

Balanced Intra- and Interchain Exciton Delocalization Enables Efficient All-Polymer Solar Cells

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(Received 22 December 2025; revised 9 April 2026; accepted 4 May 2026; published 8 June 2026)

Polymerized Y-type nonfullerene acceptors (PY-NFAs) have shown great promise for efficient and stable organic solar cells (OSCs), yet their excited-state dynamics and structure-photophysics-performance relationships remain unclear. Here, we investigate a series of PY-NFAs and distinguish between intrachain excitons (intra-Ex) and interchain excitons (inter-Ex) formed in the solid state using cryogenic transient absorption (TA) spectroscopy at 100 K. We identify the emergence of trapped intra-Ex in the PY-NFA films from approximately 100 ps onwards after photoexcitation. By comparing this low-temperature TA signal among different PY-NFA films, we uncover a strong correlation between the trapped intra-Ex signature and the performance of these PY-NFAs in donor-acceptor blend OSC devices. This correlation indicates that the low-temperature TA response provides a quantitative measure of structural disorder in the PY-NFA aggregates and in the corresponding donor-acceptor blends. Correlating these spectroscopic results with molecular packing and morphological data, we reveal that high-performance PY-NFAs simultaneously exhibit (1) extended backbone conjugation and large intrachain exciton bandwidths and (2) uniform, oriented interchain packing despite moderately increased π - π stacking distances. These findings provide new design rules for PY-NFAs and offer deeper insight into how structural disorder and exciton dynamics govern OSC performance.

DOI: [10.1103/fls9-jc34](https://doi.org/10.1103/fls9-jc34)

I. INTRODUCTION

The development of Y-type nonfullerene acceptors (Y-NFAs), which include the landmark system Y6 and its derivatives, has enabled single-junction organic solar cells (OSCs) with over 20% power conversion efficiencies (PCEs) [1–6]. However, current high-efficiency OSCs tend to show relatively fast performance degradation under continuous solar illumination, which is largely associated with the thermodynamic instability of the nanoscale donor-acceptor bulk-heterojunction morphology [7–9]. Polymerized Y-type NFAs (PY-NFAs), which are composed of Y-NFA repeat units linked by π -conjugated spacers, have emerged as promising candidates for enabling OSCs with high efficiency and stability. Compared to

their small-molecule counterparts, PY-NFAs have larger miscibility with state-of-the-art polymer donors (such as PM6 and D18) and are less prone to diffuse into the donor domains under solar-cell operation, thus leading to more stable blend morphology and devices [7–12]. Recent development of PY-NFAs has promoted the PCEs of all-polymer OSCs from approximately 13% in 2020 to approximately 19% in 2025 [13–24].

Understanding the photoexcited state properties and dynamics is crucial for rational design and optimization of OSC materials and devices. While numerous studies have examined the excited-state properties of small-molecule Y-NFAs, detailed investigations of PY-NFAs remain limited [11,25–28]. Due to the A–DA'D–A structure with a curved geometry, small-molecule Y-NFAs can form a three-dimensional intermolecular packing structure in both pure films and donor-blended films [27,29]. Such packing gives rise to intermolecular excitons with strong charge-transfer (CT) character that promote free charge generation, particularly in ordered packing regions [25–27]. In PY-NFA aggregates, excitons can be delocalized along the polymer backbone to form intrachain excitons (intra-Ex)

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and between neighboring chains to form interchain excitons (inter-Ex) [30,31]. However, the interplay between these photoexcited states, as well as their roles in optimizing OSC performance, have remained unclear. Transient absorption (TA) spectroscopy has been extensively employed to study the photoexcited state dynamics with subpicosecond temporal resolution, but overlapping spectral features of various photoexcited states often hinders detailed analysis [32].

Here we report an investigation of photoexcited state properties and dynamics in a range of neat PY-NFA films. By performing TA measurements at cryogenic temperature (100 K), we identify the presence of trapped intra-Ex in the various PY-NFA films from approximately 100 ps onwards after the initial photoexcitation. Importantly, by comparing this low-temperature TA signal among the various PY-NFA films, we discover a strong correlation between this signal and the OSC performance of these PY-NFAs when they are blended with donor polymers and made into devices. This result indicates that this low-temperature TA signal provides a measure of the degree of structural disorder (S) in these PY-NFA aggregates as well as their corresponding donor-acceptor blends. By relating these results with molecular packing and structural morphology data, our results provide new insights for PY-NFA material design and development. Specifically, we find that developing PY-NFAs that exhibit both: (1) extended backbone conjugation and large intrachain exciton bandwidth, and (2) oriented interchain packing with moderately increased π - π stacking spacings (approximately 3.90 Å), can synergistically lead to reduced structural disorder and thereby enhanced device performance. This finding challenges the prevailing notion that NFAs with smaller π - π stacking spacings (i.e., tighter

intermolecular packing) can generally lead to more efficient OSC devices.

II. RESULTS

A. Probing intra- and interchain excitons in PY-IT

We first study PY-IT, which is synthesized via polymerization of Y5-I-C20-Br molecules and thiophene linkers [chemical structures in Figs. 1(a) and 1(b)] [23]. In dilute chloroform solution (0.001 mg ml^{-1}), where PY-IT chains are dispersed and interchain electronic coupling is minimal, the photoexcited states are dominated by intra-Ex delocalized along the polymer backbone. The absorption peak of PY-IT in solution (approximately 795 nm) is significantly redshifted relative to that of Y5-I-C20-Br in solution (approximately 734 nm) [Fig. 1(c) and Fig. S1 in the Supplemental Material [33]], indicating that the intra-Ex in PY-IT are more delocalized than the localized excitons (LEs) in the monomer. In the spin-coated film of PY-IT, the absorption peak redshifts further and a low-energy tail emerges beyond approximately 860 nm. We attribute this additional feature to the emergence of inter-Ex with strong CT character formed between neighboring chains [30,31].

Figure 2(a) shows the TA data of PY-IT neat film at 100 K under 700 nm photoexcitations. We observe ground-state bleaching (GSB) signals in the ranges of approximately 630–880 nm and 500–550 nm, as well as photoinduced absorption (PIA) signals at approximately 550–630 nm, 880–910 nm, and 1100–1600 nm. We begin by focusing on 750–910 nm region, where both GSB and PIA signals are prominent and exhibit clear spectral evolution with increasing time delay. The GSB signal of PY-IT

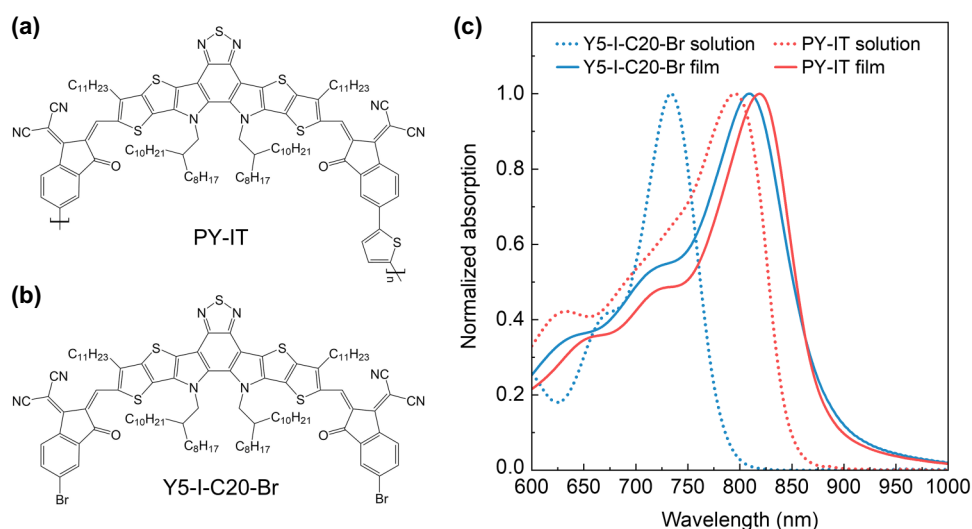


FIG. 1. (a),(b) Chemical structures of PY-IT (a) and Y5-I-C20-Br (b). (c) Absorption spectra of films and dilute solutions (0.001 mg ml^{-1} in chloroform) of PY-IT and Y5-I-C20-Br.

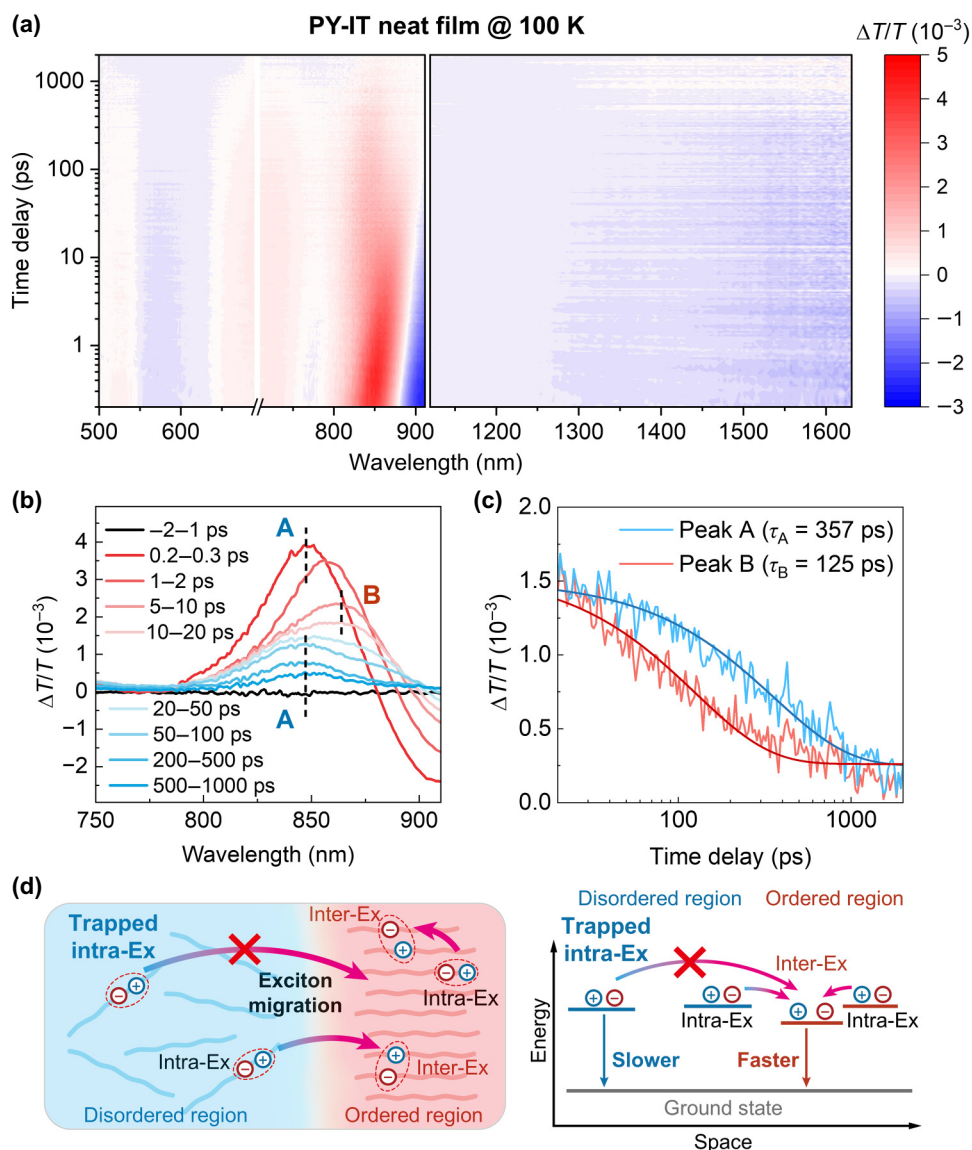


FIG. 2. (a) Broadband transient absorption (TA) data of PY-IT neat film pumped at 700 nm measured at 100 K. (b) TA spectra of PY-IT neat film at 100 K. (c) Decay kinetics and fitted lifetime of signals at Peaks A and B in TA spectra of PY-IT neat film at 100 K. (d) Schematic illustration of the excited-state transitions in PY-IT neat film at 100 K. Intra-Ex and inter-Ex represent intra- and interchain excitons, respectively.

neat film shows a significant redshift between approximately 0.2 ps to approximately 10 ps [Fig. 2(b), see TA spectra with broader regions in Fig. S2 in the Supplemental Material [33]]. For clarity, the early-time GSB peak (approximately 848 nm at <0.5 ps) is labelled Peak A, while the peak observed at later times (approximately 863 nm at >10 ps) is labelled Peak B. This redshift of GSB suggests a transition from higher-energy to lower-energy excited states within this timescale.

To understand this transition, we measure the TA spectra of a dispersed PY-IT film (1 wt.% PY-IT in polystyrene matrix). At 100 K, the TA spectra show little variation with increasing time delay (Fig. S3 in the Supplemental

Material [33]) and largely resemble the early GSB/PIA signals (i.e., 0.2–0.3 ps) observed for the neat PY-IT film. The photoluminescence spectrum and exciton lifetime of this film are similar to those of a dilute PY-IT solution (Fig. S4 in the Supplemental Material [33]), confirming that PY-IT chains are well isolated by polystyrene and interchain electronic couplings are weak, such that only intra-Ex are formed. These results confirm that intra-Ex are dominant in the neat film at early times, and the spectral redshift observed for the neat PY-IT film up to approximately 5 ps (i.e., GSB peak shift from A to B) can be assigned to the transition from intra-Ex to inter-Ex.

Between approximately 20 ps to approximately 100 ps, we find that the GSB peak position blueshifts from Peak B back to Peak A [Fig. 2(b)]. Tracking the TA decay kinetics shows a longer lifetime for signal at Peak A (approximately 357 ps) compared to that at Peak B (approximately 125 ps) [Fig. 2(c)]. Since it is unlikely that the lower-energy inter-Ex states will migrate back to populate the higher-energy intra-Ex states at this temperature, we consider that such spectral blueshift is due to the faster decay of inter-Ex back to the ground state, leaving signals from longer-lived intra-Ex states to dominate from approximately 200 ps onwards. These longer-lived intra-Ex are likely trapped in the disordered regions since they do not transition into inter-Ex.

A schematic illustration of the photoexcited state dynamics at 100 K is shown in Fig. 2(d). First, photoexcitations at 700 nm primarily generate intra-Ex in the neat film. Those created near the regions with strong intermolecular electronic coupling (i.e., with ordered chain packing) can gradually convert into inter-Ex, while those created deep in the disordered regions remain as intra-Ex. These trapped intra-Ex states outlive the inter-Ex states, thus dominating the TA signals at later times (e.g., after approximately 100 ps).

At room temperature, we observe similar redshift of GSB peak at early time but it completes at a faster rate than at 100 K, indicating faster intra-Ex to inter-Ex transition (approximately 1 ps, see Fig. S5 in the Supplemental Material [33]). Interestingly, the subsequent spectral blueshift that we associated with the tracking of trapped intra-Ex states is not observed at room temperature. This likely reflects that, at room temperature, even those intra-Ex states formed deep in the disordered regions are able to thermally migrate to the ordered regions and turn into inter-Ex. Therefore, our results suggest that studying TA dynamics at cryogenic temperatures can provide information about the morphology-dependent distribution of intra-Ex and inter-Ex states formed in neat spin-coated PY-NFA films. Specifically, we hypothesize that tracking the TA signal intensity of trapped intra-Ex at approximately 100 ps may provide a direct measure of the structural disorder of these PY-NFAs that affect their performance in OSC devices.

B. Relate trapped intra-Ex signal to structural disorder

We extend the cryogenic TA study to other model PY-NFAs including POY, PYT, PYF-T-*o*, PY-OD and PY-DT [see chemical structures in Fig. 3(a)]. Similar to PY-IT, their neat films also exhibit a red shift followed by a blue shift in TA spectral peaks at 100 K [Fig. 3(b); see Fig. S5 in the Supplemental Material [33] for TA data at 300 K], indicating the ubiquitous presence of trapped intra-Ex (Peak A at later times) in the various PY-NFAs at

100 K. Among these systems, POY and PYT films show higher intensity of trapped intra-Ex than others [Fig. 3(b); Table S1 in the Supplemental Material [33]].

We then investigate the correlation between trapped intra-Ex signal intensity of the various PY-NFAs and their optimized OSC device performance. We tentatively assign the Peak A intensity at approximately 100 ps time delay as the signal intensity due to trapped intra-Ex states in the various PY-NFAs, and divide it by the estimated number of photoexcitations initially created by pump pulse for fair comparison among samples (Table S1 in the Supplemental Material [33]). OSC device parameters of the studied PY-NFAs are taken from the literature (Table S2 in the Supplemental Material [33]) with conditions [19,21,34–36]: (1) the blend devices are binary ones based on PY-NFAs and the most commonly used donor polymer, PM6; (2) the devices were fabricated with the same device architecture, typical charge transport layers and additives and similar procedures.

Interestingly, we observe a strong correlation between the signal intensity of trapped intra-Ex of these PY-NFAs and the PCEs of their blend OSC devices [Fig. 3(c)]. Specifically, PY-NFAs with lower trapped intra-Ex intensity (e.g., PY-IT and PY-DT) generally achieve higher PCEs in devices compared to those with higher trapped intra-Ex intensity (e.g., POY and PYT). This aligns with previous findings that PY-NFAs can form similar chain packings in both neat films and blended films with PM6 [37,38]. Such strong correlation supports our hypothesis that the signal intensity of trapped intra-Ex provides a measure of structural disorder in these PY-NFAs as well as their corresponding donor-acceptor blends. The structural disorder (S) in these systems can thus be estimated by

$$S = \frac{\text{Signal intensity of Peak A at 100 ps}}{\text{Total excitations created by pump pulse}}$$

Among the device parameters, the device fill factor (FF) shows the strongest correlation with the degree of structural disorder of these PY-NFAs since it is closely related to the charge transport and recombination loss during device operation. This is supported by morphological characterization results shown below. A weaker correlation is observed for short-circuit current density (J_{SC}), which is because it depends not only on charge generation but also on the different light-absorption properties of these PY-NFAs and their blend films. The various optical gaps of these PY-NFAs (Fig. S6 in the Supplemental Material [33]) can also explain the lack of correlation between S and device V_{OC} , which is greatly affected by the energetic levels.

C. Exciton bandwidth and intra-Ex delocalization

In addition to the varying trapped intra-Ex signal intensities and S , these PY-NFAs also show different extents

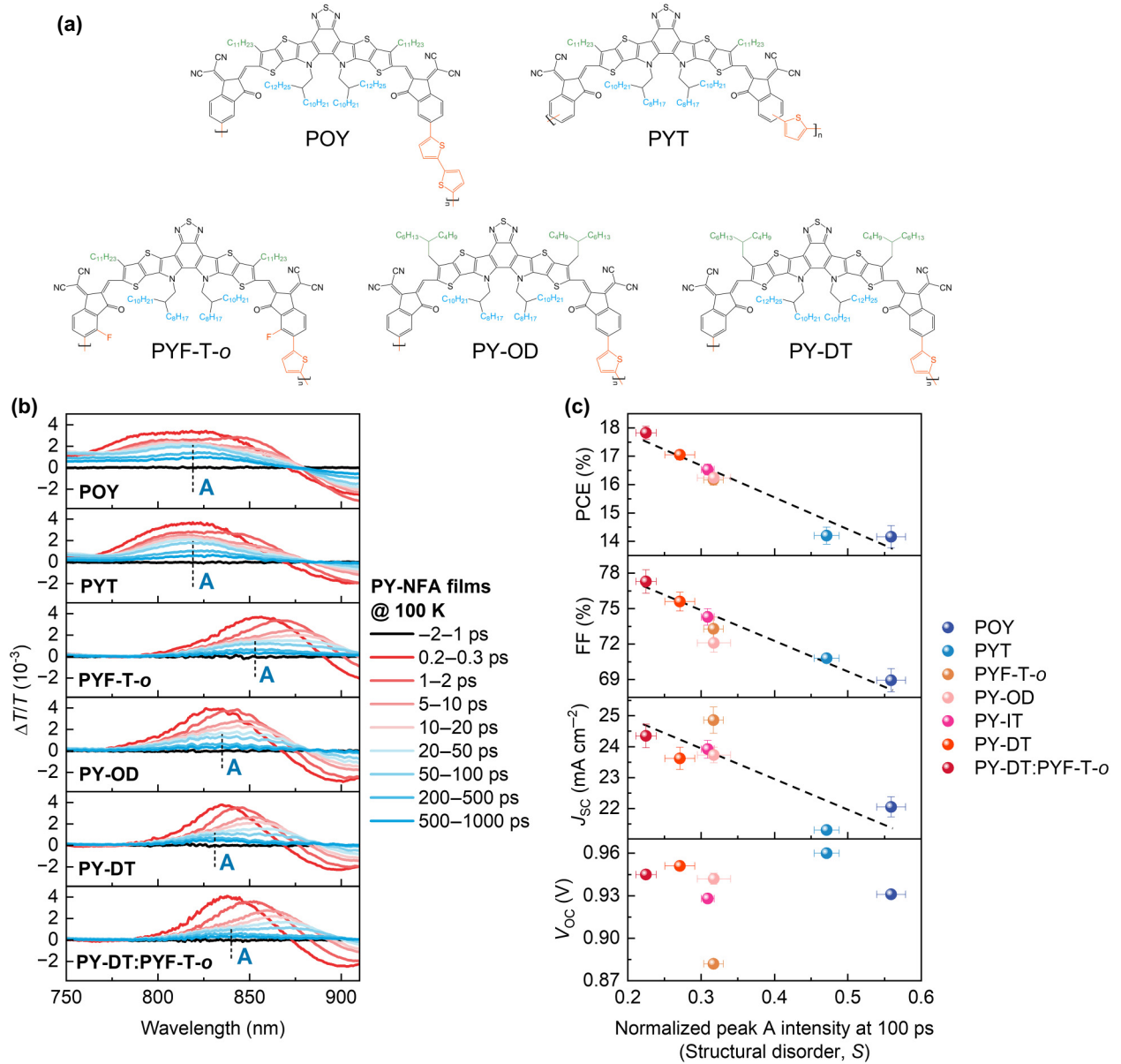


FIG. 3. (a) Chemical structures of PY-NFAs, POY, PYT, PYF-T-o, PY-OD, and PY-DT. (b) TA spectra of PY-NFA neat films pumped at 700 nm at a temperature of 100 K. (c) Plots of blend device power conversion efficiency (PCE), fill factor (FF), short-circuit current density (J_{sc}), and open-circuit voltage (V_{oc}) with respect to the signal intensity of trapped intra-Ex (Peak A intensity at approximately 100 ps) in PY-NFA neat films normalized by the total photoexcitations created by pump pulse. The black dashed lines serve as a guide to the eye. The structural disorder, S , probed by trapped intra-Ex is defined as the normalized Peak A intensity at approximately 100 ps. The device performance parameters are collected from the literature according to the selection criteria described above [19,21,34–36].

of intra-Ex delocalization. Figure 4(a) plots the neat film absorption spectra of these PY-NFAs, showing dominant 0–0 transitions over 0–1 transitions (i.e., the ratio of 0–0 to 0–1 peak absorbance $A_{0-0}/A_{0-1} > 1$). According to Spano's model [30,31,39], for J-aggregate systems with similar interchain coupling, their intrachain coupling and backbone conjugation length can be characterized by comparing their exciton bandwidth (W), which is given by

(assuming a Huang-Rhys factor of 1):

$$W \approx E_p \frac{\sqrt{A_{0-0}/A_{0-1}} - 1}{0.24 + 0.073 \sqrt{A_{0-0}/A_{0-1}}}$$

where E_p is the energy of the main intrachain vibration (assumed to be 180 meV for the dominant vinyl symmetric stretching mode) [30,31]. As shown in Fig. 4(b), PYT and

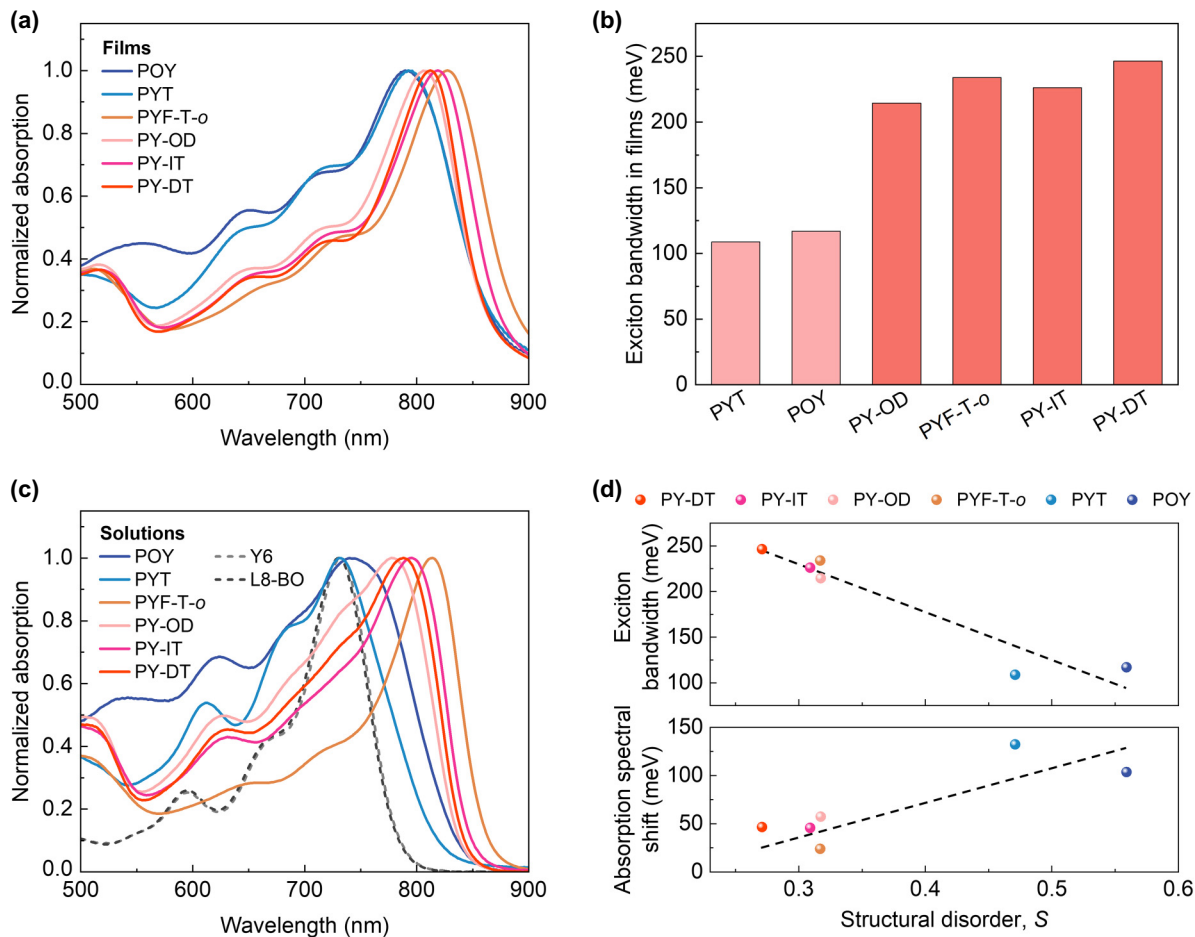


FIG. 4. (a),(b) Absorption spectra (a) and exciton bandwidths (b) of PY-NFA neat films. (c) Absorption spectra of dilute solutions of PY-NFAs and small-molecule Y-NFAs (Y6 and L8-BO). (d) Plots of exciton bandwidths of neat films (top panel) and absorption spectral shift from solutions to films (bottom panel) of PY-NFAs with respect to their structural disorder (S) in films. The black dashed lines serve as a guide to the eye.

POY have relatively small exciton bandwidths of approximately 110 meV, indicating that they have short backbone conjugation lengths and weak intrachain coupling between repeating units, hindering intra-Ex delocalization. In contrast, PY-IT, PY-DT, PY-OD, and PYF-T-*o* exhibit significantly larger exciton bandwidths of approximately 210–250 meV [Fig. 4(b)], indicating their stronger intrachain electronic coupling and thus intra-Ex delocalization that help to facilitate carrier transport [30,31,40].

The variations in backbone conjugation among the studied PY-NFAs primarily arise from differences in their linkers and connection positions [Figs. 1(a) and 3(a)]: PYT with uncertain thiophene linker positions and POY with twisted bithiophene linker have relatively large conformational freedom, limiting their backbone conjugation lengths to comparable to small-molecule Y-NFAs. In contrast, the other four systems (PY-IT, PY-DT, PY-OD, and PYF-T-*o*), with monothiophene linker and well-defined linker positions, have more planar and rigid chain conformation and better backbone conjugation. The

extended backbone conjugation of these four PY-NFAs is also supported by the absorption spectra in dilute solutions [Fig. 4(c)], which are significantly redshifted compared to those of the Y6 and L8-BO molecules. In contrast, dispersed chains of PYT and POY show similar absorption features as Y6 and L8-BO molecules, thus indicating that their intra-Ex states are mostly localized on the monomer. Critically, we find that PY-NFAs with larger exciton bandwidths generally exhibit smaller S as determined by our low-temperature TA data [Fig. 4(d), top panel].

D. Film morphology and interchain packing

We find that PY-NFAs with smaller S also show more similar absorption spectra in dilute solutions and neat films, which indicates relatively weak interchain couplings in these systems [Fig. 4(d), bottom panel; Fig. S7 in the Supplemental Material [33]]. We investigate the interchain packing of three representative PY-NFA films, PYT,

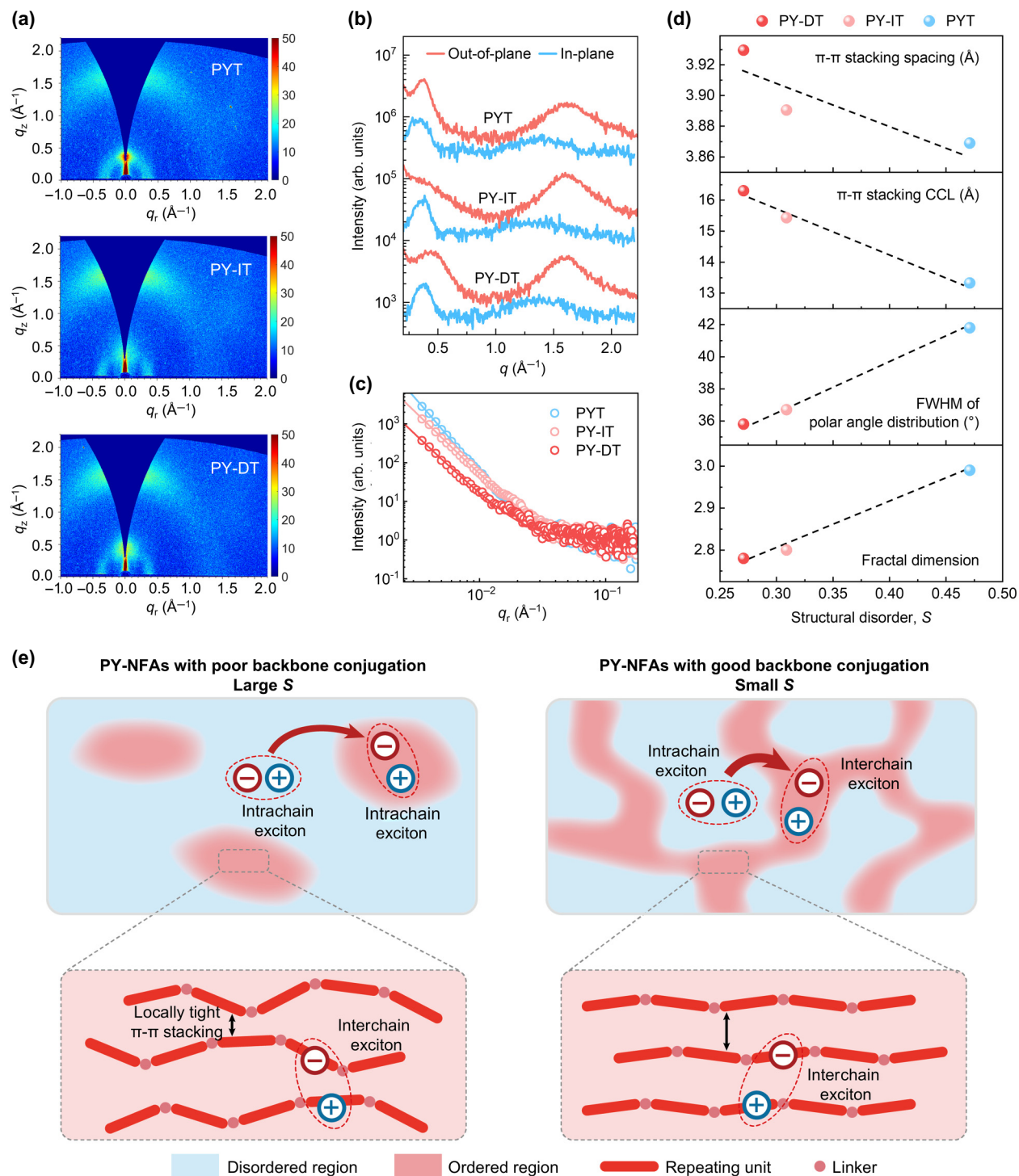


FIG. 5. (a)–(c) 2D GIWAXS patterns (a), GIWAXS line-cut profiles in in-plane and out-of-plane directions (b) and in-plane GISAXS line-cut profiles and fittings (c) of PY-NFA films. (d) Plots of π - π stacking spacings, crystal coherence lengths (CCLs), FWHM of polar angle distributions and fractal dimensions of PY-NFA films with respect to their structural disorder (S). The black dashed lines serve as a guide to the eye. (e) Schematic illustration of chain packings and excited-state transitions in aggregates of PY-NFAs with poor and good backbone conjugation.

PY-IT, and PY-DT, using grazing-incidence wide-angle x-ray scattering (GIWAXS). The two-dimensional GIWAXS patterns [Fig. 5(a)] and line-cut profiles [Fig. 5(b)] of these films show significant π - π stacking diffraction peaks in the out-of-plane direction, indicating their preferential face-on orientation. Their π - π stacking diffraction peaks are at q_z of approximately 1.60–1.63 Å⁻¹ [Fig. 5(b)], corresponding to π - π stacking spacings of approximately 3.87–3.93 Å [Fig. 5(d); Table S3 in the Supplemental Material [33]]. Among these systems, PYT shows the smallest π - π stacking spacing (approximately 3.87 Å), i.e., the strongest interchain interactions [Fig. 5(d)], consistent with its larger absorption spectral shift from solution to film states than other systems [Fig. 4(d), bottom panel]. While PYT has stronger interchain couplings in the neat film compared to PY-IT and PY-DT, it exhibits smaller exciton bandwidth, i.e., overall weaker intra- and interchain couplings. This again supports that PYT has weaker intrachain couplings and shorter backbone conjugation length than other systems. Consequently, the repeating units in PYT chains likely behave like small-molecule acceptors, forming relatively tight π - π stacking locally [Fig. 5(e)] [31]. In contrast, PY-IT and PY-DT, which have enhanced intrachain couplings and more extended intra-Ex delocalization, actually exhibit larger π - π stacking spacings, i.e., weaker interchain interactions [Figs. 5(d) and 5(e)].

While it is generally believed that OSC materials with tighter π - π stackings can generally achieve higher device performance, our results herein suggest a different trend for these PY-NFAs [Fig. 5(d)]. Although PYT forms the tightest π - π stacking among the studied systems, it exhibits the smallest crystal coherence length (CCL), i.e., the smallest crystallite size [Fig. 5(d); Table S3 in the Supplemental Material [33]]. In addition, PYT shows the largest FWHM of the polar angle distribution of π - π stacking peak among these systems [Fig. 5(d); Fig. S8 in the Supplemental Material [33]], indicating the broadest orientation distribution of chain packing. Therefore, while PYT can form tight π - π stacking locally, it can only form smaller crystallites and less-oriented chain packings compared to other systems, leading to larger S and lower device performance in blend OSCs [Fig. 3(c)]. With moderately increased π - π stacking spacings and thus weaker interchain interactions, PY-IT and PY-DT can form larger crystallites and more oriented interchain packings, contributing to reduced S [Fig. 5(d)].

We also perform grazing-incidence small-angle x-ray scattering (GISAXS) measurements to study their aggregation characteristics at larger length scales [Fig. 5(c)]. PYT with the strongest interchain interactions, exhibits the largest fractal dimension (D of approximately 2.99) among the studied systems [Fig. 5(d)], indicating the formation of agglomerated crystalline domains [Fig. 5(e)], which are surrounded by disordered regions and can act as the deep traps for charge transport [41]. In contrast, PY-IT and PY-DT show smaller fractal dimensions of

approximately 2.80 [Fig. 5(d)], indicating the formation of more extended crystalline networks [Fig. 5(e)] [41], which can separate the disordered regions into smaller domains, leading to reduced S and improved charge transport and device performance.

Moreover, we extend our study to a mixed PY-NFA film consisting of PY-DT and PYF-T-*o*, i.e., PY-DT:PYF-T-*o*, which shows smaller S than neat films of PY-DT and PYF-T-*o* [Figs. 3(b) and 3(c)]. The PY-DT:PYF-T-*o* mixed film exhibits a smaller fractal dimension compared to PY-DT and PYF-T-*o* neat films (Fig. S9 in the Supplemental Material [33]), indicating the formation of more extended crystalline network and smaller disordered regions, consistent with its smaller S (Table S1 in the Supplemental Material [33]). The improved structural order of PY-DT:PYF-T-*o* compared to PY-DT and PYF-T-*o* is consistent with the higher PCE and fill factor of the corresponding ternary device based on PY-DT:PYF-T-*o* compared to binary devices based on PY-DT and PYF-T-*o* [Fig. 3(c)], where all the devices used the same donor polymer PM6. Therefore, these results indicate that mixing PY-NFAs to construct ternary all-polymer OSCs can promote structural order in aggregates, improving charge transport and device performance.

III. DISCUSSIONS

Our results therefore establish a direct link between the molecular structure, excited-state dynamics, morphology, and OSC device performance of PY-NFAs. We identify the ubiquitous presence of trapped intra-Ex in PY-NFA films using cryogenic TA spectroscopy. Importantly, we discover a strong correlation between the signal intensity of trapped intra-Ex in various PY-NFA aggregates and their performance in donor-acceptor blended OSC devices. Such strong correlation indicates that the signal intensity of trapped intra-Ex provides a measure of the degree of structural disorder in these PY-NFA aggregates and their corresponding donor-acceptor blends. It is noted that the parameter S probed by the signal intensity of trapped intra-Ex serves as a qualitative indicator of structural disorder rather than a precise quantitative measure. This is because the GSB signal intensity of intra-Ex is inherently influenced by their delocalization degree along the chains, with more delocalized intra-Ex exhibiting higher GSB signal intensity per exciton. As mentioned above, PYT and POY with smaller exciton bandwidths form less delocalized intra-Ex compared to other systems, contributing to their weaker GSB signal intensity per exciton. Consequently, the higher overall signal intensity of trapped intra-Ex in PYT and POY than other systems implies that the difference in the actual numbers of trapped intra-Ex, i.e., the difference in degrees of structural disorder, is more significant than that suggested by the signal intensity difference. Nevertheless, the trends that PY-NFAs with larger

exciton bandwidths generally exhibit lower degrees of structural disorder [Fig. 4(d)] and achieve higher photovoltaic performance in blend devices [Fig. 3(c)] are still valid.

Among the studied PY-NFAs, despite exhibiting moderately increased π - π stacking spacings, systems with enhanced backbone conjugation and more oriented interchain packing (e.g., PY-IT and PY-DT) can generally lead to reduced structural disorder in their aggregates and achieve improved device performance. The reduced interchain interaction strength in these PY-NFAs can help mitigate the formation of overtight interchain packing observed in systems with poor backbone conjugation (e.g., PYT), thus allowing chains to organize into larger, interconnected crystalline domains [Fig. 5(e)]. This picture aligns with a recent work reporting a highly efficient PY-NFA (named PY-DT-X, with PCE up to 19.5%), which has a relatively large π - π stacking spacing of over 4.0 Å [15]. Therefore, our results suggest that high-performance PY-NFAs should exhibit both: (1) extended backbone conjugation and large intrachain exciton bandwidth, and (2) uniform and oriented interchain packings that enable large crystallite formation. Among the PY-NFAs involved in this study, the latter condition is achieved by slightly reducing the interchain coupling (i.e., moderately increased π - π stacking spacings). Critically, we consider that the extended backbone conjugation that promotes charge transport along the polymer chains may help to balance the slightly suppressed transport between polymer chains as a result of the weakened interchain coupling. Our results therefore suggest that balanced intra- and interchain electronic couplings may be critical for high-performance PY-NFAs.

While PY-NFA neat films studied herein generally exhibit a redshift followed by a blueshift of their TA spectra at low temperature (e.g., 100 K), neat films of representative small-molecule Y-NFAs (e.g., Y6 and BTP-eC9) only show a sustained spectral redshift with increasing time delay (Fig. S10 in the Supplemental Material [33]). We consider that this difference primarily arises from their distinct molecular packings: small-molecule Y-NFAs exhibit significantly smaller π - π stacking spacings (approximately 3.50–3.60 Å) compared to PY-NFAs (approximately 3.80–3.90 Å) (Fig. S11 and Table S3 in the Supplemental Material [33]) [11,25], leading to their stronger intermolecular electronic couplings and consequently more efficient energy transfer and exciton diffusion [42,43]. Therefore, even at low temperatures, excitons generated in the disordered regions of small-molecule Y-NFA aggregates can still efficiently migrate to ordered regions and transition into intermolecular CT excitons, causing the sustained TA spectral red shift. In contrast, PY-NFA aggregates with larger π - π stacking spacings and weaker interchain electronic couplings exhibit less efficient energy transfer. Consequently, at low temperatures,

only excitons formed near ordered regions can migrate and transition into inter-Ex, while those formed far away from ordered regions are trapped within disordered regions. This highlights a key difference in the photophysics of small-molecule and polymerized Y-NFAs.

In summary, we investigate the intrachain excitons and interchain excitons in a range of PY-NFA neat films using cryogenic TA spectroscopy. At 100 K, we identify the presence of trapped intrachain excitons in the various PY-NFA neat films from approximately 100 ps onwards after the initial photoexcitation. Importantly, we discover a strong correlation between this low-temperature TA signal and the performance of these PY-NFAs in donor-acceptor blend OSC devices. This result indicates that this low-temperature TA signal provides a measure of the degree of structural disorder in these PY-NFA aggregates and their corresponding donor-acceptor blends. By relating these results with morphological data, we reveal that PY-NFAs with both: (1) extended backbone conjugation and large intrachain exciton bandwidth, and (2) oriented interchain packing with moderately increased π - π stacking spacings, can synergistically lead to reduced structural disorder and enhanced device performance, thus providing insights for future material design and device performance optimization.

IV. METHODS

A. Materials and sample preparation

PY-IT and PY-DT were purchased from Hyper Chemicals Limited. PYF-T-*o* was purchased from eFlexPV Limited. PYT and PY-OD were purchased from Derthon OPV Co Limited. POY was synthesized at South China University of Technology. PY-NFA neat films were spin-coated (2500 rpm) onto precleaned quartz substrates from chloroform solutions (8 mg ml⁻¹). PY-IT dispersed film (1 wt.%) was spin-coated onto precleaned quartz substrate from a mixture solution of PY-IT and polystyrene (weight ratio of 1:99, total concentration of 8 mg ml⁻¹ in chloroform). The mixed PY-NFA film, PY-DT:PYF-T-*o* film, was spin-coated onto precleaned quartz substrate from a mixture solution of PY-DT and PYF-T-*o* (weight ratio of 9:1, total concentration of 8 mg ml⁻¹ in chloroform) [34]. Small-molecule Y-type NFA films were spin-coated onto precleaned quartz substrates from chloroform solutions (10 mg ml⁻¹). All the film samples were prepared and encapsulated inside a glovebox with a nitrogen atmosphere. The dilute solution samples were prepared by dissolving Y-type NFA materials in chloroform with concentration of 0.001 mg ml⁻¹.

B. Steady-state absorption and photoluminescence spectroscopy

The steady-state ground-state absorption spectra of neat films and dilute solutions of Y-type NFAs were measured

with a PerkinElmer Lambda 365 spectrophotometer. The photoluminescence spectra of neat films were measured with a Princeton Instrument (HRS-300) monochromator integrated with a PIXIS CCD camera, both spectrally calibrated using a standard light source.

C. Transient absorption (TA) spectroscopy

Transient absorption spectroscopy was conducted with a femtosecond transient absorption spectrometer (Ultrafast Systems, HELIOS). A femtosecond laser amplifier (Light Conversion) operating at a repetition rate of 1 kHz was used to generate 1030-nm pulses, which were split into two beams. One of the split beams was used to generate the pump beam via an optical parametric amplifier. The other split beam was focused onto a sapphire crystal to generate a white-light continuum probe pulse. The pump and probe beams were spatially overlapped in the encapsulated film samples. The time delay between the pump and probe pulses was controlled by a mechanical delay stage. Calibrated laser beam profiler and power meter were used to determine the pulse fluences (approximately $3.5 \mu\text{J cm}^{-2}$). Transient absorption measurement at low temperature was conducted using a liquid nitrogen-cooled optical cryostat (Instec).

D. Grazing incidence wide angle x-ray scattering and grazing incidence small angle x-ray scattering measurements

The GIWAXS and GISAXS measurements were conducted with a Xeuss 2.0 SAXS/WAXS laboratory beamline using a Cu x-ray source (8.05 keV, 1.54 Å) and a Pilatus3R 300 K detector with an incident angle of 0.20° . The film samples were prepared by spin coating onto precleaned silicon wafer substrates. One-dimensional GISAXS profiles along in-plane direction are fitted using the fractal network model [41].

ACKNOWLEDGMENTS

P.C.Y.C. acknowledges support from the Hong Kong Research Grant Council (Grants No. 16300023, No. 17300425), and the University Research Council of the University of Hong Kong. X.L. acknowledges financial support from the RGC Research Fellow Scheme (RFS) under Grant No. RFS2425-4S05. The authors acknowledge Dr Ziming Chen for helpful discussions.

Y.G. performed sample preparation, optical experiments and data analysis of this project. Y.F. and X.L. provided support on x-ray scattering measurements and analysis. X.L. assisted with data analysis. Y.L. and F.H. provided support on material samples. P.C.Y.C. conceived and supervised the project. P.C.Y.C. and Y.G. wrote the manuscript. All authors reviewed the manuscript.

The authors declare no competing interests.

DATA AVAILABILITY

The data that support the findings of this article are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

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