

Ultralong-range exciton transport in submillimeter-scale spherulite film of π -conjugated polymer

Corresponding Author: Professor Wei Huang

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Attachments originally included by the reviewers as part of their assessment can be found at the end of this file.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The authors present a study on long-range exciton transport in π -conjugated polymer (π CP) films treated by solvent thermal annealing (SVA), and investigate their potential for improving exciton diffusion lengths. The authors show significant advancements, including submillimeter-scale spherulite formation, longer exciton diffusion lengths, and enhanced electroluminescence in PLEDs. While the study has a wide range of characterisation methods covered, I regret that I cannot recommend this manuscript for publication in its current form due to the following major concerns:

1. The authors used photoluminescence quantum yield (PLQY) values in their calculations; however, these values are not explicitly reported in the manuscript or supporting information. The measured PLQY values are essential for the comparison between the spherulite and pristine film samples and to assess the reliability of the calculation.
2. The transient absorption (TA) measurements were measured at an intensity of up to 10 mOD, which is very high for systems with good diffusion lengths, especially in films. Under these conditions, exciton annihilation is very likely happening, making the kinetics faster and the comparison invalid. The authors should perform a fluence-dependent TA series in both the pristine and spherulite films to identify a low-fluence regime where no annihilation occurs. In this regime, the lifetimes should be compared.
3. Regarding the response time of the experimental setup, the authors should clarify whether the 0-300 ns range, where the diffusion constant is extracted, is within the response time of the system. If so, this time point may not be representative and needs careful consideration.
4. The authors extracted diffusion data for the first 300 ps despite the reported lifetime of 1.2 ns. However, Figure S7 reveals a negative trend after 300 ps, which is not adequately explained. The authors should provide a clear justification for excluding this part of the data although it is within the life time and address why the trend goes negative.
5. The Gaussian fits used in the analysis should be included in the Supplementary Information to allow readers to evaluate the robustness of the fitting procedure.
6. While the manuscript focuses on singlet exciton dynamics, it does not address the potential influence of triplet excitons in the devices. Optical excitation generates 100% singlet excitons, whilst triplet excitons only form via intersystem crossing (ISC). In contrast, electrical excitation directly produces 75% triplet excitons. The rising electroluminescence (EL) intensity trend observed in the spherulite films could be influenced by delayed triplet excitons contributing through triplet-triplet annihilation, especially given the efficient diffusion reported. The authors should discuss the role of triplet excitons in detail.
7. The authors should compare the PLQY and EQE values, as such a comparison can offer insights into the presence of trap states or dark triplet excitons, which could influence the overall device performance.

Reviewer #2

(Remarks to the Author)

This paper presents an innovative method to improve exciton transport in organic semiconductor materials. It involves creating submillimeter-scale spherulite films through solvent vapor annealing (SVA). The authors report substantial enhancements in exciton diffusion length and coefficients within π -conjugated polymer films, which show great promise for optoelectronic applications, especially in polymer light-emitting diodes (PLEDs). The study is well-structured, featuring comprehensive experimental methods, and the results offer valuable insights into how long-range ordered spherulite

structures can significantly improve exciton diffusion and optoelectronic properties. This research deepens our understanding of the structural dynamics and performance of organic semiconductor materials. Therefore, this work can be considered for publication after a minor revision by addressing the following comments.

1. The paper suggests that the introduction of branched side chains, as opposed to linear side chains, leads to the formation of large-sized spherulites. Why does the introduction of branched side chains result in the formation of spherulites, while materials with linear side chains do not form this morphology? A comparative experiment should be conducted to explore this issue.

2. The description of “solvent vapor annealing” in the paper should be standardized, as there are currently two different expressions being used, such as “solvent thermal annealing”.

3. In Fig. 3b, why is the absorption edge of the spherulite higher than that of the pristine film?

4. Page 8, line 27; “We obtained the width of the bandgap tail states (Eu) by fitting the photothermal deflection spectroscopy (PDS). The Eu value of spherulite film is 48.1 meV, lower than the 52.9 meV of pristine spin-coated film (Fig. 3e).” In the PDS test referenced in the paper, the data obtained indicates minimal differences. Might these data potentially contain errors?

5. Page 10, line 13; “As shown in Fig. 4a, the diameter of excitation spot (beam center) irradiated on the nanofiber bundles is about 238 nm, covering several single nanofibers.” This paper utilizes a laser with an excitation wavelength of 405 nm to excite the sample. How is the diameter of the light spot determined to be 238 nm? In Fig. S6, what is the role of the flip mirror?

Reviewer #3

(Remarks to the Author)

The manuscript studies exciton transport in a conjugated polymer by transient photoluminescence microscopy. Diffusion coefficients reach in the same order of magnitude as those of other reports in literature. Based on a solvent vapour annealing procedure of a spin coated film of branched side-chain modified polydiarylfuorene, the authors demonstrate improved structural order and enhanced exciton diffusivity. When incorporated into polymer light-emitting diodes, these films yield deep-blue electroluminescence with high brightness and improved color purity at low current densities.

Although the manuscript provides a detailed analysis of the structural and photophysical properties of the spherulite films, the core findings are not strikingly novel. The enhancement of exciton diffusion through improved molecular ordering and reduced defects in π -conjugated polymer films is a concept that is established in the literature. While the work confirms these relationships for the specific polymer under study, it does not introduce fundamentally novel insights or processing strategies. I am not sure about the impact of this work. In summary, the study confirms established principles rather than presenting research of great novelty that I would expect for papers in Nature Communications.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

Please find the new Reviewers Comments attached in a Word document as direct answers to the Authors' individual answers (green: new Reviewer comment).

Reviewer #2

(Remarks to the Author)

All the comments have been addressed, the reviewer suggests the manuscript can be accepted.

Version 2:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The authors have carefully addressed the reviewers comments. From my last round of comments, two of the three points have now been fully addressed: the low-fluence TA measurements and the clarification regarding exciton-exciton annihilation before 300 ps.

However, one comment remains unresolved: the Gaussian fit curves are still not shown directly overlaid on the raw diffusion data so that readers can visually assess the fit and confirm that the Gaussian model is appropriate. This should be a

straightforward figure update, but essential for transparency. Once this final point is addressed, I am satisfied with the revision and can recommend the manuscript for publication.

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Response to reviewers' comments

Answers to Reviewer 1:

The authors present a study on long-range exciton transport in π -conjugated polymer (π CP) films treated by solvent thermal annealing (SVA), and investigates their potential for improving exciton diffusion lengths. The authors show significant advancements, including submillimeter-scale spherulite formation, longer exciton diffusion lengths, and enhanced electroluminescence in PLEDs. While the study has a wide range of characterization methods covered, I regret that I cannot recommend this manuscript for publication in its current form due to the following major concerns:

Response: We thank the reviewer for your positive feedback on our manuscript.

We sincerely apologize for the inconvenience caused by our previous mistakes. According to your comments, we have carefully corrected all our mistakes and polished the entire manuscript. We also added extensive experiments to support our assumption and results in this revised manuscript. Therefore, we sincerely hope that you will re-consider our revised manuscript for publishing in *Nature Communications* journal.

1. The authors used photoluminescence quantum yield (PLQY) values in their calculations; however, these values are not explicitly reported in the manuscript or supporting information. The measured PLQY values are essential for the comparison between the spherulite and pristine film samples and to access the reliability of the calculation.

Response: Thank you for bringing these concerns to our attention.

We are very sorry to confuse you for our mistakes. As you have mentioned, the PLQY values are essential for the comparison of between the thin film and the spherulite samples. We sincerely apologize that only the PLQY values presented in Figure S4b (Page 7) were shown, without providing the numerical values in the main text. In response to your helpful suggestion, we have conducted additional experiments, and the updated PLQY data have been incorporated into the revised manuscript to provide stronger support for our conclusions and improve the overall clarity and completeness of the study.

(1) We apologize for not clearly expressing the PLQY values in the previous manuscript. Actually, we measured the PLQY values of Film and Spherulite (22% and 26%, respectively), as shown in Figure S4b (Page 7), and we find the Spherulite's PLQY higher than that of the Film, as follows:

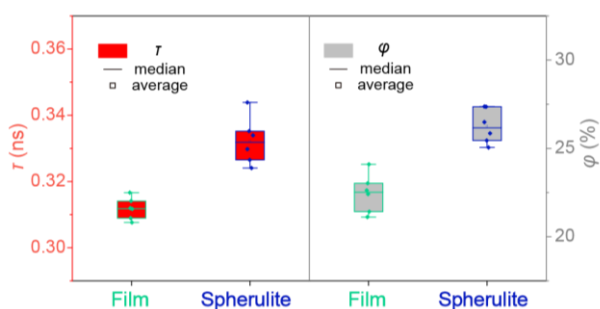


Figure 1. Summary of the τ (red) and ϕ (grey) data of the Film and Spherulite. (The PLQY of spherulite and pristine film samples were determined by FLS980 Series of Fluorescence Spectrometers.)

(2) Additionally, during the revision, we supplemented excitation energy-dependent PLQY measurements to further validate the difference between the spherulite and pristine film samples. For statistical robustness, six repeated measurements were performed for each sample (Figure 2). The PLQY of spherulite and pristine film samples were determined by a custom-built system consisting of a 375nm laser (MDL-III-375 nm, spot size is $\approx 0.13 \text{ cm}^2$), optical fibers, a spectrometer and an integrating sphere (*Adv. Mater.*, **1997**, 9, 230). All films were deposited onto quartz substrates through spin-coating. The results show that Spherulite exhibited a significantly higher average PLQY of approximately 40%, compared to 30% for Film. Moreover, the PLQY of Spherulite remains relatively stable under high excitation energy. The enhanced PLQY in Spherulite is attributed to the more ordered molecular packing in crystalline phase, which facilitates exciton diffusion, reduces nonradiative recombination, and enhances radiative decay. Based on the results of excitation energy-dependent PLQY experiments, it can be re-verified that the highly ordered spherulite film enhances photoluminescence quantum efficiency and luminescence stability.

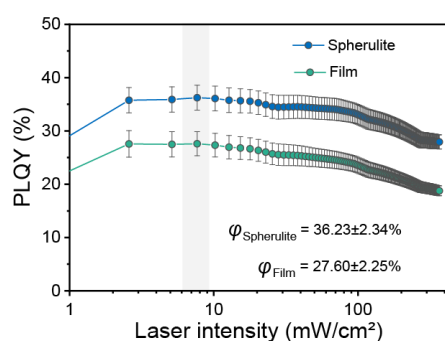


Figure 2. PLQY value of the Film and Spherulite under different excitation energy.

Revision:

We have now revised the manuscript to clarify this point on page 8, lines 5-7:

“Meanwhile, the excitation energy-dependent PLQY measurements (Fig. 3c) show that the Spherulite exhibits a higher average PLQY (~40%) than the Film (~30%) and remains stable at high excitation energies.”

The PLQY measurements has now been added to the revised Supplementary Information to clarify this point on page 4, lines 3-6:

“The excitation energy-dependent PLQY of spherulite and pristine film samples were determined by a self-made system by combining laser (MDL-III-375 nm, spot size is $\approx 0.13 \text{ cm}^2$), optical fiber, spectrometer and integrating sphere (*Adv. Mater.*, **1997**, 9, 230). All films were deposited onto quartz substrates through spin-coating.”

Thank you for your comments and suggestions again.

2. The transient absorption (TA) measurements were measured at an intensity of up to 10 mOD, which is very high for systems with good diffusion lengths, especially in films. Under these conditions, exciton annihilation is very likely happening, making the kinetics faster and the comparison invalid. The authors should perform a fluence-dependent TA series in both the pristine

and spherulite films to identify a low-fluence regime where no annihilation occurs. In this regime, the lifetimes should be compared.

Response: Thank you for your kind comments and suggestions.

We sincerely appreciate your professional and insightful review work on our manuscript. As you correctly pointed out, performing TA measurements at lower fluence regime is essential for minimizing effects of exciton-exciton annihilation and for better revealing the intrinsic exciton dynamics. According to your nice suggestions, we supplemented fluence-dependent TA series on both the pristine (Film) and spherulite (Spherulite) films. However, we sincerely apologize for not being able to reduce the TA signal intensity below 10 mOD, due to the limitations of the TA measurement system. At excitation fluence lower than $70 \mu\text{J}/\text{cm}^2$, the signal-to-noise ratio was too low, which makes it difficult to extract reliable kinetic data. Therefore, to ensure data quality and accurate analysis, we chose to perform measurements starting from $70 \mu\text{J}/\text{cm}^2$, and compared the excited-state lifetimes under low-fluence regime, as follows:

(1) To further trace the ultrafast exciton decay behavior in Spherulite and Film, the fluence-dependent femtosecond-transient absorption (*fs*-TA) technology is performed under pump fluences of 70, 140, and $280 \mu\text{J}/\text{cm}^2$ with 400 nm excitation (Figure 3a, c). The differential absorption (ΔA) spectra from 0.2 to 200 ps exhibit consistent spectral features across fluences (Figure 3b, d), including the ground state bleach (GSB) peaks at 425 nm for Film and 430 nm for Spherulite, along with stimulated emission (SE) signals at 450 nm and 480 nm. In contrast, the broad positive ΔA signals which peak at 570 nm (Film) and 580 nm (Spherulite), corresponding to polaron-pairs photoinduced absorption (PA_P). These features are similar to the ΔA spectra previously reported for related polyfluorene derivatives (Sun, C. et al., *Adv. Funct. Mater.*, **2022**, 32, 2206723. Virgili, T. et al., *J. Mater. Chem.*, **2010**, 20, 519–523.)

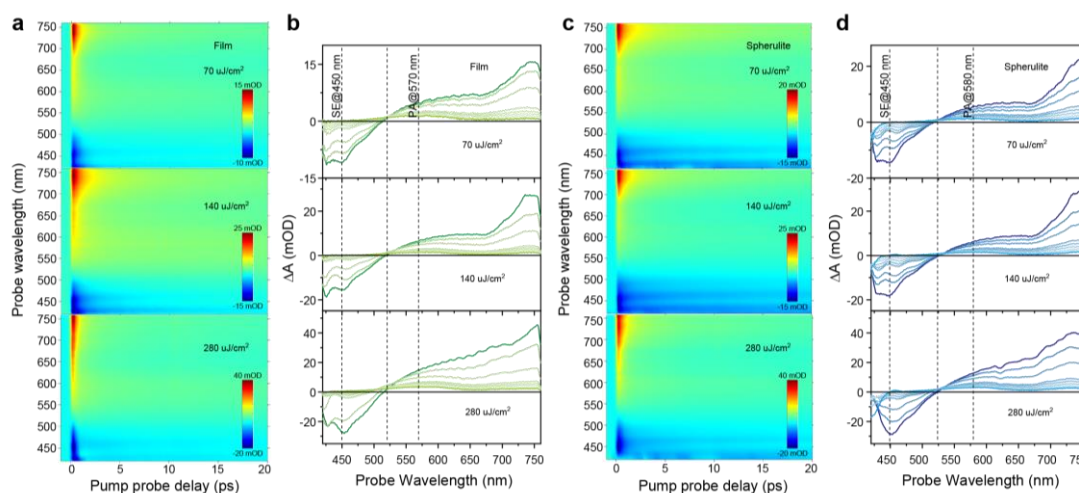


Figure 3. Transient absorption (TA) analysis of films. TA contour plots of the Film (a) and Spherulite films (c) under pump fluences of $70 \mu\text{J}/\text{cm}^2$, $140 \mu\text{J}/\text{cm}^2$, and $280 \mu\text{J}/\text{cm}^2$ using photoexcitation at 400 nm. ΔA spectra of the Film (b) and Spherulite films (d) at different time delays down to 200 ps (0.2 ps, 0.5 ps, 1 ps, 5 ps, 10 ps, 20 ps, 50 ps, 100 ps and 200 ps, respectively).

(2) Figure 4 presents the normalized SE and PA dynamics of Film and Spherulite under varying pump fluences ($70 \mu\text{J}/\text{cm}^2$, $140 \mu\text{J}/\text{cm}^2$, $280 \mu\text{J}/\text{cm}^2$). The time trace was fitted using a triexponential function with lifetimes (τ_i), and amplitudes A_i . The intensity weighted averaged lifetimes were calculated using the formula:

$$\tau = \frac{\sum A_i \tau_i^2}{\sum A_i \tau_i} \quad (1)$$

as summarized in Table 1. For the Film sample, the SE lifetime (Figure 4a) initially increased and then rapid decay with increasing excitation fluence, indicating the exciton-exciton annihilation at higher excitation fluence. In contrast, the Spherulite exhibited gradually decreased SE lifetime with increasing excitation fluence (Figure 4b). However, the decay curves at 70 and $140 \mu\text{J}/\text{cm}^2$ are nearly constant, suggesting that exciton annihilation is negligible at low fluence. Based on this observation, we infer that under $70 \mu\text{J}/\text{cm}^2$, both the pristine film and spherulite film exhibit minimal exciton-exciton annihilation.

Under $70 \mu\text{J}/\text{cm}^2$ (Figure 4c, f), **Film shows longer SE and PA_p lifetimes (11 ps and 96 ps, respectively) compared to the Spherulite (7 ps and 48 ps, respectively).** The shorter PA_p lifetimes in the Spherulite film suggests more efficient carrier extraction and reduced polaron formation, consistent with a lower density of nonradiative defects. **Combined with the increased PLQY observed in Spherulite, confirm that enhanced molecular ordering and reduced defect density effectively suppress traps and polaron-mediated nonradiative losses, enabling more efficient and faster exciton recombination.**

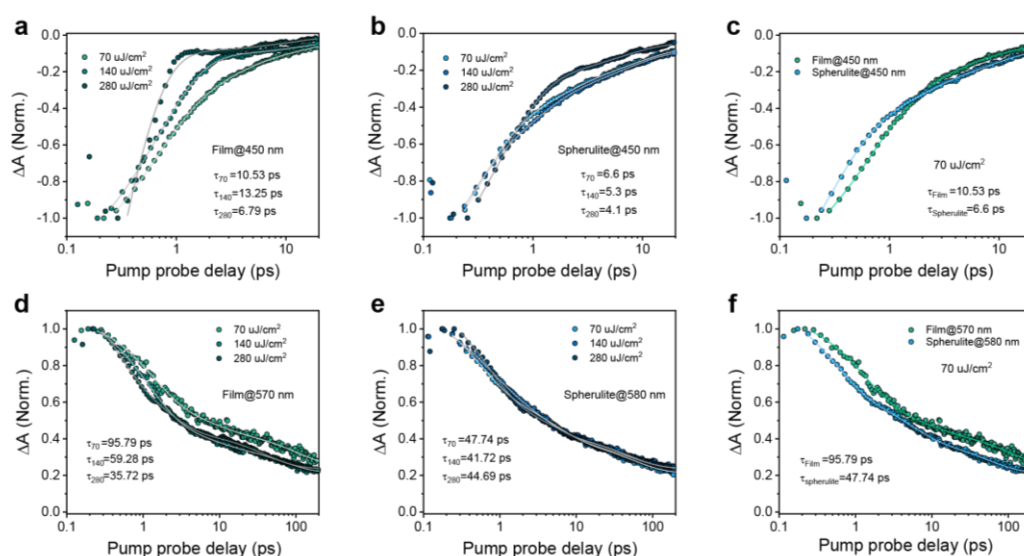


Figure 4. Normalized the TA decay kinetics of Film at 450 nm (a) and 570 nm (d), Spherulite at 450 nm (b) and 580 nm (e) with three pump fluences of $70 \mu\text{J}/\text{cm}^2$, $140 \mu\text{J}/\text{cm}^2$, $280 \mu\text{J}/\text{cm}^2$. (c) Comparison of normalized the TA decay kinetics of Film and Spherulite at 450 nm with $70 \mu\text{J}/\text{cm}^2$ fluence. (f) Comparison of normalized the TA decay kinetics of Film at 570 nm and Spherulite at 580 nm with $70 \mu\text{J}/\text{cm}^2$ fluence.

Table 1. Results of the multi-exponential global fits the lifetimes (τ_i) and amplitudes (A_i) of Film and Spherulite.

Sample	Trace wavelength (nm)	Pump Fluence ($\mu\text{J}/\text{cm}^2$)	A_1	τ_1 (ps)	A_2	τ_2 (ps)	A_3	τ_3 (ps)	τ_{average} (ps)
Film	450	70	0.84	0.58	0.30	2.32	0.16	14.91	10.53
		140	1.10	0.67	0.10	0.67	0.11	18.29	13.24
		280	2.69	0.26	0.61	0.04	0.10	11.82	6.79
	570	70	0.47	1.22	0.16	6.39	0.21	102.62	95.79
		140	0.59	1.07	0.15	5.13	0.17	66.35	59.28
		280	0.55	0.38	0.34	1.84	0.21	39.20	35.72
Spherulite	450	70	1.08	0.25	0.28	1.27	0.25	8.32	6.57
		140	0.88	0.16	0.49	0.81	0.28	6.69	5.35
		280	1.13	0.50	0.14	0.23	0.22	5.84	4.14
	580	70	0.49	0.51	0.27	4.65	0.19	54.05	47.74
		140	0.35	0.56	0.32	3.02	0.44	46.76	41.72
		280	0.60	0.65	0.21	5.03	0.17	51.56	44.69

Revision:

The TA data have been corrected and re-analyzed, this revised results and discussion has now been added to the revised manuscript on page 9, lines 10-31:

“To further trace the ultrafast exciton decay behavior in Spherulite and Film, the fluence-dependent femtosecond-transient absorption (fs-TA) technology is performed under pump fluences of 70, 140, and 280 $\mu\text{J}/\text{cm}^2$ with 400 nm excitation (**Fig. S7a, c**). The differential absorption (ΔA) spectra from 0.2 to 200 ps exhibit consistent spectral features across fluences (**Fig. S7b, d**), including the ground state bleach (GSB) peaks at 425 nm for Film and 430 nm for Spherulite, along with stimulated emission (SE) signals at 450 nm and 480 nm. In contrast, the broad positive ΔA signals which peak at 570 nm (Film) and 580 nm (Spherulite), corresponding to polaron-pairs photoinduced absorption (PA_p). These features are similar to the ΔA spectra previously reported for related polyfluorene derivatives. In **Fig. 3e** and **Fig. S8**, the normalized SE and PA_p dynamics are fitted using a tri-exponential function, and the intensity weighted averaged lifetimes are summarized in **Table S2**. For the Film, the SE lifetime initially increased and then rapid decay at high excitation fluence, suggesting exciton–exciton annihilation, while the PA_p lifetime decrease continuously, implying enhanced polaron generation. In contrast, the Spherulite shows a gradual decrease in SE lifetime with increasing pumping fluence, and nearly constant PA_p lifetime, indicating suppressed exciton-polaron interactions. At low excitation fluence, both SE and PA_p lifetimes in Spherulite (7 ps and 48 ps, respectively) are shorter than those in Film (11 ps and 96 ps, respectively), consistent with more efficient carrier extraction and fewer trap-assisted processes. These results highlight the critical role of molecular ordering in suppressing trap-assisted and polaron-mediated losses, thereby enhancing exciton recombination efficiency. Interesting, fluorescence lifetime imaging microscopy (FLIM) reveals that the longer average fluorescence decay time (τ_m) of spherulite film (470 ps) than that Film (360 ps) (**Fig. 3f** and **S9a**). The coexistence of a prolonged PL lifetime and shortened PA_p lifetimes in the spherulite film

suggests that highly ordered crystalline domains promote rapid exciton transport and delocalization, thereby reducing exciton trapping and enhancing radiative decay, in agreement with the observed increase in PLQY. Taken together, these results indicate that enhanced molecular order and suppressed defect states in Spherulite contribute to improved excitonic performance and suppressed non-radiative losses.”

The Figure 3, Figure 4 and Table 1 has now been added to the revised Supplementary Information as Fig. S7, Fig. S8 and Table S2, respectively on page 9-10.

The TA measurements has now been added to the revised Supplementary Information to clarify this point on page 4, lines 16-21:

“Time-resolved fs-TA spectroscopy is measured by using fs laser (Coherent Astrella), optical parametric amplifier (Ultrafast Systems Apollo-T) and Helios Pump-Probe System (Ultrafast Systems Helios). The laser source was the Coherent Astrella regenerative amplifier (<100 fs, 1 kHz, 800 nm, 7 mJ pulse⁻¹). The pump pulse centered at 400 nm were generate by an optical parametric amplifier. The vis-light probe pulses (420–780 nm) by focusing an attenuated fraction of the fundamental 800 nm laser pulses (Coherent Astrella, 800 nm, 1 kHz, 7 mJ pulse⁻¹). The system provides a time window of up to 8 ns and a time resolution better than 14 fs.”

Thank you for your comments and suggestions again.

3. Regarding the response time of the experimental setup, the authors should clarify whether the 0-300 ns range, where the diffusion constant is extracted, is within the response time of the system. If so, this time point may not be representative and needs careful consideration.

Response: We thank you for this important comment.

The 0-300 ns range used for extracting the diffusion constant is well within the response time of our experimental setup. Photoexcitation diffusion imaging was performed using a home-built TPLM, a 405 nm picosecond pulsed laser (ALPHALAS) with a repetition rate of 10 MHz and pulse width of 25 ps was focused onto the surface of the sample using an objective lens (Olympus, 100X, Apo, 0.95 numerical aperture). Additionally, the single-photon detecting avalanche photodiode (APD) (SPCM-AQRH, dead time of 28 ns) was used to detect the PL, and the APD was connected to timing eletronics (PicoQuant PicoHarp 3000).

Above of all, **our system features an instrument response function (IRF) with a temporal resolution of 25 ps, which enables precise detection of the fluorescence dynamics over the entire analyzed time range.** Although the single-photon detector has a dead time of 28 ns, this parameter affects only the maximum count rate and not the temporal resolution or the validity of the time rang itself.

Therefore, the extraction of the diffusion constant within the 0-300 ns window is not limited by the experimental setup’s response and reflects the intrinsic exciton diffusion of the sample.

Revision:

This explanation has now been added to the revised Supplementary Information to clarify this point on page 4, lines 22-26:

1 “Photoexcitation diffusion imaging was performed using a home-built TPLM, a 405 nm
2 picosecond pulsed laser (ALPHALAS) with a repetition rate of 10 MHz and pulse width of 25 ps
3 was focused onto the surface of the sample using an objective lens (Olympus, 100X, Apo, 0.95
4 numerical aperture). Additionally, PL was detected using a single-photon detecting avalanche
5 photodiode (APD) (SPCM-AQRH, dead time of 28 ns), which was connected to a time-correlated
6 single-photon counting module (PicoQuant PicoHarp 3000).”

7 Thank you for your comments and suggestions again.

8
9 4. The authors extracted diffusion data for the first 300 ps despite the reported lifetime of 1.2 ns.
10 However, Figure S7 reveals a negative trend after 300 ps, which is not adequately explained. The
11 authors should provide a clear justification for excluding this part of the data although it is within
12 the life time and address why the trend goes negative.

13 Response: We thank you for this important comment.

14 Our extracted diffusion data analysis is based on the following model:

$$\text{MSD}(t) = \sigma^2(t) - \sigma^2(0) = 2Dt \quad (2)$$

15 where MSD is the mean-squared displacement, which grows linearly over time, and the diffusion
16 coefficient (D) is proportional to the swath lobe. **As shown in our data, the MSD values in the**
17 **0-300 ps interval exhibit a clear linear trend, fully consistent with this theoretical model.**
18 Accordingly, we selected the 0-300 ps region of the MSD data to fitting D . Beyond 300 ps,
19 although still within the emission lifetime (~ 1.2 ns), the MSD curve shows a negative trend in
20 Figure S7. This deviation arises from exciton-exciton recombination and traps on defect, that
21 becomes increasing at longer delay times. The recombination of exciton effectively and exciton
22 trapped that reduces the spatial spread of the exciton distribution, leading to a decrease in the
23 calculated MSD values.

24 **Revision:**

25 This explanation has now been added to the revised manuscript to clarify this point on page 12,
26 lines 3-4:

27 “At longer times $t > 0.3$ ns, the recombination of exciton effectively and exciton trapped that
28 reduces the spatial spread of the exciton distribution, leading to a decrease in the calculated MSD
29 values (**Fig. S12**).”

30 Thank you for your comments and suggestions again.

31
32 5. The Gaussian fits used in the analysis should be included in the Supplementary Information to
33 allow readers to evaluate the robustness of the fitting procedure.

34 Response: Thank you for the reminder.

35 We apologize for the missing information and have now added the full set of Gaussian fitting
36 results (including fitted curves, parameters, and r^2 values) in the Supplementary Information on
37 page 13, line 1 as follows:

38
39

1 **Table S4.** The parameters of Gaussian fits Diffusion coefficient (D) and Diffusion length (L_D).

	D (cm ² /s)	L_D (nm)
Model	Gauss	Gauss
Equation	$y = y_0 + \left(\frac{A}{w * \sqrt{\frac{\pi}{2}}} \right) * \exp \left\{ -2 * \left(\frac{x - xc}{w} \right)^2 \right\}$	$y = y_0 + \left(\frac{A}{w * \sqrt{\frac{\pi}{2}}} \right) * \exp \left\{ -2 * \left(\frac{x - xc}{w} \right)^2 \right\}$
Plot	Relative Frequency	Relative Frequency
y0	0.042 ± 0.042	0.042 ± 0.044
xc	0.14 ± 0.015	186.62 ± 7.13
w	0.096 ± 0.022	52.67 ± 14.96
A	0.078 ± 0.018	39.40 ± 8.78
Reduced Chi-S	0.0035	0.0037
R-Square (COD)	0.988	0.983
Adj. R-Square	0.951	0.932

2

3 Thank you for your comments and suggestions again.

4

5 6. While the manuscript focuses on singlet exciton dynamics, it does not address the potential
6 influence of triplet excitons in the devices. Optical excitation generates 100% singlet excitons,
7 whilst triplet excitons only form via intersystem crossing (ISC). In contrast, electrical excitation
8 directly produces 75% triplet excitons. The rising electroluminescence (EL) intensity trend
9 observed in the spherulite films could be influenced by delayed triplet excitons contributing
10 through triplet-triplet annihilation, especially given the efficient diffusion reported. The authors
11 should discuss the role of triplet excitons in detail.

12 Response: We thank you for this important comment.

13 As you noted, electrical excitation generates approximately 75% triplet excitons and the rising
14 electroluminescence (EL) intensity trend could be influenced by delayed triplet excitons
15 contributing through triplet-triplet annihilation. However, our devices are based on conventional
16 fluorescent materials, and the emission originates exclusively from singlet excitons. Since no
17 phosphorescent or thermally activated delayed fluorescence (TADF) materials are involved, triplet
18 excitons generated under electrical excitation are non-radiative due to spin-forbidden transitions,
19 and thus do not contribute directly to electroluminescence. **Although triplet-triplet annihilation**
20 **(TTA) can, in principle, occur in systems with long-lived triplet excitons, it is not expected to**
21 **play a significant role in our devices.** First, the absence of delayed emission features in transient
22 EL measurements suggests a negligible contribution from TTA. Second, our polymer system lacks
23 the energy level alignment and molecular design typically required to enable efficient TTA
24 upconversion.

As your suggestion, we re-analysis the Tr-EL of Film and Spherulite. In Figure 5a, the Tr-EL intensity of the Film-based device rises and then reaches stability before showing a decaying trend with increasing current density (up to $25 \text{ mA}\cdot\text{cm}^{-2}$) at a pulse duration time of $40 \mu\text{s}$, reflecting exciton-exciton annihilation via singlet-singlet annihilation and singlet-triplet annihilation under high exciton densities, where exciton diffusion is limited and local accumulation becomes significant. Under the same condition, the EL intensity of the Spherulite-based device (Figure 5b) shows a rising trend with the increase of current density without reaching saturation or decay. This behavior is attributed to the low density of the defect structures in spherulite film, electrons are less prone to defect trapping, which enhances exciton transport and charge mobility, thereby prolonging the recombination process between holes and electrons. These findings are consistent with the improved excitonic properties of the Spherulite film observed in PLQY and fs-TA measurements.

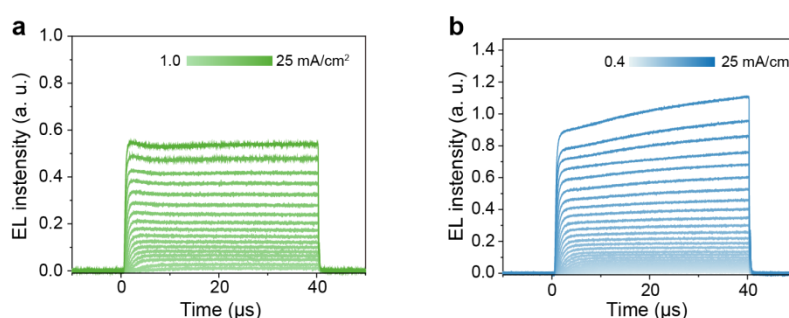


Figure 5 Transient electroluminescence spectra of PLED based on Film (a) and Spherulite (b).

Revision:

This explanation has now been added to the revised manuscript to clarify this point on page 14, lines 14-21:

“In **Fig. 5g**, the Tr-EL intensity of the Film-based device rises and then reaches stability before showing a decaying trend with increasing current density (up to $25 \text{ mA}\cdot\text{cm}^{-2}$) at a pulse duration time of $40 \mu\text{s}$, reflecting exciton-exciton annihilation via singlet-singlet annihilation and singlet-triplet annihilation under high exciton densities, where exciton diffusion is limited and local accumulation becomes significant. Under the same condition, the EL intensity of the Spherulite-based device shows a rising trend with the increase of current density without reaching saturation or decay (**Fig. 5h**). This behavior is attributed to the low density of the defect structures in spherulite film. Electrons are less prone to defect trapping, which enhances exciton transport and charge mobility, thereby prolonging the recombination process between holes and electrons.”

Thank you for your comments and suggestions again.

7. The authors should compare the PLQY and EQE values, as such a comparison can offer insights into the presence of trap states or dark triplet excitons, which could influence the overall device performance.

Response: We thank you for this helpful suggestion. As your suggestion, we compared the PLQY and EQE of the two types of films. In the experimental conditions, the Film-based device exhibits a PLQY of 30% and EQE_{max} of 0.88%, while the Spherulite-based device shows a PLQY of 40% and EQE_{max} of 1.16%. According to the EQE equation:

$$EQE = IQE \times \eta_{out} = \gamma \times \eta_r \times \phi \times \eta_{out} \quad (3)$$

where γ is hole/electron recombination efficiency, η_r is exciton formation probability (0.25 for conventional fluorescent emitters), ϕ is PLQY and η_{out} is light outcoupling efficiency. When assuming $\gamma=1$, $\eta_{out}=0.2$, $\eta_r=0.25$, $\phi_{Film}=0.3$, $\phi_{Spherulite}=0.4$, the theoretical maximum EQE_{max} for the Film device and Spherulite device are calculated to be 1.5% and 2.0%, respectively. The measured EQE_{max} (0.88% and 1.16% for the Film device and Spherulite device, respectively) are below these theoretical EQE_{max} , primarily due to limitations in our current device structure and fabrication process, which is not fully optimized. Nonetheless, this comparison clearly shows that the higher EQE in the Spherulite-based device correlates well with their increased PLQY, which results from reduced non-radiative losses, due to a lower density of trap states and suppressed structural disorder after film crystallization. The improvement in EQE further supports the role of molecular ordering in suppressing defect-induced quenching and enhancing overall device performance.

Revision:

This explanation has now been added to the revised manuscript to clarify this point on page 13, lines 23-30:

According to the EQE equation:

$$EQE = IQE \times \eta_{out} = \gamma \times \eta_r \times \phi \times \eta_{out} \quad (3)$$

where γ is hole/electron recombination efficiency, η_r is exciton formation probability (0.25 for conventional fluorescent emitters), ϕ is PLQY and η_{out} represents light outcoupling efficiency. When assuming $\gamma=1$, $\eta_{out}=0.2$, $\eta_r=0.25$, $\phi_{Film}=0.3$, $\phi_{Spherulite}=0.4$, the theoretical maximum EQE for the Film and Spherulite device are calculated to be 1.5% and 2.0%, respectively. The measured values are below these due to unoptimized device architecture. Nonetheless, the higher EQE in the Spherulite-based device correlates with its increased PLQY, indicating reduced non-radiative losses and confirming the key role of molecular ordering in suppressing defect-induced quenching and enhancing overall device performance.

Thank you for your comments and suggestions again.

Finally, thank you for your all kind comments and suggestions. We have modified all incorrect sentences in this revised manuscript. We sincerely hope that our paper can be accepted and published in *Nature Communications*.

Reviewer #2 (Remarks to the Author):

This paper presents an innovative method to improve exciton transport in organic semiconductor materials. It involves creating submillimeter-scale spherulite films through solvent vapor annealing (SVA). The authors report substantial enhancements in exciton diffusion length and coefficients within π -conjugated polymer films, which show great promise for optoelectronic applications, especially in polymer light-emitting diodes (PLEDs). The study is well-structured, featuring comprehensive experimental methods, and the results offer valuable insights into how long-range ordered spherulite structures can significantly improve exciton diffusion and optoelectronic properties. This research deepens our understanding of the structural dynamics and performance of organic semiconductor materials. Therefore, this work can be considered for publication after a minor revision by addressing the following comments.

Response: We appreciate the reviewer for the recognition of our work and the valuable comments.

1. The paper suggests that the introduction of branched side chains, as opposed to linear side chains, leads to the formation of large-sized spherulites. Why does the introduction of branched side chains result in the formation of spherulites, while materials with linear side chains do not form this morphology? A comparative experiment should be conducted to explore this issue.

Response: Thank you for the reviewer's question.

As previously reported, linear side chains at the 4-position of polydiarylfluorene (PODPF) endow the polymer with exceptional backbone planarity (β -conformation), in which the intermonomer torsion angle approaches 180° , facilitating the film with unique photophysical properties and excellent crystallinity (*Macromolecules*, **2022**, 55, 8084–8094). Besides, as mentioned above, PODPF film is self-assembled into regular nanowires when solidified from concentrated solutions under undercooling (*Cell Rep. Phys. Sci.*, **2020**, 1, 100029). However, there are rarely spherulitic structures observed. Additionally, as your suggestion, under the same conditions, the PODPF film was explored by the SVA method. Polarized optical microscopy image (Figure 1c) reveal that the small crystalline domains are formed within the PODPF film, but no spherulite can be observed.

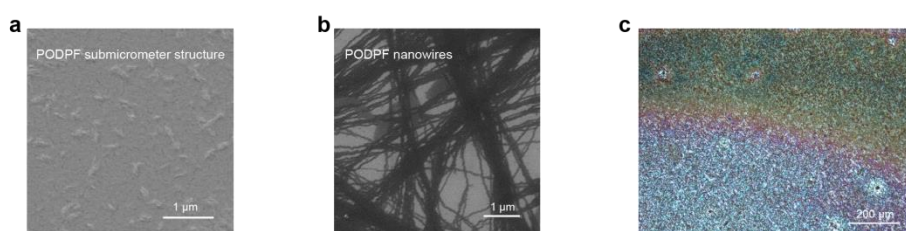
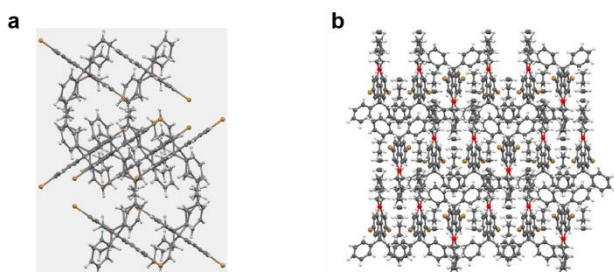


Figure 1. SEM images of PODPF film with olive-submicrometer structure (a) and nanowires (b), (c) POM image of PODPF film with small crystalline domains.

In our design principle, to obtain a “flexible random” region in crystallized processing, we introduced a branched side-chain at 4-position, named PEODPF, instead of liner-type in PODPF. The soft “steric” interaction of branched side-chain may weaken interchain π - π stacking distance, and these branched side chains can act as “self-dopants” to disrupt the periodic interchain arrangement in crystalline processing and leading to the formation of the amorphous nano-region

1 between single lamella crystalline structures, which further induced the formation of molecular
2 spherulites. The single crystal structure (Figure 2a) analysis of the branched monomer, which is
3 herringbone-like arrangement, further verifies that the introduction of the branched side chains
4 breaks the close packing of the conjugated backbone. In contrast, the monomer with linear side
5 chains adopts a linear packing motif in its single crystal structure (Figure 2b).



6
7 Figure 2. Single-crystal structure of PEODPF monomer (a) and PODPF monomer (b) (*Chem.*
8 *Mater.* **2021**, 33, 5326–5336).

9 Thank you for your comments and suggestions again.

10
11 2. The description of “solvent vapor annealing” in the paper should be standardized, as there are
12 currently two different expressions being used, such as “solvent thermal annealing”.

13 Response: Thank the reviewer for raising detailed questions. We have modified the corresponding
14 position and corrected “solvent thermal annealing” to “solvent vapor annealing”.

15 **Revision:**

16 This explanation has now been added to the revised manuscript to clarify this point on page 2,
17 lines 5:

18 “Here, large-area submillimeter-scale spherulite is achieved by treating the spin-coated film of
19 polydiaryluorene with solvent vapor annealing (SVA).”

20 Thank you for your comments and suggestions again.

21
22 3. In Fig. 3b, why is the absorption edge of the spherulite higher than that of the pristine film?

23 Response: Thank you for the reviewer’s question. Comparing with the absorption spectra of Film,
24 Spherulite has a broader spectral profile and a stronger absorption edge at longer wavelength,
25 which could be attributed from their higher order chain packing and the scattered light of their
26 crystalline structure.

27 Thank you for your comments and suggestions again.

28
29 4. Page 8, line 27; “We obtained the width of the bandgap tail states (Eu) by fitting the
30 photothermal deflection spectroscopy (PDS). The Eu value of spherulite film is 48.1 meV, lower
31 than the 52.9 meV of pristine spin-coated film (Fig. 3e).” In the PDS test referenced in the paper,
32 the data obtained indicates minimal differences. Might these data potentially contain errors?

33 Response: We appreciate the reviewer’s careful assessment of our photothermal deflection
34 spectroscopy (PDS) results. Although the difference in Urbach energy (Eu) between the spherulite
35 film (48.1 meV) and the pristine spin-coated film (52.9 meV) may seem small, it is both
36 reproducible and meaningful. It is important to note that PDS is an extremely sensitive technique,

with a spectral resolution of ~ 0.1 nm. This high precision allows for accurate detection of subtle differences in the sub-bandgap absorption edge. The ~ 5 meV reduction in Eu reflects the amount of disorder decrease in Spherulite, which is consistent with the enhanced molecular order and reduced trap states in the spherulite films.

Thank you for your comments and suggestions again.

5. Page 10, line 13; “As shown in Fig. 4a, the diameter of excitation spot (beam center) irradiated on the nanofiber bundles is about 238 nm, covering several single nanofibers.” This paper utilizes a laser with an excitation wavelength of 405 nm to excite the sample. How is the diameter of the light spot determined to be 238 nm? In Fig. S6, what is the role of the flip mirror?

Response: We appreciate the reviewer’s questions. A $\lambda = 405$ nm picosecond pulsed laser was focused onto the sample surface with an objective lens (NA=0.95), generating an in-plane Gaussian distribution of photoexcitation with a standard deviation of $\sigma_0 = 238$ nm (Figure 3).

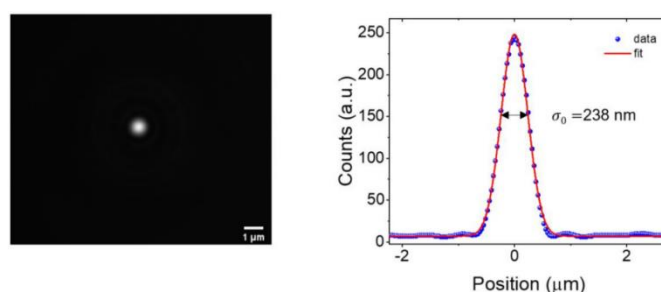


Figure 3. 405 nm pulsed excitation laser spot captured directly by CMOS camera (Left). Intensity distribution profile across the center of the laser spot (Right) (*J. Phys. Chem. Lett.* **2022**, 13, 7645–7652).

As shown in Figure 4, the measurement of time-resolved PL decay was based on the same excitation light path of the home-built TPLM. The flip mirror functions as a beam routing element. By adjusting the flip mirror, the PL signal can be sent out of the TPLM system and guide it to the TRPL system.

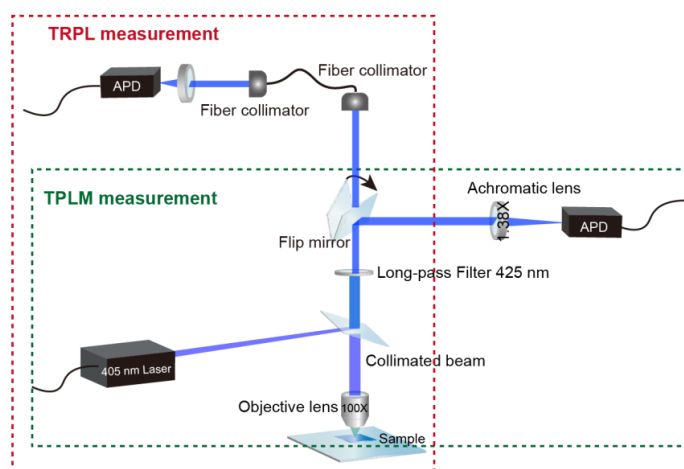


Figure 4. Schematic for TRPL measurement. By adjusting the flip mirror, the PL signal can be sent out of the TPLM system for TRPL measurement. (This figure has now been added to the revised Supplementary Information on page 11, line 10.)

1 Thank you for your comments and suggestions again.

2

3 Finally, thank you for your all kind comments and suggestions. We have modified all incorrect
4 sentences in this revised manuscript. We sincerely hope that our paper can be accepted and
5 published in *Nature Communications*.

6

Reviewer #3 (Remarks to the Author):

The manuscript studies exciton transport in a conjugated polymer by transient photoluminescence microscopy. Diffusion coefficients reach in the same order of magnitude as those of other reports in literature. Based on a solvent vapour annealing procedure of a spin coated film of branched side-chain modified polydiarylfuorene, the authors demonstrate improved structural order and enhanced exciton diffusivity. When incorporated into polymer light-emitting diodes, these films yield deep-blue electroluminescence with high brightness and improved color purity at low current densities.

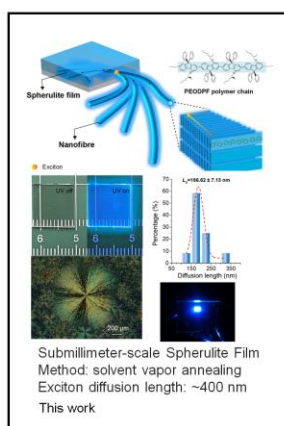
Although the manuscript provides a detailed analysis of the structural and photophysical properties of the spherulite films, the core findings are not strikingly novel. The enhancement of exciton diffusion through improved molecular ordering and reduced defects in π -conjugated polymer films is a concept that is established in the literature. While the work confirms these relationships for the specific polymer under study, it does not introduce fundamentally novel insights or processing strategies. I am not sure about the impact of this work. In summary, the study confirms established principles rather than presenting research of great novelty that I would expect for papers in *Nature Communications*.

[Response:](#) Thanks for your comments and suggestions.

We are very sorry to take your so many troubles for our mistakes. According to your comments, we have corrected all our mistakes and polished the whole manuscript. Meanwhile, we added many experiments to support our assumption and results in this revised manuscript. Therefore, we sincerely hoped that you can re-consider our revised manuscript and agree to accept and publish our work in *Nature Communications* journal.

In general, solution-processable conjugated polymer films that support ultra-long exciton migration lengths exceeding 100 nanometers are highly desirable for optoelectronic devices (Jin et al *Science* **2018**, 360, 897. Andreas T. et al *Nature* **2015**, 523, 196. Russell J. et al *Science* **2018**, 360, 854. Sneyd et al., *Sci. Adv.*, **2021**, 7, eabh4232. Shi Y. et al *Proc. Natl. Acad. Sci. U.S.A.* **2025**, 122, e2413850122.) (Figure 1). All these high-quality studies mentioned above are following an established concept that the exciton transport can be substantially improved in crystalline materials by reducing energetic disorder and exciton trapping, while also enabling a more optimized orientation of molecular transition dipole moments (S. R. Forrest et al *Adv. Mater.*, **2010**, 22, 1233). Therefore, the ability to easily fabricate the large-scale crystalline π -conjugated polymer films is key to achieving ultra-long exciton diffusion length for thin-film optoelectronic devices, yet it has rarely been reported over the past several decades. In this work, we report the ultra-long exciton diffusion length of ~400 nm achieved in our easily solution-processed, submillimeter-scale spherulite film of π -conjugated polymer represents a significant advance in organic electronics, especially for the fabrication of efficient deep-blue PLEDs (Figure 1).

Hydrocarbon fully π -conjugated polymer
without functional polar units



Heteroatomic molecular semiconductor
with functional polar units

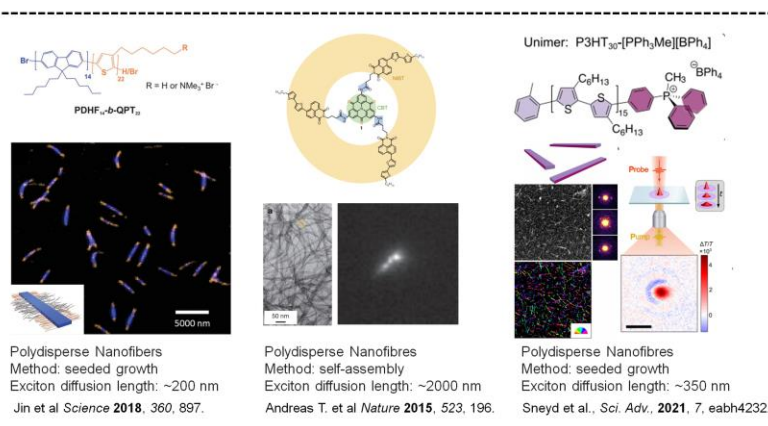


Figure 1. Summary of the prior works about the long-range exciton migration.

According to your kind comments, we have provided point-to-point responses in the following three sections. In this revised manuscript, we have also added many experimental data to further support our assumptions. We hope that our responses help to clarify the core findings of our study.

(1) Although the manuscript provides a detailed analysis of the structural and photophysical properties of the spherulite films, the core findings are not strikingly novel. Firstly, we appreciate the reviewer's recognition of the detailed analysis of the structural and photophysical properties of the spherulite films presented in our work. However, we apology any confusion regarding the core findings related to our manuscript about the structural and photophysical properties of the spherulite films. To address this, in this revised manuscript, we added extensive experimental data to better support our conclusions. We would like to highlight the three core findings as follow: (1) **Highly ordered and densely packed interchain arrangement in submillimeter-scale spherulite film.** The lattice stripe spacing is about 0.24 nm with an excellent periodic interchain arrangement, which could enhance the exciton diffusion length. The diffraction spots in SAED pattern image also further confirms the outstanding crystalline structure of interchain stacking in PEODPF spherulite film (Figure 2). (2) **Visualization of the crystallization growth process of π -conjugated polymers.** We provide the images of PEODPF spherulites at various growth stages, accompanied by a schematic illustration of the crystallization growth model (Figure 3). (3) **Ultra-fast exciton behavior in spherulite films.** The spherulitic films exhibit distinct ultrafast exciton behavior, as revealed by transient absorption spectroscopy, highlighting the impact of ordered molecular packing on excited-state processes. (4) **Ultrafast exciton dynamics and long-range transport.** For the first time, ultralong exciton diffusion with a length of ~400 nm has been observed in submillimeter-scale spherulite films of π -conjugated polymers, demonstrating exceptional exciton transport properties. In addition, efficient deep-blue polymer light-emitting diodes based on these crystalline films are also firstly fabricated with an excellent electroluminescent property.

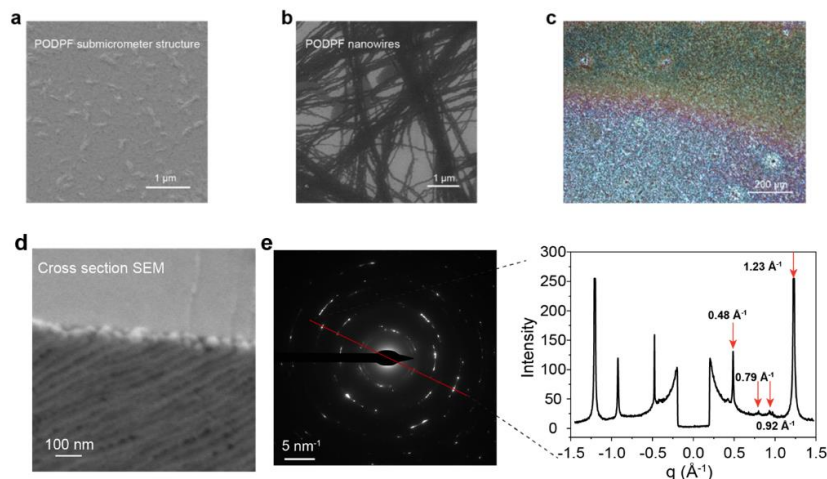


Figure 2. SEM images of PODPF film with olive-submicrometer structure (a) and nanowires (b), (c) POM image of PODPF inhomogeneous and discontinuous films with small crystalline nanodomains. (d) Cross-section scanning electron microscopy (SEM) image of PEODPF spherulite. (e) TEM selected-area electron diffraction pattern (SAED) of spherulite and the curve corresponds to SAED red line.

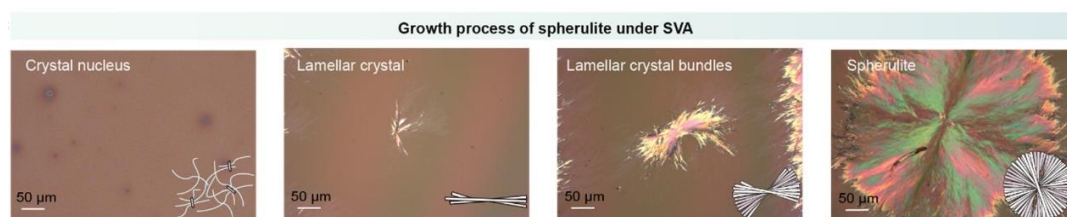


Figure 3. Polarization microscope (POM) images of PEODPF spherulite at different growth stages together with schematic illustration of the growth process model (Bottom right corner).

(2) The enhancement of exciton diffusion through improved molecular ordering and reduced defects in π -conjugated polymer films is a concept that is established in the literature.

According to your kind comment, the enhancement of exciton diffusion through improved molecular ordering and reduced defects in π -conjugated polymer films is a well-established concept in the literature. We appreciate this insightful comment; it aligns with our findings that an ordered interchain arrangement with low defect density is beneficial for exciton diffusion. However, up to date, most thin films formed from π -conjugated polymers, show short exciton diffusion lengths (L_D) of around 10 nm, due to their energetic disorder (*Energy Environ. Sci.* **2015**, *8*, 1867-1888.). In contrast, singlet excitons diffusion lengths in single crystals are known to be considerably larger (up to 220 nm), which confirms the effectiveness of improved molecular ordering as noted. More interestingly, nanofibres from amphiphilic conjugated polymers (oligomers) with a well-defined structure, prepared by living crystallization-driven self-assembly, yield an efficient exciton diffusion with coefficient of $0.5\sim 1.1\text{ cm}^2/\text{s}$ and L_D exceeding 200 nm (Jin et al., *Science* **2018**, *360*, 897-900. Sneyd et al., *Sci. Adv.*, **2021**, *7*, eabh4232.). However, in these cases, the materials are generally polydisperse in size and challenges for integration into practical devices. Therefore, solution-processable films of π -conjugated polymers, capable of transporting

excitons over lengths exceeding 100 nm, are highly desirable for a range of organic optoelectronic devices. Up to date, our work is the first work to demonstrate **ultra-long exciton transport lengths in solution-processed crystalline film of π -conjugated polymer**. Moreover, this is also the **first work to incorporate these easily processed materials, with exciton transport capacities comparable to the optical absorption depth (>100 nm) into functional electronic devices**. We also believed that realizing this commonly held assumption and concept remains a significant challenge, which lies at the core of fundamental research in this field.

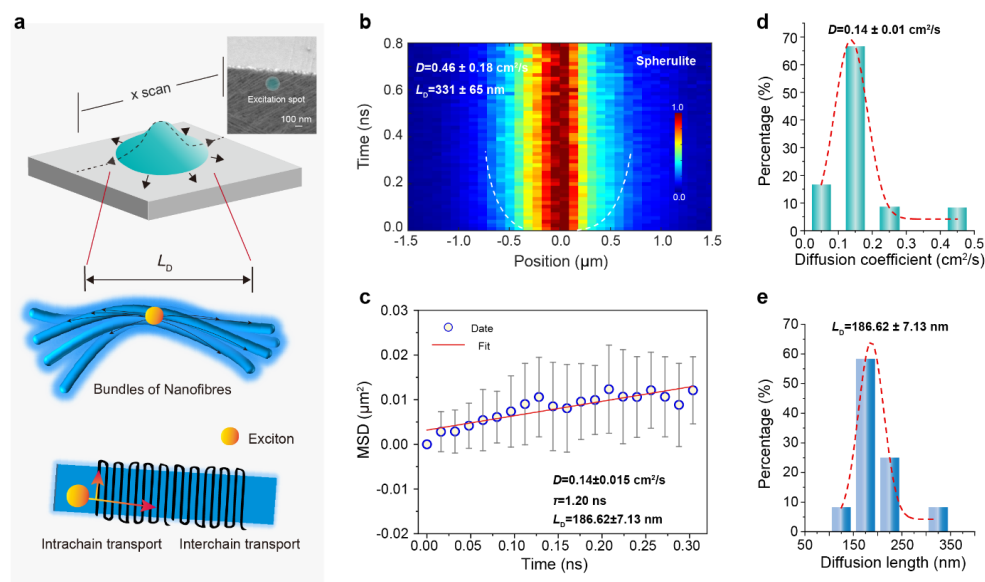


Figure 4. Long-range exciton diffusion in submillimeter-scale Spherulite.

(3) While the work confirms these relationships for the specific polymer under study, it does not introduce fundamentally novel insights or processing strategies. We thank you for the positive comment regarding the clear structure–property relationships demonstrated in our manuscript. However, we regret any confusion caused in understanding the novelty of our work. Below, we clarify the fundamentally novel insights and processing strategies presented in this study. (1) **Fundamentally novel insights:** (i) **Precisely control size-tunable submillimeter-scale spherulite via branched side-chain functionalization.** Fully π -conjugated hydrocarbons polymers (For example: PODPF and PFO) typically self-assembled into polydisperse multi-dimensional crystalline nanostructures (such as nanowires) due to their strong interchain π - π interaction, which limits their application in optoelectronic devices. Compared to the linear-type side chain at 4-position (PODPF), only branched-side chain (PEODPF) can induce the polymer self-assembled into submillimeter-scale spherulite. This branched side-chain may reduce the crystallization capacity to cause the formation of amorphous region and induce the formation of submillimeter-scale spherulite. (ii) **Prolonging exciton diffusion length for singlet excitons via the spherulite processing for optoelectronic application.** While we agree with the reviewer that enhancing exciton diffusion through improved molecular ordering and defects suppression in π -conjugated polymer films is a known concept in the literature. However, most conjugated polymers films, even with high crystallization degree, also present short exciton diffusion lengths (L_D) of around ~ 10 nm. In contrast, the densely interchain structure of our submillimeter-scale spherulite film support the ultralong exciton diffusion (~ 400 nm), far beyond previously reported

values for solution-processed films, and even comparable to or exceeding those in single crystals or oligomeric nanofibers. (2) **Novel processing strategies:** We developed a facile solvent vapor annealing (SVA) method to fabricate large-area crystalline films of π -conjugated polymers for efficient deep-blue PLEDs. To date, long-range exciton diffusion (>100 nm) has only been observed in highly ordered crystalline organic semiconductors. However, these materials are often polydisperse and difficult to integrate into practical devices. Our strategy addresses this limitation by enabling the formation of uniform, device-compatible, crystalline polymer films via a simple and scalable process. This is the first report of integrating solution-processable polymer spherulites that support ultralong exciton transport into functional optoelectronic devices.

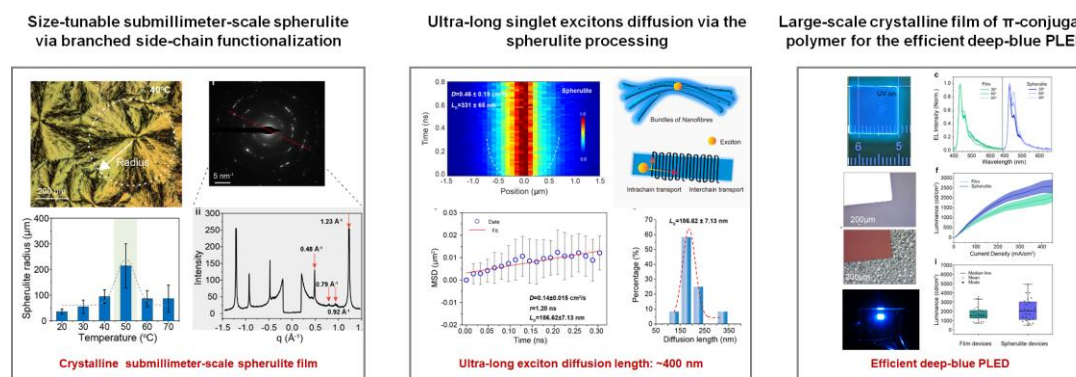


Figure 5. Fundamentally novel insights or processing strategies of our work.

Subsequently, three **strikingly core findings** for the organic optoelectronic of our works are obtained as follow:

(1) **Ultralong exciton diffusion lengths (~ 400 nm) were observed in large-scale solution-processed crystalline films.** Generally, solution-processable materials capable of transporting excitons over length exceeding 100 nm are highly desirable for a variety of light-harvesting and optoelectronic devices. We agree that enhancing molecular ordering and reducing trap densities are established strategies to improve exciton diffusion and device performance^{1,2}. However, our study tackles a challenge in organic optoelectronics by achieving ultralong exciton diffusion lengths and efficient deep-blue emission in solution-processable π -conjugated polymer thin films. This remains difficult due to the intrinsic energetic disorder and weak interchain coupling in most polymers^{1,3,4}. In contrast to previous studies that focus on single crystals or supramolecular assemblies with limited processability, we introduce a simple and scalable approach based on solvent vapor annealing to form submillimetre-scale spherulites with densely packed nanofibers and strong π - π overlap. This morphology supports singlet exciton diffusion lengths up to ~ 396 nm and a diffusion coefficient of ~ 0.63 $\text{cm}^2 \cdot \text{s}^{-1}$, which are among the highest reported for π -conjugated polymers under ambient conditions^{7,8}.

(2) **Manufacture large-scale crystalline films from π -conjugated polymers via simple and scalable solvent vapor annealing for optoelectronic applications.** Interchain π - π interactions in polymer semiconductors play a key role in fundamental optoelectronic processes such as charge transport and exciton dynamics. In particular, interchain π - π stacking significantly influences the carrier mobility and conductivity of polymer semiconductor films, which are essential for high-performance optoelectronic devices. A systematic and visual understanding of polymer chain crystallization is central to polymer physics and provides the foundation for designing

1 high-performance materials. The development of large-scale crystalline polymer films with
2 well-defined structures and outstanding properties has therefore attracted increasing attention.
3 However, due to the diverse intermolecular non-covalent interactions, obtaining large-scale
4 crystalline films of fully π -conjugated polymers via solution processing remains challenging, often
5 resulting in randomly distributed nanostructures, such as nanoparticles and nanowires. In this
6 work, we introduce a simple approach based on solvent vapour annealing to form
7 submillimetre-scale spherulites with densely packed nanofibers and strong π - π overlap.
8 Furthermore, comprehensive experimental and characterization techniques were employed to
9 investigate the structure-property relationships within Spherulite films. Therefore, we are very
10 happy about your comment that a detailed analysis of the structural and photophysical properties
11 of the spherulite films is provided in this manuscript.

12 **(3) High performance deep-blue PLED based on large-scale crystalline film.** As discussed
13 above, the key performance parameters of OLEDs include color purity, emission uniformity, EL
14 spectral stability, and efficiency, all of which are closely associated with the morphology of active
15 emission layers. Importantly, the improved molecular ordering leads to a substantial enhancement
16 in photoluminescence quantum yield (PLQY) from 30% (amorphous film) to 40% (spherulite),
17 accompanied by a notable enhancement in external quantum efficiency (EQE) from 0.88% to
18 1.16%. Finally, polymer light-emitting diodes (PLEDs) based on the large-area Spherulite films
19 present a stable and efficient deep-blue electroluminescence behavior (Brightness: 4897 $\text{cd}\cdot\text{m}^{-2}$
20 and EQE: 1.16%), enhanced about 47% and 32% compared to spin-coated ones, due to their low
21 defect density, also confirmed their uniform exciton energetic landscape for the potential
22 optoelectronic application. While the concept of ordering-induced exciton transport is established,
23 its application to deep-blue emitting and solution-processed polymer devices is rare due to
24 challenges in achieving long-range order without compromising emission properties. Our findings
25 demonstrate that controlled crystallization in π -conjugated polymers can simultaneously enhance
26 exciton transport, PLQY, and device quantum efficiency, offering a viable route toward achieving
27 high-efficiency photon output in blue-emitting OLED devices at low driving voltages.

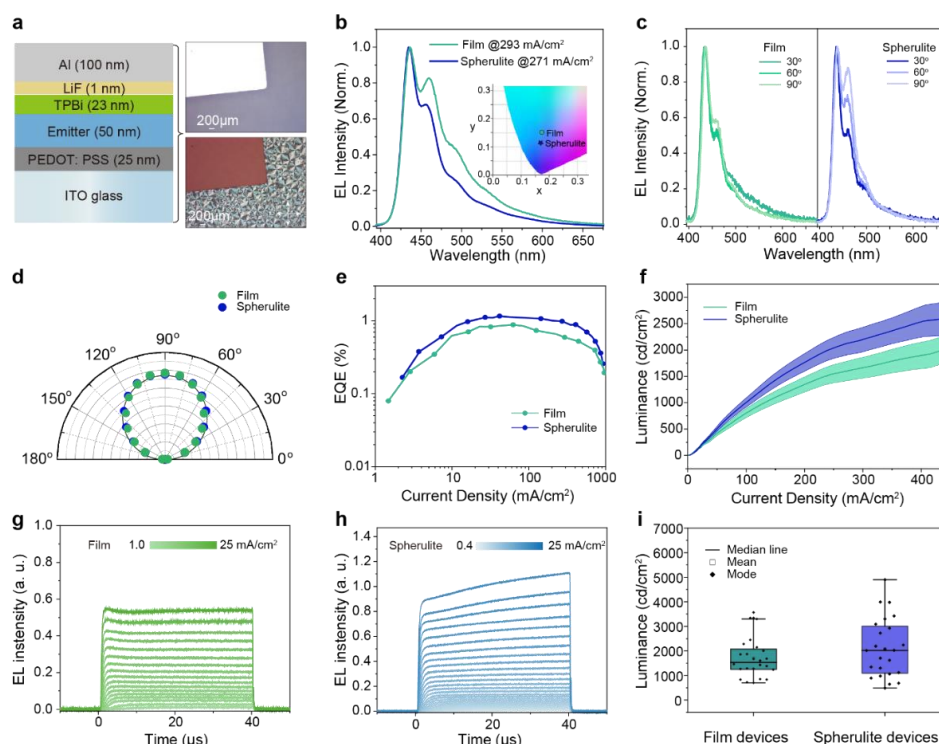


Figure 6. Device performance of PLEDs based on Spherulite and Film.

In summary, efficient exciton diffusion over long distances in semiconductor is crucial for their optoelectronic applications. However, organic semiconductor films typically exhibit exciton diffusion lengths (L_D) on the order of tens of nanometers, which are most obstacles to limit their practical optoelectronic applications. Even extremely short L_D is evaluated about ~ 10 nm in the fully π -conjugated polymers (π CPs), due to their energetic disorder in solid state. Therefore, low energetic disorder and strong π -orbital overlap in the crystalline structure can enable more efficient exciton transport and diffusion. The ability to achieve highly ordered hierarchical structures with dense interchain π -orbital overlap in solution-processed π CPs films remains a core challenge in the development of organic optoelectronics. In this work, we demonstrate ultralong-range exciton diffusion (maximum value: ~ 396 nm) in large-area ordered submillimeter-scale spherulite films of π -conjugated polydiaryluorene, enabling high brightness and narrowband deep-blue polymer light-emitting diodes (PLEDs). These self-assembled nanofibers, with molecular-scale diameters, efficiently transport singlet excitons at ambient conditions over distances exceeding hundreds of nanometers. Large-area submillimeter-scale spherulite are easily manufactured via solvent vapor annealing (SVA), which consisted of a series of nanowires with a length of ~ 3.0 μ m and width of ~ 40 nm. More interestingly, the polymer chains exhibit an extremely dense and periodic packing along the nanofibers within the spherulite, thereby facilitating excellent interchain π -orbital overlap that enhance exciton and energy transfer. Moreover, this submillimeter-scale spherulite showed an excellent and ordered hierarchical structure that effectively suppressed the formation of defect-trapping sites, leading to long-range exciton diffusion (up to ~ 396 nm) and an extremely large diffusion coefficient (~ 0.63 cm²/s). Finally, PLEDs based on large-area spherulite films present stable and efficient deep-blue electroluminescence (Brightness: 4897 cd·m⁻² and EQE: 1.16%), enhanced about 47% and 32%,

respectively, compared to spin-coated ones. This improvement is attributed to the low defect density and confirms the [uniform exciton energetic landscape for the potential optoelectronic applications](#). In a word, we believed that our solution-processed submillimeter-scale spherulite films present an ultralong exciton diffusion length (L_D) and a large diffusion coefficient in π -conjugated polymers, owing to their high degree of molecular order and strong intra/interchain π -orbital overlap. In contrast to the work by Jin (*Science* **2018**, 360, 897.) and Andreas T. Haedler (*Nature* **2015**, 523, 196.), [which relied on structurally complex nanofibers and supramolecular assemblies](#), our submillimeter-scale spherulite film can be easily manufactured a simple solution-processing method, making them highly suitable for optoelectronic device applications.. We believe [our work will attract broad attentions in materials sciences, organic photonics, nanoscience and nanotechnology, polymer science and flexible optoelectronics](#). The topic and unique conclusions of this work meet with the research scope of “*Nature Communications*”.

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8. Giannini, S. *et al.* Exciton transport in molecular organic semiconductors boosted by transient quantum delocalization. *Nat. Commun.* **13**, 2755 (2022).

[Thank you for your comments and suggestions again.](#)

Finally, we are sincerely thanks three reviewers. We have checked through carefully and corrected the errors in this revised manuscript. We sincerely hoped that our work can be accepted and published in *Nature Communications* journal.

Thank you for your kind helps again.

All changes to the manuscript have been highlighted. The revised manuscript, Supporting Information, and a list of changes & our responses to the referees’ comments have been submitted through my Author Centre.

Should you have any other questions or queries, please kindly contact me by e-mail at iamwhuang@njupt.edu.cn or by fax at (+86) 25 8586 6999.

Thank you very much.

1 With best wishes.
2 Sincerely yours,
3 Professor Wei HUANG
4 Academician of China Academy of Sciences
5 "Program of Global Experts" Distinguished Professor
6 "Changjiang Scholar" Chair Professor
7 Director-General
8 State Key Laboratory of Flexible Electronics (LoFE)
9 Nanjing University of Posts & Telecommunications
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Answers to Reviewer 1:

1.1 The transient absorption (TA) measurements were measured at an intensity of up to 10 mOD, which is very high for systems with good diffusion lengths, especially in films. Under these conditions, exciton annihilation is very likely happening, making the kinetics faster and the comparison invalid. The authors should perform a fluence-dependent TA series in both the pristine and spherulite films to identify a low-fluence regime where no annihilation occurs. In this regime, the lifetimes should be compared.

1.2 Reviewer comment: the energy is still very high for materials with good diffusion. TA is commonly measurable at least at 10 $\mu\text{J}/\text{cm}^2$ or until a fluence where no fluence-dependence is visible anymore. However, there is still a fluence dependence with 70 $\mu\text{J}/\text{cm}^2$, so the authors should record traces of fluences where no fluence dependence is visible and compare the kinetics at those fluences.

Response: Thank you for your kind comments and suggestions.

We sincerely thank the reviewer for this valuable comment and for highlighting the importance of avoiding exciton–exciton annihilation and for better revealing the intrinsic exciton dynamics in transient absorption (TA) measurements. Following your suggestion, we systematically investigated the fluence-dependent excited-state dynamics of both the pristine (Film) and spherulite (Spherulite) films using a self-built fs-TA spectrometer, ensuring that the TA signal intensity remained below 10 mOD.

(1) Fluence-dependent TA spectra: TA measurements were conducted under pump fluences of 1.5, 3, 5, 10, and 15 $\mu\text{J}/\text{cm}^2$ with 400 nm excitation (Figure 1a, c). The differential absorption (ΔA) spectra recorded from 1 to 200 ps exhibit consistent spectral features across all fluences (Figure 1b, d), including the ground state bleach (GSB) peaks at 415 nm (Film) and 416 nm (Spherulite), as well as the stimulated emission (SE) signals at 450 nm. These features are consistent with previously reported for related polyfluorene derivatives (Sun, C. et al., *Adv. Funct. Mater.* **2022**, 32, 2206723. Virgili, T. et al., *J Mater Chem* **2010**, 20, 519–523.).

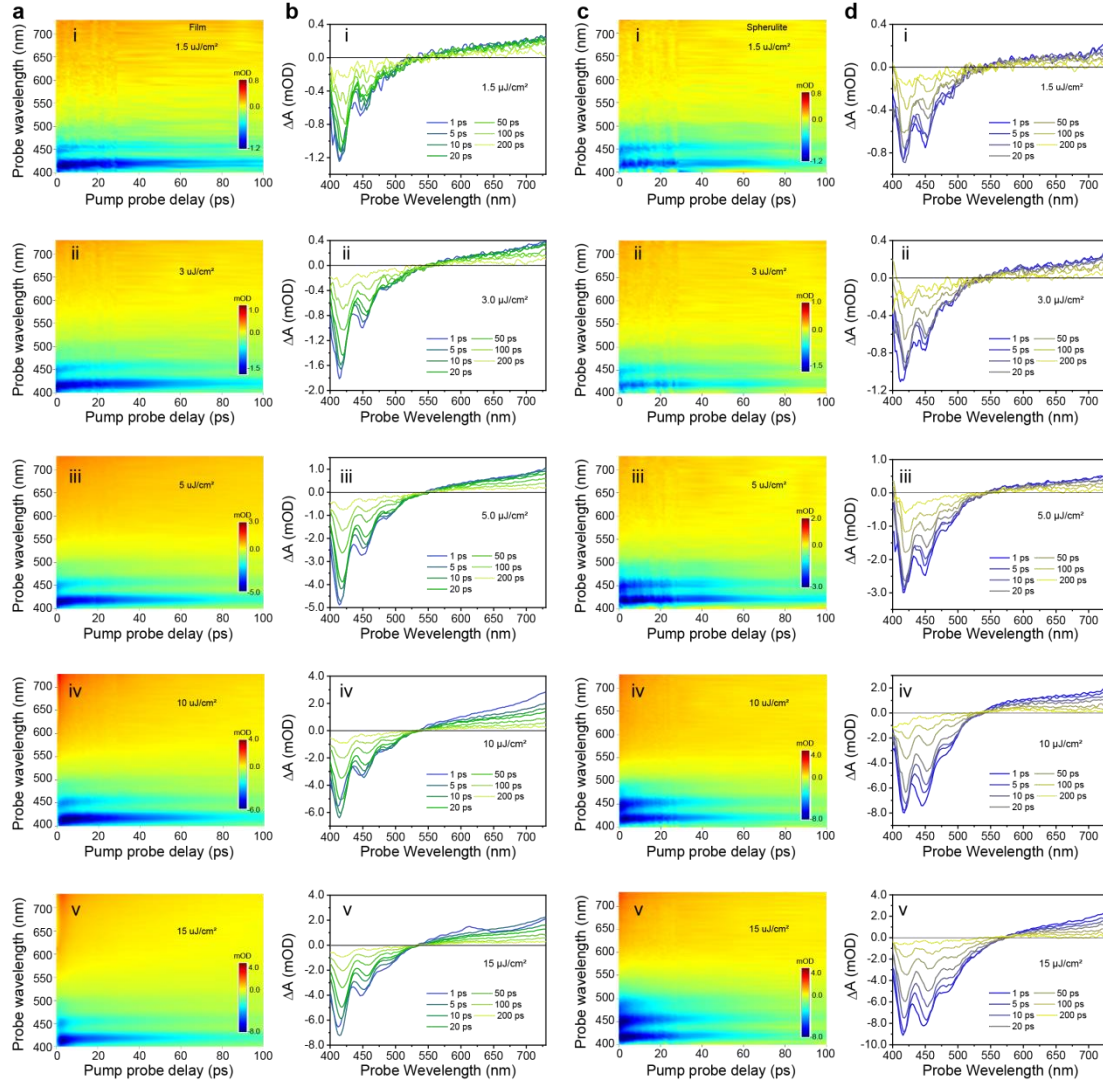


Figure 1. TA analysis of films. TA contour plots of the Film (a) and Spherulite films (c) under pump fluences of 1.5, 3, 5, 10, and 15 $\mu\text{J}/\text{cm}^2$ using photoexcitation at 400 nm. ΔA spectra of the Film (b) and Spherulite films (d) at different time delays down to 200 ps (1 ps, 5 ps, 10 ps, 20 ps, 50 ps, 100 ps and 200 ps, respectively).

(2) **Kinetic analysis and low-fluence regime identification:** Figure 2 presents the normalized SE dynamics of Film and Spherulite under varying pump fluences (1.5, 3, 5, 10, and 15 $\mu\text{J}/\text{cm}^2$). as summarized in Table 1. As shown in Figure 2a and b, the normalized SE decay kinetic of both Film and Spherulite overlap well at 1.5, 3 and 5 $\mu\text{J}/\text{cm}^2$, indicating that the system operates within the linear excitation regime, where the exciton–exciton annihilation is negligible below $\approx 5 \mu\text{J}/\text{cm}^2$. Since the signal-to-noise ratio at 1.5 $\mu\text{J}/\text{cm}^2$ was relatively low, and a slightly decay acceleration was observed at 5 $\mu\text{J}/\text{cm}^2$, therefore, we selected the data collected at 3 $\mu\text{J}/\text{cm}^2$ as the representative fluence for lifetime comparison. The decay curves were fitted using a tri-exponential function, and intensity-weighted average lifetimes (τ) were calculated the following formula and summarized in Table 1.

$$\tau = \frac{\sum A_i \tau_i^2}{\sum A_i \tau_i} \quad (1)$$

where τ_i and A_i stand for lifetimes and amplitudes.

As displayed in Figure 2c, the Spherulite film exhibits a notably longer SE lifetime (136 ps) than the amorphous Film (97 ps), suggesting that the ordered molecular packing promotes exciton diffusion and radiative recombination.

These results, together with **the increased PLQY and prolonged PL lifetimes observed in Spherulite, demonstrate that improved molecular order and reduced defect density effectively suppress nonradiative traps, facilitating more efficient exciton delocalization and radiative decay.**

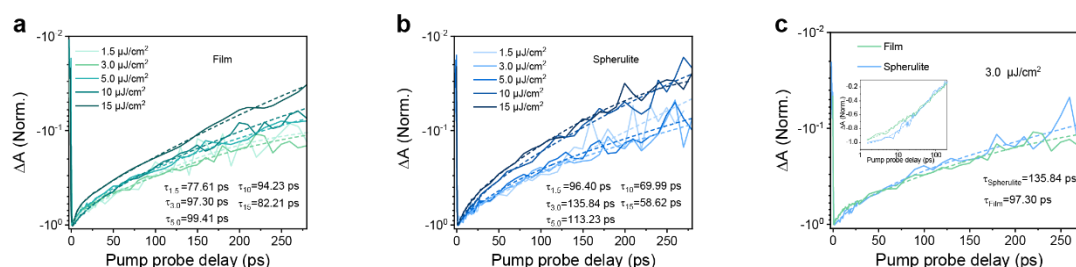


Figure 2. Normalized the TA decay kinetics of Film (a), and Spherulite at 450 nm (b) with five pump fluences of 1.5, 3, 5, 10, and 15 $\mu\text{J}/\text{cm}^2$. (c) Comparison of normalized the TA decay kinetics of Film and Spherulite at 450 nm with 3 $\mu\text{J}/\text{cm}^2$ pump fluence.

Table 1. Results of the multi-exponential decay fits the lifetimes (τ_i) and amplitudes (A_i) of Film and Spherulite.

Sample	Trace wavelength (nm)	Pump Fluence ($\mu\text{J}/\text{cm}^2$)	A_1	τ_1 (ps)	A_2	τ_2 (ps)	A_3	τ_3 (ps)	τ_{average} (ps)
Film	450	1.5	0.26	3.25	0.38	78.70	0.37	78.68	77.61
		3	0.27	5.49	0.60	103.05	0.10	37.81	97.30
		5	0.17	4.07	0.29	23.58	0.54	109.30	99.41
		10	0.15	7.01	0.54	108.65	0.39	30.24	94.23
		15	0.47	4.28	0.16	21.48	0.55	89.57	82.21
Spherulite	449	1.5	0.18	8.65	0.39	98.19	0.39	98.20	96.40
		3	0.12	9.03	0.48	36.37	0.45	161.79	135.84
		5	0.17	2.76	0.45	31.91	0.47	132.97	113.23
		10	0.10	4.75	0.43	20.31	0.54	80.60	69.99
		15	0.32	9.51	0.15	20.11	0.55	66.02	58.62

Added to the revised manuscript:

The above results and discussion have been incorporated into the revised manuscript (page 9, lines 10–31):

“To further trace the ultrafast exciton decay behavior in Spherulite and Film, the fluence-dependent femtosecond-transient absorption (f -TA) measurements were performed under pump fluences of 1.5, 3, 5, 10, and 15 $\mu\text{J}/\text{cm}^2$ with 400 nm excitation (**Fig. S7a, c**). The differential absorption (ΔA) spectra from 1 to 200 ps exhibit consistent spectral features across

fluences (**Fig. S7b, d**), including the ground state bleach (GSB) peaks at 415 nm for Film and 416 nm for Spherulite, along with stimulated emission (SE) signals at 450 nm. These features are similar to the ΔA spectra previously reported for related polyfluorene derivatives. In **Fig. 3e** and **Fig. S8**, the normalized SE dynamics are fitted using a tri-exponential function, and the intensity weighted averaged lifetimes are summarized in **Table S2**. The Spherulite film exhibits a notably longer stimulated emission (SE) lifetime (136 ps) than the amorphous Film (97 ps), suggesting that the ordered molecular packing facilitates exciton diffusion and radiative recombination. Interesting, fluorescence lifetime imaging microscopy (FLIM) reveals that the longer average fluorescence decay time (τ_m) of spherulite film (470 ps) than that Film (360 ps) (**Fig. 3f** and **S9a**), supporting that ordered crystalline domains promote rapid exciton transport and delocalization, thereby reducing exciton trapping and enhancing radiative decay rate, in agreement with the observed enhancement in PLQY. Taken together, these results indicate that enhanced molecular order and suppressed defect states in Spherulite contribute to improved excitonic performance and reduced non-radiative losses.”

Supplementary additions:

The corresponding figures and data have been added to the revised *Supplementary Information*: Figure 1, Figure 2 and Table 1 mentioned above have now been added to the revised *Supplementary Information* as Fig. S7, Fig. S8 and Table S2, respectively on page 9-10.

The experimental description of TA measurements has also been added to the revised *Supplementary Information* to clarify this point on page 4, lines 16-21:

“Ultrafast TA spectroscopy was conducted using a Ti: sapphire regenerative amplifier (Libra, Coherent Inc.). The second harmonic of the primary beam at 400 nm or an optical parametric amplifier (OperA Solo, Coherent Inc.) pumped by the regenerative amplifier was used to generate the pump beam. The probe beam was a broadband supercontinuum light source generated by focusing a small portion of the femtosecond laser beam onto either a 5 mm-thick CaF₂ plate. The TA signal was then analyzed by a silicon charge-coupled device mounted on a monochromater (Acton 2358, Princeton Instrument) at 1 kHz enabled by a home-built control board.”

Thank you for your comments and suggestions again.

2. The authors extracted diffusion data for the first 300 ps despite the reported lifetime of 1.2 ns. However, Figure S7 reveals a negative trend after 300 ps, which is not adequately explained. The authors should provide a clear justification for excluding this part of the data although it is within the life time and address why the trend goes negative.

Response: We thank you for this important comment.

Our extracted diffusion data analysis is based on the following model:

$$\text{MSD}(t) = \sigma^2(t) - \sigma^2(0) = 2Dt \quad (2)$$

where MSD is the mean-squared displacement, which grows linearly over time, and the diffusion coefficient (D) is proportional to the swsth lope. **As shown in our data, the MSD values in the 0-300 ps interval exhibit a clear linear trend, fully consistent with this theoretical model.** Accordingly, we selected the 0-300 ps region of the MSD data to fitting D . Beyond 300 ps, although still within the emission lifetime (~ 1.2 ns), the MSD curve shows a negative trend in

Figure S7. This deviation arises from exciton-exciton recombination and traps on defect, that becomes increasing at longer delay times. The recombination of exciton effectively and exciton trapped that reduces the spatial spread of the exciton distribution, leading to a decrease in the calculated MSD values.

Revision:

This explanation has now been added to the revised manuscript to clarify this point on page 11, lines 13-14:

“At longer times $t > 0.3$ ns, the recombination of exciton effectively and exciton trapped that reduces the spatial spread of the exciton distribution, leading to a decrease in the calculated MSD values (**Fig. S12**).”

Thank you for your comments and suggestions again.

➔ **Reviewer comment: should exciton-exciton annihilation now already be before 300 ps?**

Response: We thank the reviewer for this important question.

In our TPLM measurements, the excitation fluence was $11 \mu\text{J}/\text{cm}^2$. Under these conditions, exciton-exciton annihilation (EEA) is indeed expected to occur, consistent with the TA data. Previous reports on polyfluorene (PFO) films have shown that EEA processes typically occur within the first ~ 15 ps (Paul E. Shaw. et al., *Adv. Funct. Mater.* **2010**, 20, 155-161). Therefore, some degree of EEA may exist during the first 300 ps at high fluences. However, **as shown in our data, the MSD values in the 0-300 ps interval exhibit a clear linear trend, suggesting that although EEA may exist in this timescale, its contribution in this regime is minor compared to radiative recombination. The radiative decay dominates the exciton dynamics within this time window, resulting in an overall increase in MSD. At longer times ($t > 300$ ps), a decrease in intensity is observed, indicating EEA becomes more significant, and combined with defect-assisted trapping, it suppresses exciton migration and leads to the observed negative MSD trend.**

Revision:

This explanation has now been added to the revised manuscript to clarify this point on page 12, lines 3-4:

“At longer times $t > 0.3$ ns, exciton–exciton annihilation (EEA) becomes the dominant process, and together with exciton trapping, reduces the spatial spread of the exciton distribution, leading to a decrease in the calculated MSD values (**Fig. S12**).”

We appreciate the reviewer’s careful reading and constructive feedback, which has helped us clarify the interpretation of the diffusion analysis.

5. The Gaussian fits used in the analysis should be included in the Supplementary Information to allow readers to evaluate the robustness of the fitting procedure.

Response: Thank you for the reminder.

We apologize for the missing information and have now added the full set of Gaussian fitting results (including fitted curves, parameters, and r^2 values) in the Supplementary Information on page 13, line 1 as follows:

Table S4. The parameters of Gaussian fits Diffusion coefficient (D) and Diffusion length (L_D).

	D (cm ² /s)	L_D (nm)
Model	Gauss	Gauss
Equation	$y = y_0 + \left(\frac{A}{w * \sqrt{\frac{\pi}{2}}} \right) * \exp \left\{ -2 * \left(\frac{x - xc}{w} \right)^2 \right\}$	$y = y_0 + \left(\frac{A}{w * \sqrt{\frac{\pi}{2}}} \right) * \exp \left\{ -2 * \left(\frac{x - xc}{w} \right)^2 \right\}$
Plot	Relative Frequency	Relative Frequency
y0	0.042 ± 0.042	0.042 ± 0.044
xc	0.14 ± 0.015	186.62 ± 7.13
w	0.096 ± 0.022	52.67 ± 14.96
A	0.078 ± 0.018	39.40 ± 8.78
Reduced Chi-S	0.0035	0.0037
R-Square (COD)	0.988	0.983
Adj. R-Square	0.951	0.932

Thank you for your comments and suggestions again.

➔ **Reviewer comment:** Thank you for adding the fit results, however, I meant the actual fit curves in front of the data, so that the reader can evaluate if the gaussian fits are good fits for the data.

Response: We sincerely appreciate your valuable comment. We realized that our initial description was not sufficiently clear. In the revised version, we have now included both the original data (Table 2) and the processed frequency distribution data (Table 3) to provide a more intuitive presentation of the Gaussian fitting procedure. Following examples in similar works¹⁻⁴, we performed frequency histogram analyses to obtain the diffusion coefficient (D) and diffusion length (L_D) distributions, summarized in Tables 3 and 4.

Based on these data, we constructed the bar charts shown in Figure 4, where the x -axis represents the interval centers and the y -axis corresponds to the relative frequencies derived from Table 3. The experimental data points are plotted together with the Gaussian fit curves, showing only small deviations, which confirms the good consistency between the data and the fitting results. For D , the 0.1~0.2 bin exhibits the highest frequency (8 out of 12 samples, 66.67%), and the fitted mean value (fitted parameter xc , Table 4) is 0.14 ± 0.015 cm²/s. Similarly, L_D values are most frequently distributed within the 150~200 interval (7 out of 12 samples, 58.33%), and the fitted mean (xc) is 186.62 ± 7.13 nm. The corresponding relative frequency distribution curves are displayed in Figure 4, with the fitted mean values are also inset for clarity.

We apologize for this oversight and appreciate your careful attention.

Table 2. Summary of D and L_D for different samples at different locations.

Spherulite	D (cm ² /s)	L_D (nm)
1	0.4566±0.1813	331.03±65.73
2	0.2108±0.0670	224.92±35.75
3	0.0948±0.0438	150.81±34.82
4	0.1477±0.1265	188.00±80.66
5	0.1778±0.1209	206.56±70.26
6	0.1126±0.0448	164.39±32.72
7	0.1433±0.0391	185.45±25.32
8	0.1733±0.0492	203.93±28.97
9	0.1231±0.0669	171.89±46.69
10	0.1616±0.0714	196.91±43.50
11	0.1217±0.0629	170.87±44.21
12	0.0928±0.0639	149.21±51.40
Mean values	0.14±0.015	186.62±7.13

Table 3. The processed frequency distribution data of D and L_D .

	Interval Center	Interval range	Count	Cumulative Count	Relative Frequency (%)
Diffuse coefficient (D, cm²/s)	0.05	0.0~0.1	2	2	16.67
	0.15	0.1~0.2	8	10	66.67
	0.25	0.2~0.3	1	11	8.33
	0.35	0.3~0.4	0	11	0
	0.45	0.4~0.5	1	12	8.33
Diffuse length (L_D, nm)	125	100~150	1	1	8.33
	175	150~200	7	8	58.33
	225	200~250	3	11	25
	275	250~300	0	11	0
	325	300~350	1	12	8.33
Total	-	-	12	-	100

Table 4. The parameters of Gaussian fits Diffusion coefficient (D) and Diffusion length (L_D).

	D (cm ² /s)	L_D (nm)
Model	Gauss	Gauss
Equation	$y = y_0 + \left(\frac{A}{w * \sqrt{\frac{\pi}{2}}} \right) * \exp \left\{ -2 * \left(\frac{x-xc}{w} \right)^2 \right\}$	
Plot	Relative Frequency	Relative Frequency
y0	0.042±0.042	0.042±0.044
xc	0.14±0.015	186.62±7.13
w	0.096±0.022	52.67±14.96
A	0.078±0.018	39.40±8.78

Reduced Chi-S	0.0035	0.0037
R-Square (COD)	0.988	0.983
Adj. R-Square	0.951	0.932

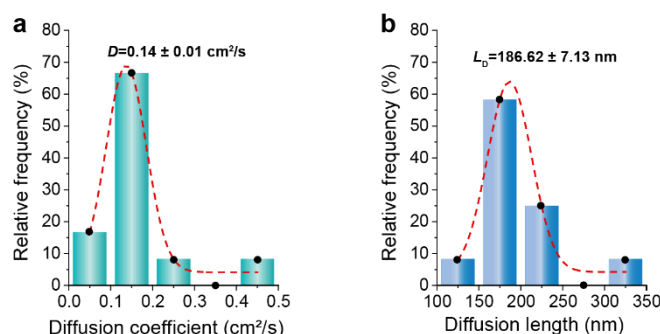


Figure 4. Relative frequency distribution curves of (a) diffusion coefficient (D) and (b) diffusion length (L_D) from Table 2. The mean value (μ), derived from the dashed fitted curve, is labeled in the figure.

Revision:

The corresponding data have been added to the revised *Supplementary Information*: Table 2, Table 3 and Table 4 mentioned above have now been added to the revised *Supplementary Information* as **Table S3**, **Table S4** and **Table S5**, respectively on page 13-14.

The experimental description of relative frequency distribution analysis has also been added to clarify this point in the revised *Supplementary Information* on page 14, lines 2-7:

“To more intuitively illustrate the diffusion coefficients (D) and diffusion length (L_D), we performed frequency histogram analyses summarized in Table S3 and Table S4, following examples in similar works¹⁻⁴. For D , the 0.1~0.2 bin exhibits the highest frequency (8 out of 12 samples, 66.67%), and the fitted mean value (fitted parameter μ , Table S5) obtained from the Gaussian fit is $0.14 \pm 0.015 \text{ cm}^2/\text{s}$. Similarly, L_D values are most frequently distributed within the 150~200 interval (7 out of 12 samples, 58.33%), and the fitted mean (μ) is $186.62 \pm 7.13 \text{ nm}$. The corresponding relative frequency distribution curves are displayed in **Fig. 4d, e**, with the fitted mean values are also inset for clarity.”

References

1. Cai, Y. *et al.* Vertically optimized phase separation with improved exciton diffusion enables efficient organic solar cells with thick active layers. *Nat. Commun.* **13**, 2369 (2022).
2. Sneyd, A. J. *et al.* Efficient energy transport in an organic semiconductor mediated by transient exciton delocalization. *Sci. Adv.* **7**, eabh4232 (2021).
3. Li, M. *et al.* Acceleration of radiative recombination for efficient perovskite LEDs. *Nature* **630**, 631–635 (2024).
4. Wang Yongshuai *et al.* Highly fluorescent semiconducting two-dimensional conjugated polymer films achieved by side-chain engineering showing large exciton diffusion length. *CCS Chem.* **5**, 2366–2377 (2022).

Thank you again for your insightful suggestion, which helped us significantly improve the clarity and completeness of our analysis.

Finally, thank you very much for your thoughtful comments and suggestions. We have corrected all issues in this revised manuscript and sincerely hope that our paper will be accepted and published in *Nature Communications*.

All changes to the manuscript have been highlighted. The revised manuscript, Supporting Information, and a list of changes & our responses to the referees' comments have been submitted through my Author Centre.

Should you have any other questions or queries, please kindly contact me by e-mail at iamwhuang@njupt.edu.cn or by fax at (+86) 25 8586 6999.

Thank you very much.

With best wishes.

Sincerely yours,

Professor Wei HUANG

Academician of China Academy of Sciences

"Program of Global Experts" Distinguished Professor

"Changjiang Scholar" Chair Professor

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Answers to Reviewer 1:

The authors have carefully addressed the reviewers comments. From my last round of comments, two of the three points have now been fully addressed: the low-fluence TA measurements and the clarification regarding exciton-exciton annihilation before 300 ps.

However, one comment remains unresolved: the Gaussian fit curves are still not shown directly overlaid on the raw diffusion data so that readers can visually assess the fit and confirm that the Gaussian model is appropriate. This should be a straightforward figure update, but essential for transparency. Once this final point is addressed, I am satisfied with the revision and can recommend the manuscript for publication.

Response: We thank the reviewer for their careful evaluation and for highlighting this important issue. We regret that our previous response did not clearly convey our intent.

In the earlier version of the manuscript, statistical analyses of the exciton diffusion length (L_D) and diffusion coefficient (D) were performed based on twelve datasets, and Gaussian functions were applied to fit the corresponding frequency distributions, to obtain average values ($L_D = 186.62 \pm 7.13$ nm, $D = 0.14 \pm 0.015$ cm²/s). This approach was initially adopted to facilitate data visualization, consistent with related reports (e.g., Fig. 1). However, we acknowledge that, given the relatively small sample size, such fitting may introduce bias and therefore lacks of sufficient statistical rigor.

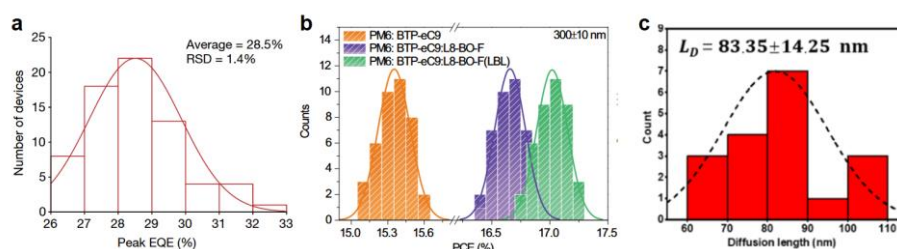


Figure 1. Similar to data treatment in the other papers (Li, M. *et al.*, *Nature*, **2024**, 630, 631-635; Cai, Y. *et al.*, *Nat. Commun.* **2022**, 13, 2369; Wang, Y. *et al.*, *CCS Chem.* **2023**, 5, 2366-2377).

To avoid potential misinterpretation and in line with the editor's recommendation that "For all data presented in a plot, chart or other visual representation, ensure that individual data points are shown when possible, and always for $n \leq 10$. The format shows data distribution clearly (e.g. dot plots, box-and-whisker plots)", we have revised the data presentation. Specifically, box plots are now employed to display the distributions of the exciton diffusion length and diffusion coefficient, as shown in the Figure 2. The average values were recalculated after excluding the highest and lowest data points ($L_D = 186.37$ nm, $D = 0.146$ cm²/s). The results remain consistent with the previously reported values and do not alter the analysis or the conclusions of this work.

Therefore, to ensure transparency and physical accuracy, the revised Figure 2 now directly displays the experimental data. As shown, the diffuse coefficients are mainly distributed in the range of 0.1~0.2 cm²/s, while the corresponding diffusion lengths are primarily concentrated in the range of 150~200 nm.

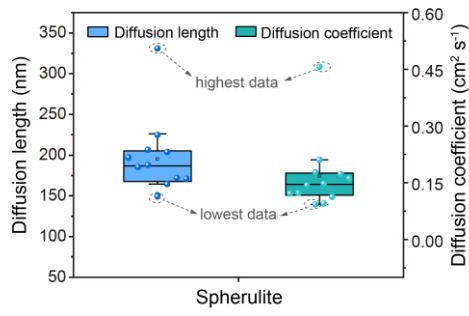


Figure 2. Statistical distribution of the diffuse coefficient (D , green) and diffusion length (L_D , blue) of bundles nanofibers (Data are presented as mean values $\pm$ s.d. $n=12$).

Thank you again for your insightful suggestion, which helped us significantly improve the clarity and completeness of our analysis.

Finally, we thank the reviewers and editors again for their thoughtful comments and constructive feedback. We have corrected all issues in this revised manuscript and sincerely hope that our paper will be accepted and published in *Nature Communications*.

All changes to the manuscript have been highlighted. The revised manuscript, Supporting Information, and a list of changes & our responses to the referees' comments have been submitted through my Author Centre.

Should you have any other questions or queries, please kindly contact me by e-mail at iamwhuang@njupt.edu.cn or by fax at (+86) 25 8586 6999.

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With best wishes.

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Response to reviewers' comments

Answers to Reviewer 1:

The authors present a study on long-range exciton transport in π -conjugated polymer (π CP) films treated by solvent thermal annealing (SVA), and investigates their potential for improving exciton diffusion lengths. The authors show significant advancements, including submillimeter-scale spherulite formation, longer exciton diffusion lengths, and enhanced electroluminescence in PLEDs. While the study has a wide range of characterization methods covered, I regret that I cannot recommend this manuscript for publication in its current form due to the following major concerns:

Response: We thank the reviewer for your positive feedback on our manuscript.

We sincerely apologize for the inconvenience caused by our previous mistakes. According to your comments, we have carefully corrected all our mistakes and polished the entire manuscript. We also added extensive experiments to support our assumption and results in this revised manuscript. Therefore, we sincerely hope that you will re-consider our revised manuscript for publishing in *Nature Communications* journal.

1. The authors used photoluminescence quantum yield (PLQY) values in their calculations; however, these values are not explicitly reported in the manuscript or supporting information. The measured PLQY values are essential for the comparison between the spherulite and pristine film samples and to access the reliability of the calculation.

Response: Thank you for bringing these concerns to our attention.

We are very sorry to confuse you for our mistakes. As you have mentioned, the PLQY values are essential for the comparison of between the thin film and the spherulite samples. We sincerely apologize that only the PLQY values presented in Figure S4b (Page 7) were shown, without providing the numerical values in the main text. In response to your helpful suggestion, we have conducted additional experiments, and the updated PLQY data have been incorporated into the revised manuscript to provide stronger support for our conclusions and improve the overall clarity and completeness of the study.

(1) We apologize for not clearly expressing the PLQY values in the previous manuscript. Actually, we measured the PLQY values of Film and Spherulite (22% and 26%, respectively), as shown in Figure S4b (Page 7), and we find the Spherulite's PLQY higher than that of the Film, as follows:

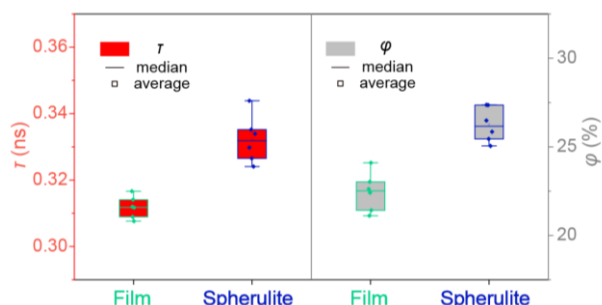


Figure 1. Summary of the τ (red) and ϕ (grey) data of the Film and Spherulite. (The PLQY of spherulite and pristine film samples were determined by FLS980 Series of Fluorescence Spectrometers.)

(2) Additionally, during the revision, we supplemented excitation energy-dependent PLQY measurements to further validate the difference between the spherulite and pristine film samples. For statistical robustness, six repeated measurements were performed for each sample (Figure 2). The PLQY of spherulite and pristine film samples were determined by a custom-built system consisting of a 375nm laser (MDL-III-375 nm, spot size is $\approx 0.13 \text{ cm}^2$), optical fibers, a spectrometer and an integrating sphere (*Adv. Mater.*, **1997**, 9, 230). All films were deposited onto quartz substrates through spin-coating. The results show that Spherulite exhibited a significantly higher average PLQY of approximately 40%, compared to 30% for Film. Moreover, the PLQY of Spherulite remains relatively stable under high excitation energy. The enhanced PLQY in Spherulite is attributed to the more ordered molecular packing in crystalline phase, which facilitates exciton diffusion, reduces nonradiative recombination, and enhances radiative decay. Based on the results of excitation energy-dependent PLQY experiments, it can be re-verified that the highly ordered spherulite film enhances photoluminescence quantum efficiency and luminescence stability.

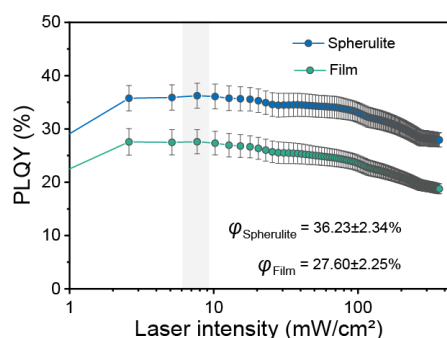


Figure 2. PLQY value of the Film and Spherulite under different excitation energy.

Revision:

We have now revised the manuscript to clarify this point on page 8, lines 5-7:

“Meanwhile, the excitation energy-dependent PLQY measurements (**Fig. 3c**) show that the Spherulite exhibits a higher average PLQY ($\sim 40\%$) than the Film ($\sim 30\%$) and remains stable at high excitation energies.”

The PLQY measurements has now been added to the revised Supplementary Information to clarify this point on page 4, lines 3-6:

“The excitation energy-dependent PLQY of spherulite and pristine film samples were determined by a self-made system by combining laser (MDL-III-375 nm, spot size is $\approx 0.13 \text{ cm}^2$), optical fiber, spectrometer and integrating sphere (*Adv. Mater.*, **1997**, 9, 230). All films were deposited onto quartz substrates through spin-coating.”

Thank you for your comments and suggestions again.

➔ Reviewer comment: ok

2. The transient absorption (TA) measurements were measured at an intensity of up to 10 mOD, which is very high for systems with good diffusion lengths, especially in films. Under these

conditions, exciton annihilation is very likely happening, making the kinetics faster and the comparison invalid. The authors should perform a fluence-dependent TA series in both the pristine and spherulite films to identify a low-fluence regime where no annihilation occurs. In this regime, the lifetimes should be compared.

Response: Thank you for your kind comments and suggestions.

We sincerely appreciate your professional and insightful review work on our manuscript. As you correctly pointed out, performing TA measurements at lower fluence regime is essential for minimizing effects of exciton-exciton annihilation and for better revealing the intrinsic exciton dynamics. According to your nice suggestions, we supplemented fluence-dependent TA series on both the pristine (Film) and spherulite (Spherulite) films. However, we sincerely apologize for not being able to reduce the TA signal intensity below 10 mOD, due to the limitations of the TA measurement system. At excitation fluence lower than $70 \mu\text{J}/\text{cm}^2$, the signal-to-noise ratio was too low, which makes it difficult to extract reliable kinetic data. Therefore, to ensure data quality and accurate analysis, we chose to perform measurements starting from $70 \mu\text{J}/\text{cm}^2$, and compared the excited-state lifetimes under low-fluence regime, as follows:

(1) To further trace the ultrafast exciton decay behavior in Spherulite and Film, the fluence-dependent femtosecond-transient absorption (fs-TA) technology is performed under pump fluences of 70, 140, and $280 \mu\text{J}/\text{cm}^2$ with 400 nm excitation (Figure 3a, c). The differential absorption (ΔA) spectra from 0.2 to 200 ps exhibit consistent spectral features across fluences (Figure 3b, d), including the ground state bleach (GSB) peaks at 425 nm for Film and 430 nm for Spherulite, along with stimulated emission (SE) signals at 450 nm and 480 nm. In contrast, the broad positive ΔA signals which peak at 570 nm (Film) and 580 nm (Spherulite), corresponding to polaron-pairs photoinduced absorption (PAP). These features are similar to the ΔA spectra previously reported for related polyfluorene derivatives (Sun, C. et al., *Adv. Funct. Mater.*, **2022**, 32, 2206723. Virgili, T. et al., *J. Mater. Chem.*, **2010**, 20, 519–523.)

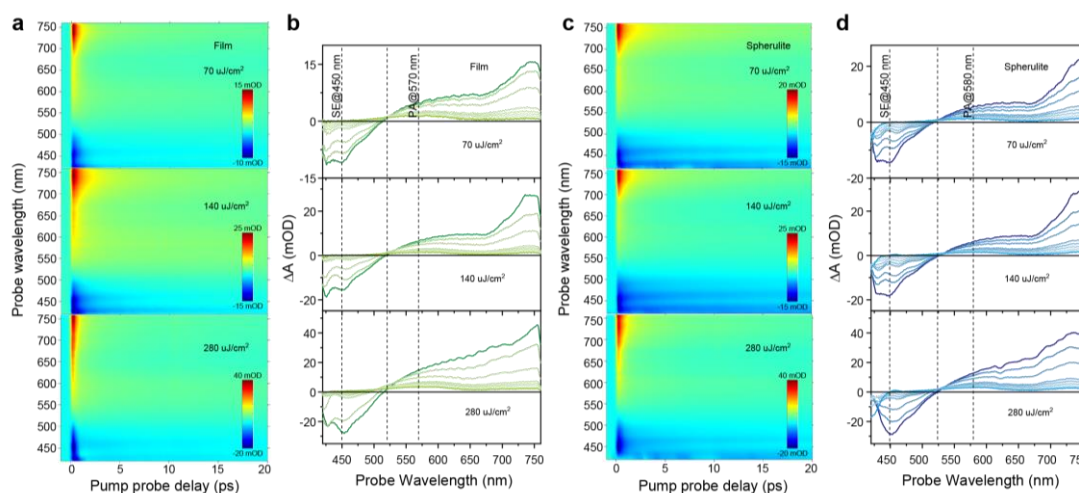


Figure 3. Transient absorption (TA) analysis of films. TA contour plots of the Film (a) and Spherulite films (c) under pump fluences of $70 \mu\text{J}/\text{cm}^2$, $140 \mu\text{J}/\text{cm}^2$, and $280 \mu\text{J}/\text{cm}^2$ using photoexcitation at 400 nm. ΔA spectra of the Film (b) and Spherulite films (d) at different time delays down to 200 ps (0.2 ps, 0.5 ps, 1 ps, 5 ps, 10 ps, 20 ps, 50 ps, 100 ps and 200 ps, respectively).

(2) Figure 4 presents the normalized SE and PA dynamics of Film and Spherulite under varying pump fluences ($70 \mu\text{J}/\text{cm}^2$, $140 \mu\text{J}/\text{cm}^2$, $280 \mu\text{J}/\text{cm}^2$). The time trace was fitted using a triexponential function with lifetimes (τ_i), and amplitudes A_i . The intensity weighted averaged lifetimes were calculated using the formula:

$$\tau = \frac{\sum A_i \tau_i^2}{\sum A_i \tau_i} \quad (1)$$

as summarized in Table 1. For the Film sample, the SE lifetime (Figure 4a) initially increased and then rapid decay with increasing excitation fluence, indicating the exciton-exciton annihilation at higher excitation fluence. In contrast, the Spherulite exhibited gradually decreased SE lifetime with increasing excitation fluence (Figure 4b). However, the decay curves at 70 and $140 \mu\text{J}/\text{cm}^2$ are nearly constant, suggesting that exciton annihilation is negligible at low fluence. Based on this observation, we infer that under $70 \mu\text{J}/\text{cm}^2$, both the pristine film and spherulite film exhibit minimal exciton-exciton annihilation.

Under $70 \mu\text{J}/\text{cm}^2$ (Figure 4c, f), **Film shows longer SE and PA_p lifetimes (11 ps and 96 ps, respectively) compared to the Spherulite (7 ps and 48 ps, respectively).** The shorter PA_p lifetimes in the Spherulite film suggests more efficient carrier extraction and reduced polaron formation, consistent with a lower density of nonradiative defects. **Combined with the increased PLQY observed in Spherulite, confirm that enhanced molecular ordering and reduced defect density effectively suppress traps and polaron-mediated nonradiative losses, enabling more efficient and faster exciton recombination.**

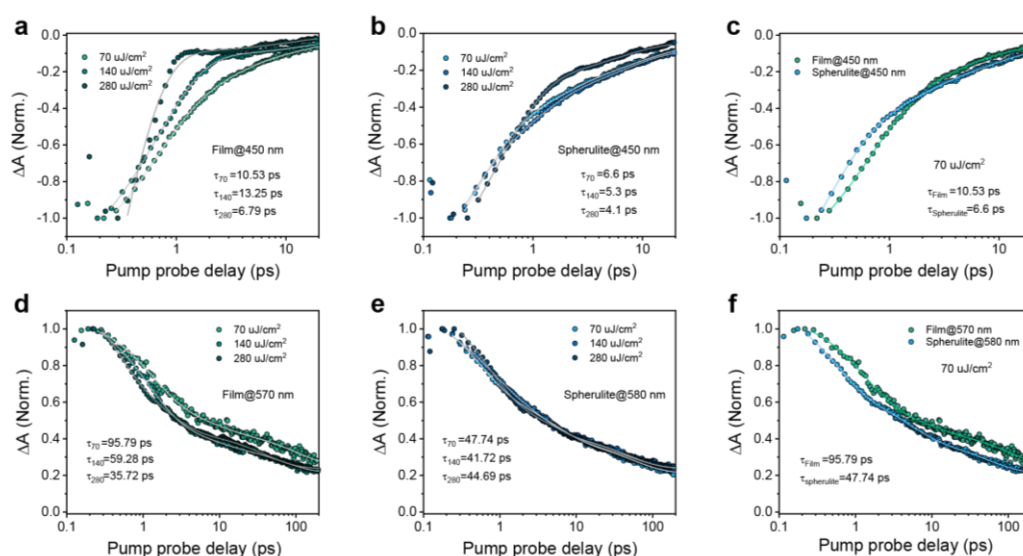


Figure 4. Normalized the TA decay kinetics of Film at 450 nm (a) and 570 nm (d), Spherulite at 450 nm (b) and 580 nm (e) with three pump fluences of $70 \mu\text{J}/\text{cm}^2$, $140 \mu\text{J}/\text{cm}^2$, $280 \mu\text{J}/\text{cm}^2$. (c) Comparison of normalized the TA decay kinetics of Film and Spherulite at 450 nm with $70 \mu\text{J}/\text{cm}^2$ fluence. (f) Comparison of normalized the TA decay kinetics of Film at 570 nm and Spherulite at 580 nm with $70 \mu\text{J}/\text{cm}^2$ fluence.

Table 1. Results of the multi-exponential global fits the lifetimes (τ_i) and amplitudes (A_i) of Film and Spherulite.

Sample	Trace wavelength (nm)	Pump Fluence ($\mu\text{J}/\text{cm}^2$)	A_1	τ_1 (ps)	A_2	τ_2 (ps)	A_3	τ_3 (ps)	τ_{average} (ps)
Film	450	70	0.84	0.58	0.30	2.32	0.16	14.91	10.53
		140	1.10	0.67	0.10	0.67	0.11	18.29	13.24
		280	2.69	0.26	0.61	0.04	0.10	11.82	6.79
	570	70	0.47	1.22	0.16	6.39	0.21	102.62	95.79
		140	0.59	1.07	0.15	5.13	0.17	66.35	59.28
		280	0.55	0.38	0.34	1.84	0.21	39.20	35.72
Spherulite	450	70	1.08	0.25	0.28	1.27	0.25	8.32	6.57
		140	0.88	0.16	0.49	0.81	0.28	6.69	5.35
		280	1.13	0.50	0.14	0.23	0.22	5.84	4.14
	580	70	0.49	0.51	0.27	4.65	0.19	54.05	47.74
		140	0.35	0.56	0.32	3.02	0.44	46.76	41.72
		280	0.60	0.65	0.21	5.03	0.17	51.56	44.69

Revision:

The TA data have been corrected and re-analyzed, this revised results and discussion has now been added to the revised manuscript on page 9, lines 10-31:

“To further trace the ultrafast exciton decay behavior in Spherulite and Film, the fluence-dependent femtosecond-transient absorption (fs-TA) technology is performed under pump fluences of 70, 140, and 280 $\mu\text{J}/\text{cm}^2$ with 400 nm excitation (**Fig. S7a, c**). The differential absorption (ΔA) spectra from 0.2 to 200 ps exhibit consistent spectral features across fluences (**Fig. S7b, d**), including the ground state bleach (GSB) peaks at 425 nm for Film and 430 nm for Spherulite, along with stimulated emission (SE) signals at 450 nm and 480 nm. In contrast, the broad positive ΔA signals which peak at 570 nm (Film) and 580 nm (Spherulite), corresponding to polaron-pairs photoinduced absorption (PA_P). These features are similar to the ΔA spectra previously reported for related polyfluorene derivatives. In **Fig. 3e** and **Fig. S8**, the normalized SE and PA_P dynamics are fitted using a tri-exponential function, and the intensity weighted averaged lifetimes are summarized in **Table S2**. For the Film, the SE lifetime initially increased and then rapid decay at high excitation fluence, suggesting exciton–exciton annihilation, while the PA_P lifetime decrease continuously, implying enhanced polaron generation. In contrast, the Spherulite shows a gradual decrease in SE lifetime with increasing pumping fluence, and nearly constant PA_P lifetime, indicating suppressed exciton-polaron interactions. At low excitation fluence, both SE and PA_P lifetimes in Spherulite (7 ps and 48 ps, respectively) are shorter than those in Film (11 ps and 96 ps, respectively), consistent with more efficient carrier extraction and fewer trap-assisted processes. These results highlight the critical role of molecular ordering in suppressing trap-assisted and polaron-mediated losses, thereby enhancing exciton recombination efficiency. Interesting, fluorescence lifetime imaging microscopy (FLIM) reveals that the longer average fluorescence decay time (τ_m) of spherulite film (470 ps) than that Film (360 ps) (**Fig. 3f** and **S9a**). The coexistence of a prolonged PL lifetime and shortened PA_P lifetimes in the spherulite film suggests that highly ordered crystalline domains promote rapid

exciton transport and delocalization, thereby reducing exciton trapping and enhancing radiative decay, in agreement with the observed increase in PLQY. Taken together, these results indicate that enhanced molecular order and suppressed defect states in Spherulite contribute to improved excitonic performance and suppressed non-radiative losses. ”

The Figure 3, Figure 4 and Table 1 has now been added to the revised Supplementary Information as Fig. S7, Fig. S8 and Table S2, respectively on page 9-10.

The TA measurements has now been added to the revised Supplementary Information to clarify this point on page 4, lines 16-21:

“Time-resolved fs-TA spectroscopy is measured by using fs laser (Coherent Astrella), optical parametric amplifier (Ultrafast Systems Apollo-T) and Helios Pump-Probe System (Ultrafast Systems Helios). The laser source was the Coherent Astrella regenerative amplifier (<100 fs, 1 kHz, 800 nm, 7 mJ pulse⁻¹). The pump pulse centered at 400 nm were generate by an optical parametric amplifier. The vis-light probe pulses (420–780 nm) by focusing an attenuated fraction of the fundamental 800 nm laser pulses (Coherent Astrella, 800 nm, 1 kHz, 7 mJ pulse⁻¹). The system provides a time window of up to 8 ns and a time resolution better than 14 fs.”

Thank you for your comments and suggestions again.

➔ Reviewer comment: the energy is still very high for materials with good diffusion. TA is commonly measurable at least at 10 μJ/cm² or until a fluence where no fluence-dependence is visible anymore. However, there is still a fluence dependence with 70 μJ/cm², so the authors should record traces of fluences where no fluence dependence is visible and compare the kinetics at those fluences.

3. Regarding the response time of the experimental setup, the authors should clarify whether the 0-300 ns range, where the diffusion constant is extracted, is within the response time of the system. If so, this time point may not be representative and needs careful consideration.

Response: We thank you for this important comment.

The 0-300 ns range used for extracting the diffusion constant is well within the response time of our experimental setup. Photoexcitation diffusion imaging was performed using a home-built TPLM, a 405 nm picosecond pulsed laser (ALPHALAS) with a repetition rate of 10 MHz and pulse width of 25 ps was focused onto the surface of the sample using an objective lens (Olympus, 100X, Apo, 0.95 numerical aperture). Additionally, the single-photon detecting avalanche photodiode (APD) (SPCM-AQRH, dead time of 28 ns) was used to detect the PL, and the APD was connected to timing electronics (PicoQuant PicoHarp 3000).

Above of all, **our system features an instrument response function (IRF) with a temporal resolution of 25 ps, which enables precise detection of the fluorescence dynamics over the entire analyzed time range.** Although the single-photon detector has a dead time of 28 ns, this parameter affects only the maximum count rate and not the temporal resolution or the validity of the time rang itself.

Therefore, the extraction of the diffusion constant within the 0-300 ns window is not limited by the experimental setup’s response and reflects the intrinsic exciton diffusion of the sample.

1 **Revision:**

2 This explanation has now been added to the revised Supplementary Information to clarify this point
3 on page 4, lines 22-26:

4 “Photoexcitation diffusion imaging was performed using a home-built TPLM, a 405 nm picosecond
5 pulsed laser (ALPHALAS) with a repetition rate of 10 MHz and pulse width of 25 ps was focused
6 onto the surface of the sample using an objective lens (Olympus, 100X, Apo, 0.95 numerical
7 aperture). Additionally, PL was detected using a single-photon detecting avalanche photodiode
8 (APD) (SPCM-AQRH, dead time of 28 ns), which was connected to a time-correlated single-photon
9 counting module (PicoQuant PicoHarp 3000).”

10 Thank you for your comments and suggestions again.

11
12 → Reviewer comment: ok

13
14 4. The authors extracted diffusion data for the first 300 ps despite the reported lifetime of 1.2 ns.
15 However, Figure S7 reveals a negative trend after 300 ps, which is not adequately explained. The
16 authors should provide a clear justification for excluding this part of the data although it is within
17 the life time and address why the trend goes negative.

18 Response: We thank you for this important comment.

19 Our extracted diffusion data analysis is based on the following model:

$$\text{MSD}(t) = \sigma^2(t) - \sigma^2(0) = 2Dt \quad (2)$$

20 where MSD is the mean-squared displacement, which grows linearly over time, and the diffusion
21 coefficient (D) is proportional to the swath lobe. **As shown in our data, the MSD values in the 0-
22 300 ps interval exhibit a clear linear trend, fully consistent with this theoretical model.**
23 Accordingly, we selected the 0-300 ps region of the MSD data to fitting D . Beyond 300 ps, although
24 still within the emission lifetime (~ 1.2 ns), the MSD curve shows a negative trend in Figure S7.
25 This deviation arises from exciton-exciton recombination and traps on defect, that becomes
26 increasing at longer delay times. The recombination of exciton effectively and exciton trapped that
27 reduces the spatial spread of the exciton distribution, leading to a decrease in the calculated MSD
28 values.

29 **Revision:**

30 This explanation has now been added to the revised manuscript to clarify this point on page 12, lines
31 3-4:

32 “At longer times $t > 0.3$ ns, the recombination of exciton effectively and exciton trapped that reduces
33 the spatial spread of the exciton distribution, leading to a decrease in the calculated MSD values
34 (Fig. S12).”

35 Thank you for your comments and suggestions again.

36
37 → Reviewer comment: should exciton-exciton annihilation now already be before 300ps?

38
39 5. The Gaussian fits used in the analysis should be included in the Supplementary Information to
40 allow readers to evaluate the robustness of the fitting procedure.

Response: Thank you for the reminder.

We apologize for the missing information and have now added the full set of Gaussian fitting results (including fitted curves, parameters, and r^2 values) in the Supplementary Information on page 13, line 1 as follows:

Table S4. The parameters of Gaussian fits Diffusion coefficient (D) and Diffusion length (L_D).

	D (cm ² /s)	L_D (nm)
Model	Gauss	Gauss
Equation	$y = y_0 + \left(\frac{A}{w * \sqrt{\frac{\pi}{2}}} \right) * \exp \left\{ -2 * \left(\frac{x - xc}{w} \right)^2 \right\}$	$y = y_0 + \left(\frac{A}{w * \sqrt{\frac{\pi}{2}}} \right) * \exp \left\{ -2 * \left(\frac{x - xc}{w} \right)^2 \right\}$
Plot	Relative Frequency	Relative Frequency
y0	0.042 ± 0.042	0.042 ± 0.044
xc	0.14 ± 0.015	186.62 ± 7.13
w	0.096 ± 0.022	52.67 ± 14.96
A	0.078 ± 0.018	39.40 ± 8.78
Reduced Chi-S	0.0035	0.0037
R-Square (COD)	0.988	0.983
Adj. R-Square	0.951	0.932

Thank you for your comments and suggestions again.

➔ Reviewer comment: Thank you for adding the fit results, however, I meant the actual fit curves in front of the data, so that the reader can evaluate if the gaussian fits are good fits for the data.

6. While the manuscript focuses on singlet exciton dynamics, it does not address the potential influence of triplet excitons in the devices. Optical excitation generates 100% singlet excitons, whilst triplet excitons only form via intersystem crossing (ISC). In contrast, electrical excitation directly produces 75% triplet excitons. The rising electroluminescence (EL) intensity trend observed in the spherulite films could be influenced by delayed triplet excitons contributing through triplet-triplet annihilation, especially given the efficient diffusion reported. The authors should discuss the role of triplet excitons in detail.

Response: We thank you for this important comment.

As you noted, electrical excitation generates approximately 75% triplet excitons and the rising electroluminescence (EL) intensity trend could be influenced by delayed triplet excitons contributing through triplet-triplet annihilation. However, our devices are based on conventional fluorescent materials, and the emission originates exclusively from singlet excitons. Since no phosphorescent or thermally activated delayed fluorescence (TADF) materials are involved, triplet excitons generated under electrical excitation are non-radiative due to spin-forbidden transitions, and thus do not contribute directly to electroluminescence. **Although triplet-triplet annihilation (TTA) can, in principle, occur in systems with long-lived triplet excitons, it is not expected to play a significant role in our devices.** First, the absence of delayed emission features in transient EL measurements suggests a negligible contribution from TTA. Second, our polymer system lacks the energy level alignment and molecular design typically required to enable efficient TTA upconversion.

As your suggestion, we re-analysed the Tr-EL of Film and Spherulite. In Figure 5a, the Tr-EL intensity of the Film-based device rises and then reaches stability before showing a decaying trend with increasing current density (up to $25 \text{ mA}\cdot\text{cm}^{-2}$) at a pulse duration time of $40 \mu\text{s}$, reflecting exciton-exciton annihilation via singlet-singlet annihilation and singlet-triplet annihilation under high exciton densities, where exciton diffusion is limited and local accumulation becomes significant. Under the same condition, the EL intensity of the Spherulite-based device (Figure 5b) shows a rising trend with the increase of current density without reaching saturation or decay. This behavior is attributed to the low density of the defect structures in spherulite film, electrons are less prone to defect trapping, which enhances exciton transport and charge mobility, thereby prolonging the recombination process between holes and electrons. These findings are consistent with the improved excitonic properties of the Spherulite film observed in PLQY and fs-TA measurements.

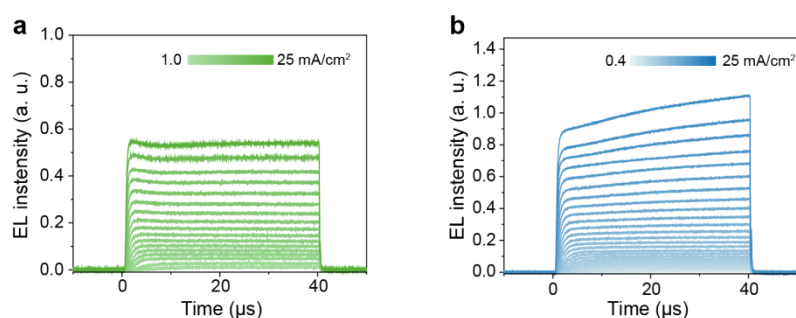


Figure 5 Transient electroluminescence spectra of PLED based on Film (a) and Spherulite (b).

Revision:

This explanation has now been added to the revised manuscript to clarify this point on page 14, lines 14-21:

“In **Fig. 5g**, the Tr-EL intensity of the Film-based device rises and then reaches stability before showing a decaying trend with increasing current density (up to $25 \text{ mA}\cdot\text{cm}^{-2}$) at a pulse duration time of $40 \mu\text{s}$, **reflecting exciton-exciton annihilation via singlet-singlet annihilation and singlet-triplet annihilation under high exciton densities, where exciton diffusion is limited and local accumulation becomes significant.** Under the same condition, the EL intensity of the Spherulite-based device shows a rising trend with the increase of current density without reaching saturation or decay (**Fig. 5h**). **This behavior is attributed to the low density of the defect structures in spherulite**

film. Electrons are less prone to defect trapping, which enhances exciton transport and charge mobility, thereby prolonging the recombination process between holes and electrons.”

Thank you for your comments and suggestions again.

→ Reviewer comment: ok

7. The authors should compare the PLQY and EQE values, as such a comparison can offer insights into the presence of trap states or dark triplet excitons, which could influence the overall device performance.

Response: We thank you for this helpful suggestion. As your suggestion, we compared the PLQY and EQE of the two types of films. In the experimental conditions, the Film-based device exhibits a PLQY of 30% and EQE_{max} of 0.88%, while the Spherulite-based device shows a PLQY of 40% and EQE_{max} of 1.16%. According to the EQE equation:

$$EQE = IQE \times \eta_{out} = \gamma \times \eta_r \times \phi \times \eta_{out} \quad (3)$$

where γ is hole/electron recombination efficiency, η_r is exciton formation probability (0.25 for conventional fluorescent emitters), ϕ is PLQY and η_{out} is light outcoupling efficiency. When assuming $\gamma=1$, $\eta_{out}=0.2$, $\eta_r=0.25$, $\phi_{Film}=0.3$, $\phi_{Spherulite}=0.4$, the theoretical maximum EQE_{max} for the Film device and Spherulite device are calculated to be 1.5% and 2.0%, respectively. The measured EQE_{max} (0.88% and 1.16% for the Film device and Spherulite device, respectively) are below these theoretical EQE_{max}, primarily due to limitations in our current device structure and fabrication process, which is not fully optimized. Nonetheless, this comparison clearly shows that the higher EQE in the Spherulite-based device correlates well with their increased PLQY, which results from reduced non-radiative losses, due to a lower density of trap states and suppressed structural disorder after film crystallization. The improvement in EQE further supports the role of molecular ordering in suppressing defect-induced quenching and enhancing overall device performance.

Revision:

This explanation has now been added to the revised manuscript to clarify this point on page 13, lines 23-30:

According to the EQE equation:

$$EQE = IQE \times \eta_{out} = \gamma \times \eta_r \times \phi \times \eta_{out} \quad (3)$$

where γ is hole/electron recombination efficiency, η_r is exciton formation probability (0.25 for conventional fluorescent emitters), ϕ is PLQY and η_{out} represents light outcoupling efficiency. When assuming $\gamma=1$, $\eta_{out}=0.2$, $\eta_r=0.25$, $\phi_{Film}=0.3$, $\phi_{Spherulite}=0.4$, the theoretical maximum EQE for the Film and Spherulite device are calculated to be 1.5% and 2.0%, respectively. The measured values are below these due to unoptimized device architecture. Nonetheless, the higher EQE in the Spherulite-based device correlates with its increased PLQY, indicating reduced non-radiative losses and confirming the key role of molecular ordering in suppressing defect-induced quenching and enhancing overall device performance.

Thank you for your comments and suggestions again.

1 Finally, thank you for your all kind comments and suggestions. We have modified all incorrect
2 sentences in this revised manuscript. We sincerely hope that our paper can be accepted and
3 published in *Nature Communications*.

4

5 Reviewer comment: The authors significantly improved the manuscript within the revision. I can
6 recommend the article for publication after the remaining comments are sufficiently addressed.