region (0.1–1 nm$^{-1}$) probably corresponds to the aggregates in the film. The excessively long fibers are not favorable for exciton dissociation and charge transport, which result in the low $J_{SC}$ of the P3HT:ZY-4Cl film. Additionally, the P3HT:IDTBR blend shows obvious phase separation morphology with the large and uneven aggregate size. For the Y6 blend, the predominant characteristic size is larger than that of P3HT:ZY-4Cl. Moreover, there are obvious short fiber aggregates with a size scale of 15 nm in the P3HT:Y6 film. The difference in device performance may be caused by the different morphologies. Next, we will investigate the thermal stability from the evolution of molecular stacking and morphology with the annealing time.

2.4  |  Molecular stacking and morphology evolution

To further reveal the origin of the distinct thermal stability observed for the four P3HT:NFA systems, GIWAXS was used to compare the nanoscale packing of the blend films after short-term (24 h) and long-term (200 h) annealing. The 2D GIWAXS patterns and 1D GIWAXS profiles of the short- and long-term annealed films are displayed in Figures 4A,B and S3. Compared with the optimized films, the active layers that are thermally annealed at 80°C for a short or long time possess basically no new diffraction peaks with slight changes in the shape and intensity of OOP π–π stacking diffraction peaks or IP lamellar stacking peak. To quantify
FIGURE 4 Two-dimensional grazing incidence wide-angle X-ray scattering (GIWAXS) patterns of four poly(3-hexylthiophene) (P3HT):nonfullerene acceptor (NFA) blends with (A) short-term annealing and (B) long-term annealing. (C) Transmission electron microscopy (TEM) images of four P3HT:NFA blends with long-term annealing. The histogram of relative degree of crystallinity (rDoC) values of (D) (010) π–π stacking peaks and (E) (100) lamellar stacking peaks of P3HT in the four P3HT:NFA blends as a function of annealing time, and the rDoC of P3HT:ZY-4Cl in the optimized condition is normalized to 1. (F) The characteristic spacing of phase separation in optimized and long-term annealing blends.

The changes in crystalline morphology of the blend films, we extracted the rDoCs from pole figures of the (010) π–π stacking peak of P3HT under the thermal stress as a function of annealing time. It is known that the rDoC analysis captures the peak intensity of all crystallite orientations (ω from 0° to 90°) and not just the (010) diffraction peak in OOP direction. As depicted in Figure S5, the intensities of the pole figures of P3HT in P3HT:ITIC and P3HT:Y6 blend films were increased in all crystallite orientations under the thermal stress. While the intensity of the pole figures of P3HT in P3HT:IDTBR and P3HT:ZY-4Cl blend films only slightly increased near the direction of OOP. Therefore, as shown in Figure 4D, the gradually increased rDoC values of (010) of P3HT in P3HT:ITIC and P3HT:Y6 blend films under thermal stress may correspond to the growth and rearrangement of P3HT during annealing. The instability of nanoscale molecular stacking and the micrometer-scale crystals probably results in the gradual degradation of $J_{SC}$ and PCE. By contrast, the rDoC values of P3HT in P3HT:IDTBR and P3HT:ZY-4Cl blend films changed slightly, indicating the more stable morphology at the nanometer scale and thermal stability of the $J_{SC}$ with a slight degradation. The pole figures and rDoC values of P3HT in the (100) of P3HT also displayed similar results (Figures S6 and 4E).

Furthermore, the mesoscale morphology evolution of the films was investigated by TEM. Figure 4C displayed the morphology of four P3HT:NFA blends during long-term annealing at 80°C. Compared with the optimized blends, the contrast of the long-term annealed films enhanced significantly, indicating the increase of the phase purity for the blend films. To quantitatively compare the influence of thermal stress on the domain sizes, PSD analysis was carried out for the TEM microscopy images (Figure S8). The characteristic spacings of optimized and long-term annealing as shown...
in Figure 4F and the values are shown in Table S4. With the increase of annealing time, the characteristic spacings in all blend films increased. For P3HT:ZY-4Cl blend, the characteristic spacing increases slightly (from ~50 to ~53 nm) after long-term annealing. The morphologic evolution at mesoscopic scale is consistent with the crystallization evolution at nanoscale by GIWAXS results. In addition, the domain of the long-term annealed P3HT:IDTBR blends were more uniform and the characteristic spacings of P3HT:IDTBR has a slight increase. Thus, we speculated that the later annealing at 80°C optimized the phase separation structure of the blend, which is the possible reason for the burn-in-free performance of this system within 200 h. In other words, the morphology evolution in P3HT:IDTBR within thermal annealed 200 h induced the purer phase domain and promoted more efficient exciton dissociation and charge transport, resulting in the enhancement of FF and $J_{SC}$.[65] In particular, as shown in Figure S9, the fiber size and aggregation in the P3HT:ITIC films increased rapidly under thermal stress. Specifically, the PSD analysis of TEM images showed that the positions of the characteristic peaks moved to lower-q gradually with the extension of annealing time, indicating that the characteristic sizes increased gradually. The oversized aggregates and micrometer-scale crystals increase the charge recombination probability and significantly affect the charge collection efficiency, thereby leading to sharp degradation of device performance even after annealing at 80°C for 1 h. These changes of characteristic spacings could be considered the coarsening of ITIC aggregates and the crystallization of P3HT supported by GIWAXS results.

2.5 Kinetic vitrification and thermodynamic mixing

To gain insight into the evolution of molecular stacking and nanomorphology, we utilized differential scanning calorimetry (DSC) to analyze the enthalpy of crystallization ($\Delta H_{P3HT}$) of P3HT fraction in the various blends. The $\Delta H_{P3HT}$ is directly correlated to the degree of molecular order of P3HT, which reflects how strongly the NFA hinders the crystallization of P3HT. A lower $\Delta H_{P3HT}$ signifies a stronger vitrifying effect of NFA on the polymer, resulting in a highly intermixed amorphous phase of the blend.[66] As displayed in Figure 5A, the crystallization of P3HT is hindered increasingly in the order ZY-4Cl < IDTBR < Y6 < ITIC. Due to the increasing influence of the liquid–liquid demixing to the crystal–melt transition with the increasing volume fraction of the NFA,[67] we chose the ratios of 9:1, 8:2, and 7:3 for P3HT and NFA materials. Accordingly, ITIC has the highest kinetic vitrification contribution on P3HT, indicating the strong hindering of the P3HT crystallization during the casting process.

The miscibility of a blend system and the crystallinity of photovoltaic materials that can be used to predict morphologic stability, which is the onset of backbone relaxation processes.[72] The $T_g$ of P3HT is ~25°C,[46] which is lower than the thermal annealing temperature ($T_{annl}$, 80°C), indicating that the molecular segment movement and rearrangement of the P3HT will occur during the thermal annealing of the active layer, according to the GIWAXS results. To elucidate the differences in morphological stability and device thermal stability, the thermal motions of four NFAs are needed to be delineated. The $T_g$s of NFAs are associated with the mobility and crystallization of NFAs,[26] which can be explored by ultraviolet (UV)–Vis absorption spectroscopy for semi-crystalline materials.[21,60] A discernible change in the absorption spectrum can be observed when the annealing temperature surpassed the $T_g$; thus, the deviation metric ($\Delta T_g$) is generally used to estimate the $T_g$ values of NFAs.[73,74] As displayed in Figures 5D–F and S11, the thermal transition temperatures of ITIC, IDTBR, Y6, and ZY-4Cl are 124°C, 97°C, 107°C, and 90°C, respectively. Prior studies have shown that D-A type conjugated polymer donors with higher $T_g$ often deliver higher stability.[21,22] While for P3HT-based OSCs, which have the three-phase morphology (pure polymer phase, pure acceptor phase, and the mixed phase)[75] and lower $T_g$ of P3HT, the thermal stability may not be simply determined by the $T_g$ of the acceptors. The relationship between $T_g$ and the thermal stability of blends will be discussed below.

3 DISCUSSION

3.1 Morphology–performance–thermal stability relationships

Having understood the thermodynamic properties, kinetic factors, and morphological properties of the four P3HT:NFA systems, we attempted to connect them with device performance and thermal stability by assessing the above results collectively. We can therefore depict the schematic diagrams for the four blend systems (Figure 6A). Kinetic vitrification and thermodynamic mixing significantly influence the optoelectronic conversion processes.[66] Due to the relatively low $\chi_{aa}$ value of P3HT:ITIC in the four systems and the high $T_g$ of ITIC, the high miscibility and stronger vitrifying effect hindered the crystallization of P3HT and thus the inefficient charge extraction, which result in the lowest photon response with EQE about 25% in the range from 300 to 800 nm. Similarly, the P3HT:Y6 system was in accordance with the
FIGURE 5  (A) The enthalpies of crystallization of poly(3-hexylthiophene) (P3HT) as measured for the four different blends with various acceptor fractions. (B) Estimates of the miscibility from measurements of the melting point depression as a function of acceptor’s volume fraction. (C) The plot of $\chi_{aa}$ of the four systems. (D) Absorption spectra of ZY-4Cl thin films annealed at various temperatures. (E) Ultraviolet (UV)–Vis deviation metric results of ZY-4Cl. (F) The plot of the thermal transition temperatures of the four nonfullerene acceptors (NFAs).

FIGURE 6  (A) Schematic illustrations of the $\chi$–$\phi$ phase diagrams of poly(3-hexylthiophene) (P3HT):nonfullerene acceptor (NFA) systems. The blue and red lines are binodal curves and liquidus, respectively. The solid lines correspond to thermodynamic equilibrium, whereas the dashed lines are meta-stable states. The gray shadow marks the percolation threshold ($\phi_p$) of blend systems, and $\phi_i$ indicates the acceptor volume fraction of blends in the cast solutions. The square, spherical, dots, and triangles represent the states in initial blends in the cast solutions, optimized and long-term annealed and final devices, respectively. The arrows from optimized positions to final state represent the evolution of the composition of mixed phases during the continuous thermal annealing. (B) Schematic illustrations of two paths of nanomorphology evolution as a function of time. In this work, P3HT:ITIC ($T_{Dg}$ of crystalline polymer donor) $< T_{annl} < 0.8 \times T_{Ag}$ ($T_{Ag}$ of small molecule acceptor)) and P3HT:ZY-4Cl ($T_{Dg} < 0.8 \times T_{Ag} < T_{annl} < T_{Ag}$) belongs to the typical cases of paths I and II, respectively. P3HT:ITIC. In sharp contrast, for P3HT:ZY-4Cl blend, the weak vitrification effect leads to the highly ordered stacking for both polymer and acceptor. Additionally, driven by the high $\chi_{aa}$ of P3HT and ZY-4Cl, the acceptor composition of its amorphous mixed phase can be quenched close to the electrical percolation threshold through precise regulation of the processing conditions (e.g., annealing temperature and time), resulting in the high $J_{SC}$ and FF. We also found that although P3HT:IDTBR and P3HT:ZY-4Cl had the similar vitrification effect (Figure 5A), the crystallization of P3HT was still inhibited by IDTBR. Based on the results, the mixing thermodynamic contribution appears to dominate over the effect of kinetics vitrification, which is consistent with the P3HT:ICBA results. In brief, efficient charge separation and transport rely on the presence of a pure crystalline phase, which is the combined effect of thermodynamic miscibility and kinetic vitrification.

During the continuous thermal annealing at 80°C, the $T_{80}$ is estimated to be 1, 1500, 100, and 6350 h for ITIC, IDTBR, Y6, and ZY-4Cl-based solar cells, respectively. The significant differences of the four systems in thermal stability indeed encourage us to analyze the underlying causes. For the most stable system P3HT:ZY-4Cl, the PCE dropped by about 14% of its initial efficiency after thermal annealing more than...
1500 h. The excellent morphological stability of P3HT:ZY-4Cl blends may be attributed to the diffusion-limited crystallization process\[76] of ZY-4Cl, which appears to induce the kinetic equilibrium state of mutual restriction. More specifically, ZY-4Cl diffuses locally since the $T_{\text{annl}}$ (80°C) is higher than $0.8 \times T_g$ ($\sim 72$°C) but lower than $T_g$ ($\sim 90$°C) of ZY-4Cl, resulting in the fine-grained nanostructure that does not evolve further with time (Figure 6B, path II). Similarly, the $T_g$ of IDTBR is close to that of ZY-4Cl, which also undergoes a diffusion-limited crystallization process during the long-term thermal annealing. Different from P3HT:ZY-4Cl system, the crystallization of P3HT is imperfect due to the vitrification effect and better miscibility of P3HT:IDTBR. Therefore, the polymer rearranges and the mixed phase purifies during long-term thermal annealing, resulting in the device performance degradation. Nevertheless, what made matters worse was that the stronger vitrification effect caused the intermixed amorphous polymer-rich phase in the P3HT:ITIC, resulting in the crystallized and purified P3HT under continuously thermal annealing to form larger crystals and isolated ITIC aggregates (Figure 6B, path I).\[77] Consequently, dramatic decreases in $J_{\text{SC}}$ and $PCE$ (Figure S1) were observed.

Obviously, not only the miscibility of the systems and the $T_g$ of the materials affect the thermal stability of OSCs, but also the external conditions such as $T_{\text{annl}}$ plays an important role. In general, when the $T_{\text{annl}}$ (e.g., up to 100°C) is much higher than the $T_g$ of NFAs, NFAs will change from diffusion-limited crystallization to long-range diffusion and crystallization.\[76] The crystallization of P3HT and NFAs will lead to the appearance of micrometer-scale crystals in the blend films, which affects the photovoltaic performance. To investigate the effect of high-temperature thermal annealing on the device performance of P3HT:NFA systems, we tested the device performance of P3HT:ZY-4Cl system annealed at 130°C for different times. The experimental data are shown in Figure S12 and Table S5. Clearly, thermal annealing at 130°C results in rapid degradation of device performance. Therefore, considering the practical application of OSCs (outdoor temperature generally does not exceed 100°C), the design and synthesis of new fused ring electron acceptors with high $T_g$ (much greater than 100°C) are conducive to promoting the commercial application of low-cost OSCs.

3.2 | Guide and regulation methods for highly efficient and thermally stable blends

The low-cost P3HT-based solar cells are different from the mainstream high-efficiency systems because of the strong crystallization and the low $T_g$ characteristic of P3HT. Noteworthy, it is essential to maintain hypo-miscibility of P3HT and acceptors as well as weak vitrification effect to form more favorable pathways for charge transport.\[53] Additionally, optimizing the crystallization process and phase separation structure of P3HT:NFA blends by enhancing the crystallization of P3HT can further improve the PCE, which has been recently demonstrated by Han and coworkers.\[78] Complementary to the prior studies, our work provides an in-depth explanation of the reason why preferential crystallization of P3HT can significantly improve the device performance of P3HT:IDTBR. Due to the miscibility and vitrification effect, the crystallization of P3HT is inhibited to form pure phases. We thus considered a higher regioregularity (95%) of P3HT (P3HT-H) to pair with IDTBR and achieved an increase in $PCE$ from 6.5% to 7.3%, which is the record PCE of P3HT:IDTBR system (Figure 7 and Table S6). Simultaneously, the thermal stability also has been dramatically improved (Figure 7D) with the extrapolated $T_{\text{80}}$ increased from ~1500 to 2700 h (Figure S13). It is largely attributed to the fact that the higher regioregularity of P3HT is conducive to the formation of more pure phases of P3HT, which is mainly manifested in the significantly improved FF from 0.58 to 0.66. Such a change in the crystallization kinetics and mixing thermodynamics is important to meet the requirements for realizing efficient and thermally stable P3HT:NFA solar cells. Though this work focused primarily on P3HT:NFA systems, the guidelines gained here could be also useful to the much broader range of polythiophene and poly(thiophene vinylene) solar cells.\[35,45]

Lastly, we note that Y6 and ZY-4Cl have similar molecular backbone structures, but the optimized device performance and thermal stability of P3HT:Y6 and P3HT:ZY-4Cl are significantly different. For device performance, there is no doubt that the cyanosubstituted compound of Y6 has much higher miscibility with P3HT compared to the hydroxy-substituted compound of ZY-4Cl. The $T_g$ of ZY-4Cl is lower than that of Y6, Qin et al. also discovered that the use of chlorine leads to a lower $T_g$ than fluorine.\[21] From these studies, one may think Y6-based devices are more stable, while our stability results pointed to a contrasting trend. The reasons behind this are noted in the following: (i) the morphology of the P3HT:Y6 film formed under the driver of mixing thermodynamics; (ii) the $T_g$ of P3HT is lower than that of acceptor small molecules. The results indicate that the above factors should be considered in the study of thermal stability in polythiophene-based OSCs.

4 | CONCLUSIONS

To promote the device performance and thermal stability of semi-crystalline P3HT:nonfullerene solar cells, a multi-technique approach based on X-ray scattering, real-space microscopy, calorimetry, and UV–Vis spectroscopy was utilized. Encouragingly, a microstructure–thermal stability picture emerges and connects the thermodynamic mixing, kinetics vitrification, the evolution of nanostructure, and device performance and stability of a set of P3HT:nonfullerene systems with notable differences in the chemical structures of NFAs. The molecular matching rules are summarized as follows: (i) the weak vitrification effect and hypo-miscibility of materials are beneficial to achieve high device performance; (ii) regulating the diffusion-limited crystallization process of NFA and the movement of chain segments of semi-crystalline polymer donors can realize excellent morphological stability. Benefiting from the highly ordered molecular stacking and low miscibility, the P3HT:ZY-4Cl system reached the highest $PCE$ of over 10% and the record-high $T_{\text{80}}$ lifetime of >6000 h for P3HT solar cells. Such exceptional results showcase the great potential of P3HT:ZY-4Cl solar cell. By contrast, P3HT:ITIC held the hindered P3HT crystallization and inefficient charge transport due to the stronger vitrification effect and relatively low $\chi_\infty$ value. Importantly, motivated by the above blending guidelines, a higher regioregularity batch
of P3HT sets a PCE record of 7.3% and yields improved thermal stability in the binary P3HT:IDTBR system. Additionally, the multi-technique approach and strategies displayed in this work would help reduce the strong reliance on trial-and-error screening for achieving highly efficient, cheap, and operationally stable OSCs based on polythiophene or analogous semi-crystalline polymers,[80] especially in the combinations of new materials.

5 | EXPERIMENTAL

5.1 | Materials

P3HT ($M_w = 26$ kg mol$^{-1}$, polydispersity index = 1.49) was synthesized in our laboratory using an eco-friendly direct arylation protocol.[71] ITIC, Y6, and ZY-4Cl were synthesized according to the procedures as previously reported.[52,54,55] IDTBR was commercially available from Solarmer Materials Inc. PEDOT:PSS (Baytron PVP A14083) and N,N'-Bis(N,N-dimethylprop-1-amine oxide)perylene-3,4,9,10-tetracarboxylic diimide (PDINO) were purchased from the CleviosTM and Derthon Optoelectronic Materials Science Technology Co. Ltd, respectively. All solvents were purchased from Sigma Aldrich or Heowns, and used without further purification.

5.2 | Photovoltaic device fabrication and characterization

Devices were fabricated with the conventional device structure of ITO/PEDOT:PSS/P3HT:NFA/PDINO/Al. The ITO substrates were cleaned ultrasonically with detergent, deionized water, acetone, and isopropanol for 10 min each and then dried by argon flow. P3HT:NFA (1:1, wt/wt) were dissolved in tetrahydrofuran (THF) with a total concentration of 16 mg mL$^{-1}$ and stirred at 50$^\circ$C for 4 h without any solvent additives. A 30 nm layer of PEDOT:PSS was spin-coated on ITO at 4000 rpm after 25 min of UV-ozone treatment. After annealing at 150$^\circ$C for 20 min, all PEDOT:PSS-coated ITO substrates were transferred to the nitrogen-filled glove box. The active layers were deposited by spin-coating the P3HT:NFA blend solutions at 2000–3000 rpm with a thickness of about 100 nm, as measured by Bruker Dektak 150 profilometer. The active layers were then thermally annealed at 130$^\circ$C except P3HT:IDTBR was thermally annealed at 100$^\circ$C for the optimized performance.[79] The PDINO in methanol solution was spin-coated onto the active layers at 3000 rpm as the electron transporting layer. Finally, the aluminum electrode was thermally deposited on the top surface (100 nm) under a pressure of $<1.5 \times 10^{-4}$ Pa to acquire an area of 4 mm$^2$ solar cell with a metal aperture.

$J$–$V$ curves of the four P3HT:NFA systems were measured by Keithley 2400 source meter under the standard AM 1.5G spectrum, 100 mW cm$^{-2}$, provided by an AAA solar simulator (SS-F5-3A, Enli Technology Co. Ltd., Taiwan). The light intensity was calibrated with a standard photovoltaic cell equipped with a KG5 filter in a glove box. EQE curves were measured through the solar cell spectral response measurement system (QE-R, Enli Technology Co. Ltd.), which was calibrated using a standard monocrystalline silicon solar cell before the performance measurements. For the thermal stability of the active layer, the active layers were kept under N$_2$ in dark conditions to limit the extrinsic degradation and intrinsic photodegradation.
5.3 Physical properties and morphology characterizations

The UV–Vis–NIR absorption spectra were recorded on a Shimadzu UV-3600 Plus spectrometer. The procedures of UV–Vis deviation metric results for the four NFAs were detailed in the literature.[73] DSC samples were dissolved in THF with a concentration of 24 mg mL⁻¹ and stirred at 50°C for 4 h. Then the solution was drop-cast on a clean glass substrate and kept in high vacuum for 24 h to remove the residual solvent prior to transfer to the DSC pan. The DSC thermograms were all acquired on a Q25 differential scanning calorimeter (TA Instruments) using a heating/cooling rate of 10°C min⁻¹. GIWAXS measurements were carried out at beamline 1W1A, Beijing Synchrotron Radiation Facility (BSRF) and beamline BL02U2, Shanghai Synchrotron Radiation Facility (SSRF). The energy of the X-ray beam is 10 keV with an incidence angle of ~0.15° to allow for complete penetration of X-ray into the films. The beam center and sample-to-detector distance were calibrated with LiF. The active layers were directly prepared on Si substrates with the same conditions as the device preparation. Nanoscale morphology of the active layers was characterized by a Bruker MultiMode 8 AFM in tapping mode. TEM images of active layers were obtained by a JEOL JEM-2100 PLUS electron microscope operating at an accelerating voltage of 120 kV.

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AUTHOR CONTRIBUTIONS

Long Ye and Mengyuan Gao conceived the idea and designed the experimental protocols. Mengyuan Gao performed the device fabrication and characterization, morphology characterization, and thermodynamic analysis. Yang Liu supplied the photovoltaic materials. Kailu Xian assisted the beamline and sample-to-detector distance were calibrated with LaB₆. The active layers were directly prepared on Si substrates with the same conditions as the device preparation. Nanoscale morphology of the active layers was characterized by a Bruker MultiMode 8 AFM in tapping mode. TEM images of active layers were obtained by a JEOL JEM-2100 PLUS electron microscope operating at an accelerating voltage of 120 kV.

ETHICS STATEMENT

There are no ethical issues in this work.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available on request from the corresponding authors.

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