

Water-oil interfacial kinetics control enables water-based organic solar cells with 12.59% certified efficiency

Corresponding Author: Professor Wei Ma

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

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The manuscript deals with the development of organic solar cells needed to produce electric energy.

The authors propose an environmentally friendly protocol that avoids hazardous organic solvents. This protocol is based on the formation of semiconductor nanoparticles at a water/oil interface.

The photovoltaic efficiency was measured and found to be quite good. The interfacial tension guided protocol is proposed as very efficient.

The interfacial tensions are measured by the Wilhelmy plate method, although for some surface tension measurements, a drop profile tensiometer was available. This sounds quite strange as the plate tensiometry is not very reliable for interfacial tension measurements due to the required contact angle. Instead, drop profile analysis is a perfect method for these measurements.

Else, the manuscript provides many important data and results and can therefore be recommended for publication.

Reviewer #2

(Remarks to the Author)

In this article, Ma et al. report a water-processed OSC based on PM6:Y6 heterojunction nanoparticles (NPs), with a champion PCE of 12.64% and a certified PCE of 12.59%. The main advance, in my view, is not only the device efficiency itself, but also the attempt to control the internal structure of the NPs through the water/oil interfacial tension during particle formation. By using DPE, the authors tune the interfacial-tension contrast between PM6- and Y6-containing oil phases, which changes the PM6/Y6 segregation at the water/oil interface. As a result, the NPs evolve from a donor-dominated and highly ordered shell structure to a more mixed polycrystalline surface. This structural change is proposed to improve particle fusion, phase connectivity, and charge-carrier processes in the final films. The work is quite systematic. The authors combine interfacial-tension measurements, Cryo-TEM, SANS, in situ PL spectroscopy, GIWAXS, AFM and device characterization to build a reasonably complete picture of how the NPs form and how their structure affects device performance. I especially appreciate the in-situ PL study, which gives useful information on the evolution of structure during NP solidification.

Overall, I consider this manuscript to be a meaningful advance in water-processed OSCs. The use of water/oil interfacial tension to manipulate heterojunction NP structure is an interesting and important idea, and it addresses a real bottleneck in this field. The certified PCE of 12.59% is also very impressive and, to the best of my knowledge, represents the highest reported value for water-processed OSCs so far. I therefore support publication in Nature Communications after the authors address the following points.

1. In the Introduction section, the scalability of photovoltaic material synthesis and device fabrication should be commented and cited (such as Joule 2025, 9, 102173), which is very important to the industrialization of OPVs.
2. The authors consistently use the term "water-processed organic solar cells" in the title and introduction, implying a predominantly aqueous fabrication route. In practice, however, the NP preparation involves dissolving the active materials in chloroform, injecting the solution into an aqueous surfactant phase (with an optimal chloroform:water ratio of 1:6), and subsequently evaporating the solvent. Thus, the process still relies on chloroform, and the only difference is that the chloroform is removed during NP synthesis rather than during final film casting. This critical detail is omitted from the narrative of authors in abstract and introduction. The term "water-processed" should therefore be revised appropriately to

more accurately reflect the actual fabrication process. Additionally, the GSK solvent sustainability assessment should be amended to explicitly account for chloroform consumption, to explicitly quantify the consumption and associated environmental hazards of chloroform and provide an honest evaluation of the true environmental impact of the proposed technology.

3. The additive-containing emulsions seem to maintain good processability at high solid contents, as suggested by the successful film coating and device fabrication. However, the colloidal stability is not directly shown. Zeta-potential measurements and storage-stability data should be added.
4. The neat PM6 and neat Y6 NP dispersions show different emission evolution during evaporation (Fig. S17), and PM6 behavior is different from that of the PM6:Y6 samples. This difference deserves more discussion. The authors should also describe the in-situ PL setup more clearly, so that the experiment can be better understood and reproduced by readers.
5. In stage 2 (Fig. 3e), the DPE-treated emulsion shows a clear two-step decrease in PL intensity compared with the control sample. A weaker two-step feature is also seen for the 1-PN-treated sample. Is this related to a stage mainly governed by additive evaporation? The authors should give a more detailed analysis of this point.
6. The PM6:Y6 films prepared from NP inks show different GIWAXS features under different additive conditions (Fig. 3g). In particular, the 1-PN film shows two pronounced peaks at $q = 0.32$ and $0.48 \text{ \AA}^{-1}$. To make the assignment more reliable, it would be useful to include GIWAXS data for films prepared from neat PM6 NP ink and neat Y6 NP ink.
7. For the SANS measurements, the sample-preparation conditions should be specified more clearly. The fitted model parameters should also be provided in the Supporting Information.
8. The manuscript states that the as-cast DPE-treated devices outperform the control and 1-PN devices. However, I could not find the corresponding photovoltaic parameters in the Supporting Information. The authors should provide the full photovoltaic parameters for the as-cast devices.
9. Some terms are used interchangeably for the same concept. For example, the manuscript uses “BHJ organic nanoparticles”, “blend NPs” and “NP blends”, as well as “water-processed OSCs”, “nanoparticle OSCs” and “WNP-OSCs”. To avoid unnecessary confusion, the authors should choose one term and use it consistently throughout the manuscript. “heterojunction nanoparticles” and “water-processed OSCs” or “WP-OSCs” would be suitable choices.
10. There are still a few formatting and wording issues in the manuscript. For example, the reference format on page 25 should be corrected; the description of Fig. 3e should be added on page 31; the intensity scales in the GIWAXS patterns on page 32 should be made more consistent where possible; and the fs-TA signal near 900 nm on page 34 should be described consistently with the figure.

Reviewer #3

(Remarks to the Author)

This manuscript reports a facile liquid-liquid interfacial tension regulation strategy via DPE additive to tailor the intrinsic nanostructure of PM6:Y6 aqueous NPs for WNP-OSCs. Comprehensive characterizations including cryo-TEM and SANS verify that DPE effectively inhibits the undesired donor-rich core-shell structure and generates homogeneous polycrystalline NP surfaces, which facilitates interparticle fusion and the construction of continuous charge transport networks after thermal annealing. Correlated GIWAXS, AFM, RSoXS and femtosecond transient absorption measurements collectively demonstrate enhanced molecular stacking order, balanced carrier mobilities, and suppressed non-radiative recombination as well as accelerated exciton dissociation in DPE-modified blend films. Benefiting from the optimized nanoparticle morphology, the optimized device achieves a certified PCE of 12.59%, outperforming all previously reported water-based OSC benchmarks. Meanwhile, unencapsulated devices exhibit greatly improved thermal stability with a T80 lifetime exceeding 2000 h at 85 °C. This work establishes a clear mechanistic correlation between oil-water interfacial tension, nanoparticle solidification kinetics and final thin-film morphology, and provides instructive molecular engineering guidelines for environmentally friendly printable photovoltaic manufacturing. Although the overall structure-property relationship is well supported by systematic characterizations and certified photovoltaic data, several critical experimental and mechanistic details remain insufficiently discussed, which requires appropriate revisions before acceptance. The key questions to be addressed are listed as follows:

1. What is the molecular weight of PM6 adopted in this work? How does its molecular weight affect solubility in chloroform?
2. What concentration/dosage of SDS was used during nanoparticle synthesis? Residual SDS inside active films acts as insulating impurity and deteriorates charge transport. The authors should characterize residual SDS content and systematically discuss its negative impacts on device performance.
3. Which preparation parameters (e.g., organic solution concentration, SDS loading, ultrasonic power, processing temperature) exert dominant effects on nanoparticle size and microphase separation? Corresponding control experiments are suggested to clarify the influence law.
4. Will DPE and 1-PN additives remain inside the active layer after spin-coating and thermal annealing?
5. How do chloroform evaporation rate and temperature regulate nanoparticle size, internal component distribution and phase-separated nanostructure during miniemulsion preparation? The underlying kinetic mechanism needs further elaboration.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The revision answers all my questions so that I recommend the manuscript to publish in its present state.

Reviewer #2

(Remarks to the Author)

I have carefully read the revised manuscript and response letter. The authors have sufficiently addressed all my concerns. I therefore support the acceptance this manuscript at its current form.

Reviewer #3

(Remarks to the Author)

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REVIEWER REPORT(S)

We thank the reviewers for their much-valued suggestions, which have enabled us to improve the manuscript. The following are the detailed revisions based on the reviewers' comments:

Reviewer #1 (Remarks to the Author):

The manuscript deals with the development of organic solar cells needed to produce electric energy.

The authors propose an environmentally friendly protocol that avoids hazardous organic solvents. This protocol is based on the formation of semiconductor nanoparticles at a water/oil interface.

The photovoltaic efficiency was measured and found to be quite good. The interfacial tension guided protocol is proposed as very efficient.

Reply: We thank the reviewer for the valuable comment on our work.

The interfacial tensions are measured by the Wilhelmy plate method, although for some surface tension measurements, a drop profile tensiometer was available. This sounds quite strange as the plate tensiometry is not very reliable for interfacial tension measurements due to the required contact angle. Instead, drop profile analysis is a perfect method for these measurements.

Else, the manuscript provides many important data and results and can therefore be recommended for publication.

Reply: We thank the reviewers' recognition and suggestions of our work. We agree that the measured force can be affected by the wetting state and contact angle of the plate. To address this concern, we repeated the relevant interfacial tension measurements using pendant-drop profile analysis.

At the concentration used for nanoparticle preparation, the PM6 CF droplets rapidly developed precipitation and non-axisymmetric deformation in the SDS aqueous phase, preventing reliable fitting of the drop profile. We therefore used diluted PM6 and Y6 solutions in chloroform (0.5 mg mL^{-1}), while maintaining the same additive fraction and SDS concentration, to obtain stable axisymmetric droplets. These measurements were used to compare the relative interfacial tendencies of PM6 and Y6 under controlled conditions.

For the semiconductor-free organic phases, both additives reduced the CF-SDS interfacial tension, with a larger reduction observed for DPE (2.87, 2.68, and 2.23 mN m^{-1} for control, 1-PN, and DPE, respectively.). More importantly, the additives produced different effects when PM6 or Y6 was present in the organic phase. The PM6-

SDS interfacial tension (3.06 mN m^{-1}) decreases to 2.86 mN m^{-1} with 1-PN, but increases to 3.26 mN m^{-1} with DPE. In contrast, the Y6-SDS interfacial tension decreased from 3.66 mN m^{-1} to 3.35 and 3.19 mN m^{-1} with 1-PN and DPE, respectively. Accordingly, the interfacial-tension contrast, defined as $\Delta\gamma = \gamma_{\text{Y6-SDS}} - \gamma_{\text{PM6-SDS}}$, decreased from 0.60 mN m^{-1} (control) to 0.49 mN m^{-1} (1-PN) and -0.07 mN m^{-1} (DPE). The positive $\Delta\gamma$ values for the control and 1-PN conditions indicate that PM6 retains a lower interfacial tension with the SDS aqueous phase than Y6, whereas the small magnitude of the negative value suggests a limited interfacial selectivity for donor-acceptor partition at the interface for the DPE condition.

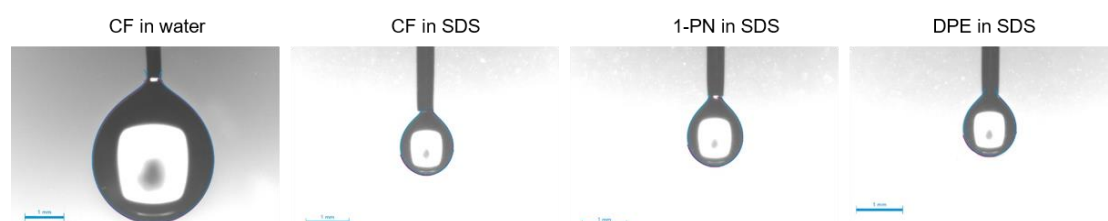


Figure R1. Pendant-drop interfacial tension measurement of CF without and with additives (1.5 vol%) in water and SDS aqueous solution, respectively.

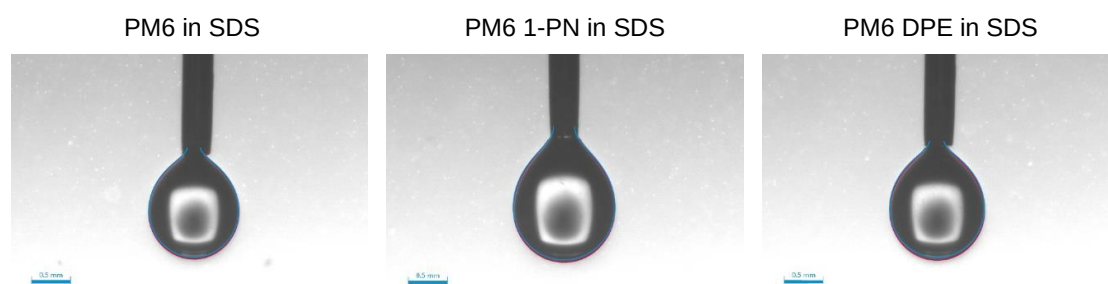


Figure R2. Pendant-drop interfacial tension measurement of PM6 solution (0.5 mg/ml in CF) without and with additives (1.5 vol%) in SDS aqueous solution.

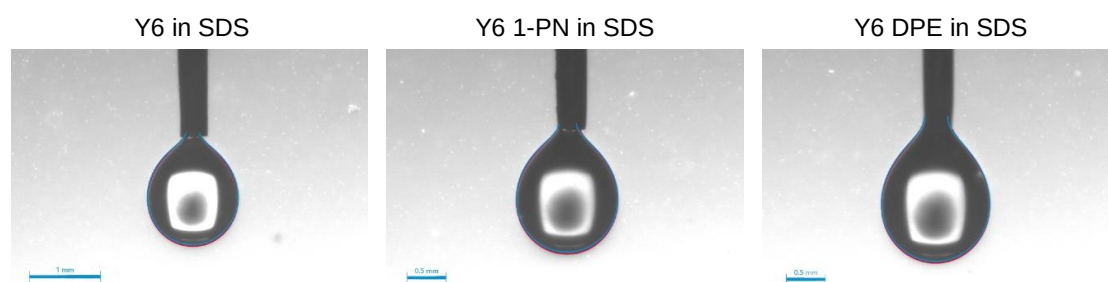


Figure R3. Pendant-drop interfacial tension measurement of Y6 solution (0.5 mg/ml in CF) without and with additives (1.5 vol%) in SDS aqueous solution.

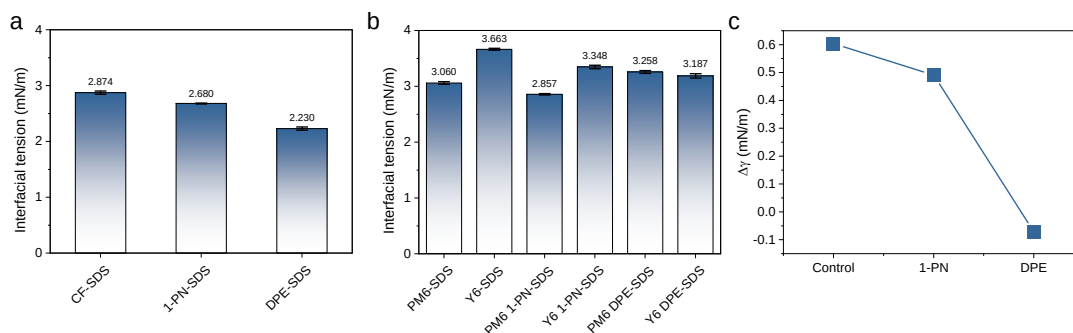


Figure R4. a, Interfacial tension between CF (with and without additives) and SDS aqueous solution. **b**, Interfacial tension between PM6 or Y6 CF solution (with and without additives) and SDS aqueous solution. **c**, Additive-dependent differences in liquid-liquid interfacial tension between PM6 and Y6 chloroform solutions and SDS aqueous solution.

Our modification to the manuscript:

On page 5, please read “Pendant-drop measurements in the presence of SDS suggest that the CF-SDS interfacial tension (2.87 mN m^{-1}) decreases to 2.68 and 2.23 mN m^{-1} upon the addition of 1-PN and DPE, respectively (Supplementary Figs. 5-9). The oxygen-containing DPE may preferentially reside near the aqueous-organic boundary through weak polar interactions, which could stabilize the interfacial adsorption layer and reduce γ . By contrast, 1-PN only show a slight change on γ , suggesting its limited influence on the interfacial composition. More importantly, the additives exerted distinct effects on the PM6- and Y6-containing organic phases. The interfacial-tension contrast, defined as $\Delta\gamma = \gamma_{\text{Y6-SDS}} - \gamma_{\text{PM6-SDS}}$, decreased from 0.60 mN m^{-1} (control) to 0.49 mN m^{-1} (1-PN) and -0.07 mN m^{-1} (DPE), respectively (Supplementary Figs. 6-9). The positive $\Delta\gamma$ values for the control and 1-PN conditions indicate that PM6 retains a lower interfacial tension with the SDS aqueous phase than Y6, whereas the small magnitude of the negative value suggests a limited interfacial selectivity for donor-acceptor partition at the interface for the DPE condition”.

On page 21-22, please read “Liquid-liquid interfacial tensions between the chloroform-based organic phase and the aqueous phase were measured using the pendant-drop method (Kruss DSA100S) at room temperature A droplet of the chloroform-based organic phase was generated from a superhydrophobic needle immersed in an aqueous SDS solution (10 mg mL^{-1}). PM6 or Y6 was dissolved separately in chloroform at a concentration of 0.5 mg mL^{-1} . Where applicable, DPE or 1-PN was added at 1.5 vol%. The drop profiles were fitted using the Young-Laplace equation. Corresponding results are shown in Supplementary Figs. 5-9”.

Reviewer #2 (Remarks to the Author):

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Reply: We appreciate very much the recognition from reviewer 2 for our work's advance and impact. We have carefully considered the suggested improvements and conducted the necessary experiments and analyses to address these comments, and updated the manuscript accordingly.

1. In the Introduction section, the scalability of photovoltaic material synthesis and device fabrication should be commented and cited (such as Joule 2025, 9, 102173), which is very important to the industrialization of OPVs.

Reply: We thank the reviewer for this suggestion. We have added a discussion on the critical factors in OPV industrialization, emphasizing that, in addition to device efficiency, the scalable synthesis of photovoltaic materials and the environmental impact of the manufacturing process also warrant consideration. Furthermore, we have cited relevant articles and studies.

Our modification to the manuscript:

On page 2, please read “Practical translation further requires high-performance photovoltaic materials to be accessible through scalable and reproducible synthesis, together with device fabrication routes compatible with large-area coating and module manufacturing”.

2. The authors consistently use the term “water-processed organic solar cells” in the title and introduction, implying a predominantly aqueous fabrication route. In practice, however, the NP preparation involves dissolving the active materials in chloroform, injecting the solution into an aqueous surfactant phase (with an optimal chloroform:water ratio of 1:6), and subsequently evaporating the solvent. Thus, the process still relies on chloroform, and the only difference is that the chloroform is removed during NP synthesis rather than during final film casting. This critical detail is omitted from the narrative of authors in abstract and introduction. The term “water-processed” should therefore be revised appropriately to more accurately reflect the actual fabrication process. Additionally, the GSK solvent sustainability assessment should be amended to explicitly account for chloroform consumption, to explicitly quantify the consumption and associated environmental hazards of chloroform and provide an honest evaluation of the true environmental impact of the proposed technology.

Reply: We thank the reviewer for this important and thoughtful comment. We agree that the term “water-processed” may obscure the use of chloroform during nanoparticle synthesis. In this work, PM6 and Y6 are first dissolved in chloroform, and the organic solution is emulsified into an aqueous SDS phase at a chloroform-to-water volume ratio of 1:6. Chloroform is subsequently removed during nanoparticle formation, after which the concentrated aqueous nanoparticle ink is used for active-layer deposition. Thus, although the final active layer is deposited from aqueous ink, the nanoparticle-synthesis step still involves chloroform. To avoid overstatement, we have revised the title, abstract and introduction to describe the devices as water-based OSCs processed from aqueous nanoparticle inks, and we have also explicitly stated that chloroform is used during nanoparticle synthesis.

In addition, to account quantitatively for chloroform consumption, we revised the solvent-sustainability assessment using the actual chloroform-to-water volume ratio of 1:6. For each assessment category, we calculated a volume-weighted GSK-derived index based on the relative processing volumes of the two liquids. This index is not a standard GSK score, but rather a simplified process-level metric describing the impact per unit volume of the mixed solvent. Because water accounts for 6/7 of the total liquid volume, the calculated index is closer to that of water. It should be noted that, during the synthesis of nanoparticles, chloroform still remains the primary source of solvent-

related health and environmental concerns. Accordingly, the development of closed-loop chloroform capture and reuse, or its replacement with a less hazardous solvent, represents an important direction for improving the sustainability of future water-based OSC fabrication.

Solvent Name	Innovation	Recycling	Bioremediation	VOC Emissions	Aquatic Impact	Air Impact	Health Hazard	Exposure potential	Flammability & Explosion	Reactivity & stability	Life Cycle Analysis	Overall ranking
Water	4	2	4	6	10	8	10	9	8	10	10	Recommended
p-Xylene	10	9	6	7	5	2	7	7	5	10	7	Hazardous
Toluene	10	7	6	7	7	2	7	6	5	10	7	Hazardous
2-Methyltetrahydrofuran	6	5	3	4	7	4	4	3	4	6	4	Problematic
Tetrahydrofuran ^a	5	5	2	3	9	3	7	5	4	6	4	Hazardous
Chlorobenzene ^{*a}	4	9	7	7	7	2	4	4	8	10		Hazardous
Dichlorobenzene	4	8	6	7	6	1	7	6	8	10		Hazardous
Chloroform ^{*a}	3	9	5	3	7	5	4	1	5	10	6	Hazardous
CF/water process index ^b	3.9	3.0	4.1	5.6	9.6	7.6	9.1	8	7.6	10.0	9.4	Not classified

^{*} Carcinogenic; ^a Reproductive harm. ^b Volume-weighted index of the water-chloroform mixture

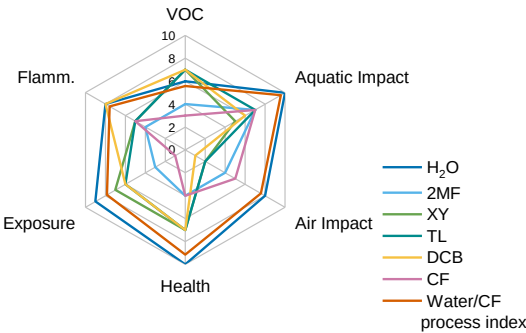


Figure R5. Solvents GSK scores and corresponding radar plots on VOC emissions, aquatic impact, air impact, health hazard, exposure potential, and flammability & explosion. 2MF denotes 2-Methyltetrahydrofuran. Flamm. denotes Flammability & Explosion. The GSK-derived process index was calculated for each category by weighting the chloroform and water scores according to their processing volume ratio of 1:6, which is used to describe the relative impact of the solvents and do not represent a standard GSK score.

Our modification to the manuscript:

On page 3, please read “Among water-based approaches, heterojunction nanoparticle organic solar cells (HNP-OSCs) are distinctive in that donor and acceptor semiconductors are emulsified into an aqueous surfactant phase, converted into surfactant-stabilized nanoparticles (NPs), and subsequently converted into active layers via a particle-to-film pathway (Fig. 1a). In this context, water-based processing refers to active-layer deposition from aqueous NP inks; chloroform is commonly used as a volatile solvent during NP synthesis and is subsequently removed during solvent evaporation.”

On page 4 in Supporting Information, please read “It should be noted that, although the final active layer is deposited from aqueous ink, the nanoparticle-synthesis step still

involves chloroform. Therefore, to account quantitatively for chloroform consumption, we revised the solvent-sustainability assessment using the actual chloroform-to-water volume ratio of 1:6. For each assessment category, we calculated a volume-weighted GSK-derived index based on the relative processing volumes of the two liquids. The calculated values describe the relative impact of the solvents and do not represent a standard GSK score. Water and chloroform are therefore also reported separately to retain visibility of the intrinsic hazards associated with chloroform.”

3. The additive-containing emulsions seem to maintain good processability at high solid contents, as suggested by the successful film coating and device fabrication. However, the colloidal stability is not directly shown. Zeta-potential measurements and storage-stability data should be added.

Reply: Thanks for the reviewer’s comment. To evaluate the colloidal stability of the NP dispersions, we measured their zeta-potentials and their hydrodynamic diameters during storage at room temperature for 10 days (Figure R6). The control, 1-PN and DPE NP dispersions exhibited negative zeta-potentials of -45.1, -61.6 and -39.5 mV, respectively, consistent with negatively charged SDS-stabilized particle surfaces. After storage at room temperature for 10 days, the DLS size of all three dispersions changed by only approximately 4-7 nm, with no appreciable broadening of the size distributions. These results indicate that the addition of 1-PN or DPE does not measurably compromise the colloidal stability of the NP dispersions over the tested storage period and supports their suitability for subsequent film deposition.

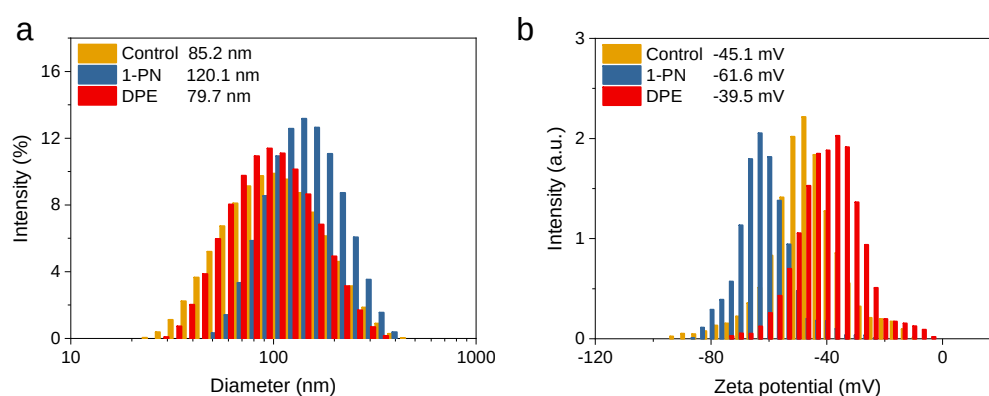


Figure R6. a, DLS size distribution of PM6:Y6 NP dispersions after storage at room temperature for 10 days. **b,** Zeta potentials of the PM6:Y6 NP dispersions.

Our modification to the manuscript:

On page 6, please read “Moreover, the hydrodynamic diameters of all three NP dispersions show only minor changes of about 4-7 nm after storage at room temperature for 10 days, indicating that neither 1-PN nor DPE compromised their colloidal stability

over the tested period (Supplementary Fig. 10a). This stability is further supported by the negative zeta-potentials of all three dispersions, which were more negative than -30 mV (Supplementary Fig. 10b)".

4. The neat PM6 and neat Y6 NP dispersions show different emission evolution during evaporation (Fig. S17), and PM6 behavior is different from that of the PM6:Y6 samples. This difference deserves more discussion. The authors should also describe the in-situ PL setup more clearly, so that the experiment can be better understood and reproduced by readers.

Reply: We thank the reviewer for raising this concern. We have expanded the discussion of the distinct PL evolution observed for the neat PM6, neat Y6 and PM6:Y6 nanoparticle dispersions and have provided a more detailed description of the in situ PL setup.

The neat-component measurements reveal different molecular responses to solvent evaporation and nanoparticle densification. Neat PM6 initially exhibits a gradual blue shift followed by a modest red shift, with only small changes in the emission bandwidth (Figure R7a-b). This continuous evolution suggests progressive changes in polymer-chain conformation and interchain coupling as the nanoparticles densify. In contrast, neat Y6 displays an induction period followed by a redistribution of spectral from the high-energy emission at approximately 830 nm to a lower-energy band near 923 nm (Figure R7d-e). The decrease in the high-energy contribution and narrowing of the overall spectral envelope are consistent with the formation of more strongly coupled Y6 aggregates (Nat. Commun. 2024, 15, 2393). Although PM6 and Y6 exhibit different spectral pathways, their most pronounced changes occur within a similar time window of approximately 60-70 min (Figure R7c,f). We therefore interpret this temporal coincidence as evidence that solvent depletion imposes a common processing window, while the PM6 and Y6 respond through different molecular packing pathways.

In the PM6:Y6 dispersion, the PM6 emission is quenched by more than 85% relative to that of neat PM6 (Supplementary Fig. 12), consistent with efficient excited-state quenching following donor-acceptor contact through energy-transfer and charge-transfer pathways. Consequently, the emission spectra of PM6:Y6 dispersion is dominated by Y6. Its temporal evolution therefore reflects not only the aggregation of Y6 but also the donor-acceptor contact, phase segregation and associated exciton-quenching processes. The neat-component measurements can serve as references for identifying the aggregation behaviors of PM6 and Y6, whereas the blend measurements report their coupled structural and photophysical evolution.

For the in-situ PL setup, we combined the stirring equipment with the fluorescence

setup as shown in Figure 3a to perform in situ measurement. The sample was excited at 532 nm and the emission was collected using an optical fiber and directed to Ocean Optics spectrometer, which is controlled via the OceanView software. Spectra were acquired continuously at fixed time intervals of 1 minute throughout the 180-min evaporation period. The detailed description of the in-situ PL setup was added in the methods section in the revised manuscript.

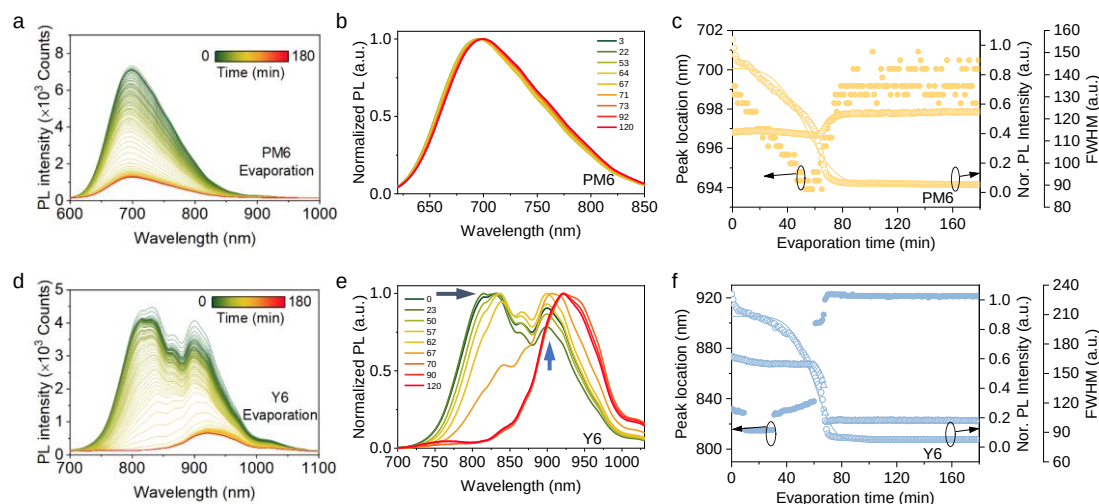


Figure R7. a-c, Evolution of in situ PL spectra during CF evaporation (a), normalized PL spectra measured at different minute time points (b), and time evolution of emission-peak position, intensity, and full width at half maximum (FWHM) during NP formation (c) for neat PM6 NP dispersion. **d-f,** Evolution of in situ PL spectra during CF evaporation (d), normalized PL spectra measured at different minute time points (e), and time evolution of emission- peak position, intensity, and FWHM during NP formation (f) for neat Y6 NP dispersion.

Our modification to the manuscript:

On page 9, please read “Neat PM6 dispersions show a gradual blue shift followed by a modest red shift, with comparatively small changes in the emission bandwidth. This suggests gradual adjustment of polymer-chain conformation and interchain coupling during nanoparticle densification (Supplementary Fig. 21a-c). Neat Y6 dispersions show a pronounced red shift of emission from approximately 830 nm to a lower-energy band near 923 nm, consistent with the formation of more strongly coupled Y6 aggregates (Supplementary Fig. 21d-f)”.

On page 22, please read “In situ PL spectra were recorded during chloroform evaporation from the aqueous emulsion using the configuration illustrated in Fig. 3a. The freshly prepared emulsion was stirred continuously at 1500 r.p.m. under ambient conditions. The time at which evaporation begins is defined as $t = 0$. The sample was excited using a 532-nm laser. The PL emission was collected using an optical fiber and

directed to Ocean Optics spectrometer controlled using OceanView software. Spectra were acquired continuously at fixed time intervals of 1 minute throughout the 180-min evaporation period.”

5. In stage 2 (Fig. 3e), the DPE-treated emulsion shows a clear two-step decrease in PL intensity compared with the control sample. A weaker two-step feature is also seen for the 1-PN-treated sample. Is this related to a stage mainly governed by additive evaporation? The authors should give a more detailed analysis of this point.

Reply: We thank the reviewer for this insightful observation. To investigate whether the two-step PL decrease is governed by additive evaporation, we performed thermogravimetry analysis (TGA) to monitor the evaporation curves of the control, 1-PN- and DPE-containing emulsions at 40 °C. All three emulsions exhibited continuous mass-loss profiles, without a resolvable secondary mass-loss in the additive-containing samples (Figure R8). This indicates that the second PL decrease is unlikely to be governed primarily by additive evaporation, although minor additive loss below the resolution of the gravimetric measurement cannot be excluded.

We further analyzed the normalized PL spectra to identify the possible causes of the two-stage intensity decline through a comparison of aggregation states and the kinetics of intensity quenching (Figure R9). The DPE sample shows a small early red shift of the emission maximum within the first 10 min, indicating an early adjustment of the local Y6 packing. During the first approximately 40 min, all three emulsions showed comparable decreases in absolute PL intensity. However, the normalized spectra of the 1-PN and DPE remained largely unchanged, suggesting that this initial decrease mainly reflects nanoparticle densification. After the intensity inflection, the contribution of the low-energy Y6 emission near 900 nm increased and became pronounced at approximately 55 min in the additive-treated emulsions, consistent with the later development of more strongly coupled Y6 aggregates. In the control sample, however, this spectral change occurred earlier and overlapped with the initial intensity decrease from about 40 min, resulting in a more continuous PL decay. We therefore attribute the two-step behavior primarily to the temporal separation between initial densification-driven quenching and the subsequent evolution of the low-energy Y6 aggregate state. This separation is most pronounced for DPE and weaker for 1-PN, accounting for their different two-step features.

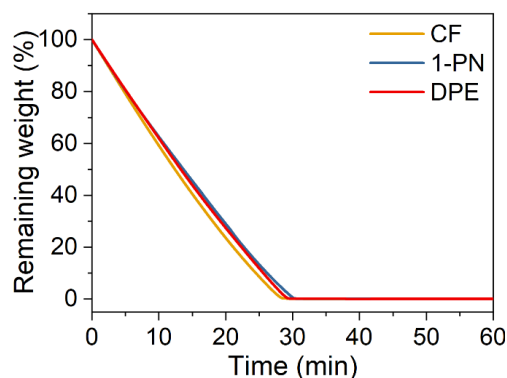


Figure R8. TGA evaporation curves denoting the remaining weight over time for a 15 μl droplet of each emulsion.

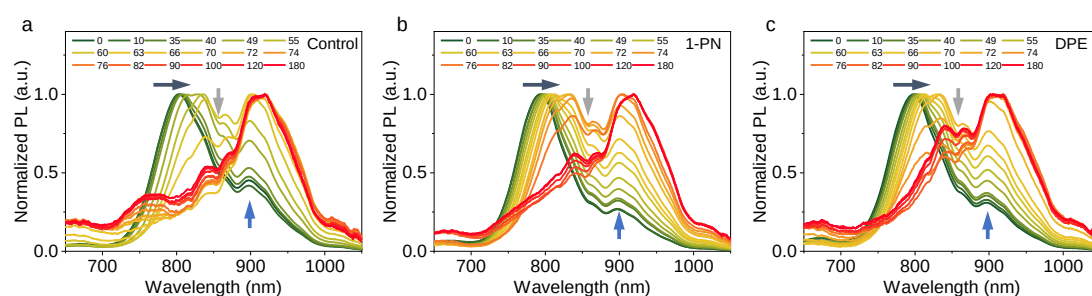


Figure R9. The normalized PL spectra of PM6:Y6 dispersions without additives (b) and with 1-PN (c) or DPE (d) measured at different minute time points during the evaporation process.

Our modification to the manuscript:

On page 9-10, please read “During solidification stage, DPE exhibits a two-step PL decrease, whereas a weaker feature is observed with 1-PN. Isothermal gravimetric measurements show continuous single-stage mass loss for all three emulsions, without a resolvable additive-specific evaporation stage (Supplementary Fig. 23a). Combined with the normalized PL spectra (Supplementary Fig. 23b-c), these results attribute the two-step response to the temporal separation between initial densification-driven quenching and the subsequent development of the low-energy Y6 aggregate state”.

6. The PM6:Y6 films prepared from NP inks show different GIWAXS features under different additive conditions (Fig. 3g). In particular, the 1-PN film shows two pronounced peaks at $q = 0.32$ and $0.48 \text{ \AA}^{-1}$. To make the assignment more reliable, it would be useful to include GIWAXS data for films prepared from neat PM6 NP ink and neat Y6 NP ink.

Reply: We thank the reviewer for this helpful suggestion. To clarify the origin of the pronounced low- q scattering features observed in the film prepared from 1-PN-treated

PM6:Y6 emulsion, we performed GIWAXS measurements of films prepared from neat PM6 and neat Y6 NP inks under the corresponding control, 1-PN and DPE conditions. As shown in Figure R10, the neat PM6 NP-derived films exhibit out-of-plane (OOP) scattering features near $q = 0.32$ and $0.48 \text{ \AA}^{-1}$. Related features are also observed in the neat Y6 NP-derived films, and they are broader and partially overlap with an additional low- q contribution near $q = 0.26 \text{ \AA}^{-1}$. The 1-PN-treated neat PM6 and neat Y6 films both show more pronounced scattering in this region than their corresponding control films. The neat-component measurements therefore show that neither the $q = 0.32 \text{ \AA}^{-1}$ nor the $q = 0.48 \text{ \AA}^{-1}$ feature is unique to one component. Therefore, the enhanced low- q scattering from 1-PN-treated PM6:Y6 sample most likely contains overlapping contributions from the ordered packing of PM6 and Y6. This interpretation is consistent with the more extensive local ordering observed in both the outer region and the interior of the 1-PN nanoparticles by cryo-TEM. We have revised the manuscript accordingly and have added the neat-component GIWAXS data to Supplementary Fig. 27.

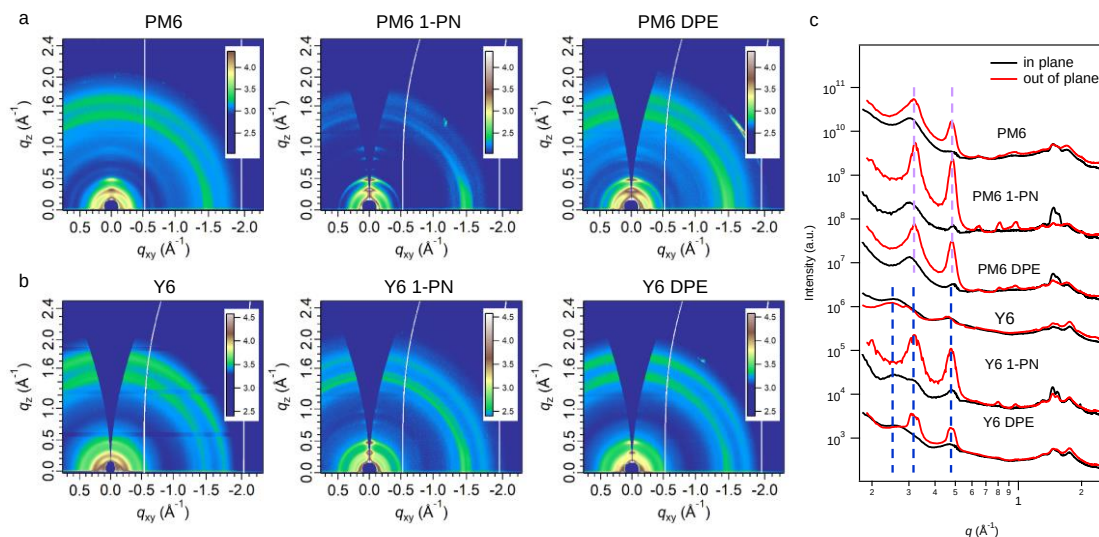


Figure R10. Two-dimensional GIWAXS patterns (a, b) and corresponding linecuts (c) of neat PM6 and neat Y6 NP films deposited from concentrated NP inks without and with additives.

Our modification to the manuscript:

On page 10, please read “Measurements of films prepared from neat PM6 and neat Y6 NP inks show scattering contributions from both components at similar positions, indicating that these peaks reflect overlapping contributions from PM6 and Y6 ordered packing (Supplementary Fig. 27). The enhanced low- q features are consistent with the extended ordering observed within 1-PN NPs by cryo-TEM.”

7. For the SANS measurements, the sample-preparation conditions should be specified more clearly. The fitted model parameters should also be provided in the Supporting

Information.

Reply: We thank the reviewer’s comments. For the SANS measurements, Y6 was replaced with deuterated Y6 (*d*-Y6) to enhance the neutron-scattering contrast between PM6 and the acceptor (Nat. Commun. 2024, 15, 2784). Contrast variation was further achieved by preparing the continuous aqueous phase with varied H₂O/D₂O ratio. Except for the isotopic substitution of Y6 and the H₂O/D₂O composition, all other parameters were identical to those used for the device-grade nanoparticle inks. The sample-preparation condition has now been added to the Methods section. We have also added the fitted model parameters for all SANS profiles to Supplementary Table 4-5, reproduced below as Table R1-2.

Table R1. The parameters and results of fitting the SANS profiles of PM6:*d*-Y6 NP dispersions in 25% D₂O water with the combination of fractal-like network model and core-shell model.

25% D ₂ O	afrac	rfrac (Å)	zfrac	b (cm ⁻¹)	ccfrac (Å)	ddfrac	<i>R_g</i> (nm)	thickness (nm)
Control	1.33×10 ⁻⁴	24.99	5.21	0.10	275.51	2.39	33.59	6.35
1-PN	2.99×10 ⁻⁴	33.19	4.57	0.10	262.21	2.82	35.15	8.33
DPE	3.31×10 ⁻⁴	10.01	23.75	0.11	113.19	2.95	27.57	--

Table R2. The parameters and results of fitting the SANS profiles of PM6:*d*-Y6 NP dispersions in 100% D₂O water with the fractal-like network model.

100% D ₂ O	afrac	rfrac (Å)	zfrac	b (cm ⁻¹)	ccfrac (Å)	ddfrac	<i>R_g</i> (nm)
Control	7.01×10 ⁻⁴	50.00	2.14	0.50	115.13	2.97	27.95
1-PN	3.34×10 ⁻⁴	93.33	0.81	0.81	168.20	2.78	38.55
DPE	1.24×10 ⁻⁴	130.05	1.16	1.30	132.30	2.35	26.23

Our modification to the manuscript:

On page 22, please read “PM6:*d*-Y6 NP dispersions for small-angle neutron scattering (SANS) measurements were prepared using the same protocol as the device-grade NP inks, with Y6 replaced by *d*-Y6 to enhance the neutron-scattering contrast. Contrast variation was achieved using aqueous phases containing varied H₂O/D₂O ratio, while all other preparation conditions were kept unchanged.”

8. The manuscript states that the as-cast DPE-treated devices outperform the control and 1-PN devices. However, I could not find the corresponding photovoltaic parameters in the Supporting Information. The authors should provide the full photovoltaic parameters for the as-cast devices.

Reply: We thank the reviewer for identifying this omission, and we apologize that the corresponding photovoltaic parameters were not included in the original Supporting Information. We have now added the photovoltaic parameters of the as-cast devices to Supplementary Table 18, which is reproduced below as Table R3. The as-cast DPE devices delivered an improved PCE of 6.20%, compared with 4.08% for the control and 3.56% for the 1-PN devices. The improved performance of the DPE-treated devices arose primarily from the increased J_{sc} and V_{oc} .

Table R3. Photovoltaic performance parameters of as-cast PM6:Y6 WB-OSCs processed with and without additives under AM1.5G 100 mW cm⁻² illumination.

As-cast	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)
Control	0.717	13.24	43.06	4.08 (3.69±0.31)
1-PN	0.545	16.01	40.75	3.56 (3.28±0.21)
DPE	0.744	18.84	44.23	6.20 (5.66±0.31)

9. Some terms are used interchangeably for the same concept. For example, the manuscript uses “BHJ organic nanoparticles”, “blend NPs” and “NP blends”, as well as “water-processed OSCs”, “nanoparticle OSCs” and “WNP-OSCs”. To avoid unnecessary confusion, the authors should choose one term and use it consistently throughout the manuscript. “heterojunction nanoparticles” and “water-processed OSCs” or “WP-OSCs” would be suitable choices.

Reply: We thank the reviewer for this helpful suggestion. We have standardized the terminology throughout the revised manuscript. The donor-acceptor nanoparticles containing both PM6 and Y6 are now consistently referred to as “heterojunction nanoparticles” (HNPs). Single-component nanoparticles are described separately as “neat PM6 NPs” or “neat Y6 NPs”. Accordingly, the previous terms “BHJ organic nanoparticles”, “blend NPs” and “NP blends” have been changed. In addition, devices fabricated by depositing the active layer from aqueous HNP inks are now consistently termed “water-based nanoparticle organic solar cells” (water based NP-OSCs).

10. There are still a few formatting and wording issues in the manuscript. For example, the reference format on page 25 should be corrected; the description of Fig. 3e should be added on page 31; the intensity scales in the GIWAXS patterns on page 32 should be made more consistent where possible; and the fs-TA signal near 900 nm on page 34

should be described consistently with the figure.

Reply: We thank the reviewer for carefully identifying these formatting and wording issues. We have corrected each of the points raised and have further checked the manuscript and Supplementary Information for consistency.

Our modification to the manuscript:

- 1) The reference formatting on page 25 has been corrected.
- 2) A description of the PL-intensity evolution shown in Fig. 3e has been added.
- 3) The intensity scales of GIWAXS patterns have been made consistent.
- 4) The description of the fs-TA feature near 900 nm has been revised.
- 5) Figure citations, captions and related terminology have been rechecked throughout the manuscript and Supplementary Information.

Reviewer #3 (Remarks to the Author):

This manuscript reports a facile liquid-liquid interfacial tension regulation strategy via DPE additive to tailor the intrinsic nanostructure of PM6:Y6 aqueous NPs for WNP-OSCs. Comprehensive characterizations including cryo-TEM and SANS verify that DPE effectively inhibits the undesired donor-rich core-shell structure and generates homogeneous polycrystalline NP surfaces, which facilitates interparticle fusion and the construction of continuous charge transport networks after thermal annealing. Correlated GIWAXS, AFM, RSoXS and femtosecond transient absorption measurements collectively demonstrate enhanced molecular stacking order, balanced carrier mobilities, and suppressed non-radiative recombination as well as accelerated exciton dissociation in DPE-modified blend films. Benefiting from the optimized nanoparticle morphology, the optimized device achieves a certified PCE of 12.59%, outperforming all previously reported water-based OSC benchmarks. Meanwhile, unencapsulated devices exhibit greatly improved thermal stability with a T80 lifetime exceeding 2000 h at 85 °C. This work establishes a clear mechanistic correlation between oil-water interfacial tension, nanoparticle solidification kinetics and final thin-film morphology, and provides instructive molecular engineering guidelines for environmentally friendly printable photovoltaic manufacturing. Although the overall structure-property relationship is well supported by systematic characterizations and certified photovoltaic data, several critical experimental and mechanistic details remain insufficiently discussed, which requires appropriate revisions before acceptance. The key questions to be addressed are listed as follows:

Reply: We are grateful to the reviewer for the recognition of our work and for the constructive comments. In response, we have addressed each comment point-by-point and revised the manuscript carefully to ensure that our discussions with sufficient experimental and mechanistic details. We hope these changes address the reviewer's concerns and will meticulously revise the manuscript to address each of the points you raised, ensuring the work meets higher academic standards.

1. What is the molecular weight of PM6 adopted in this work? How does its molecular weight affect solubility in chloroform?

Reply: We thank the reviewer for this question. The gel-permeation chromatography (GPC) measurements showed that the PM6 used in this work has a molecular weight (M_n) of 43.3 kDa (Figure R11). We did not compare PM6 batches with different molecular weights in this work. In general, increasing the molecular weight of a conjugated polymer reduces the entropic contribution to polymer-solvent mixing and increases chain entanglement and pre-aggregation, which may slow dissolution and lower the solubility under a fixed dissolution protocol (*J. Mater. Chem. C* 2015, 3, 7394-

7404; J. Am. Chem. Soc. 2021, 143, 1822). Under the conditions used in this study, the PM6 batch was fully and reproducibly dissolved in chloroform at the concentration required for nanoparticle preparation.

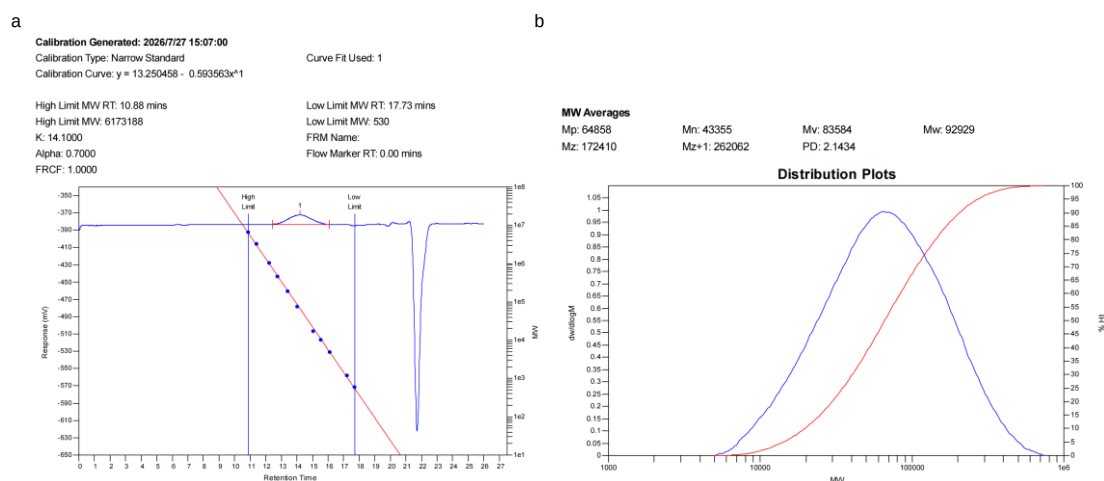


Figure R11. The GPC trace of PM6.

Our modification to the manuscript:

On page 17, please read “The molecular weight (M_n) of PM6 is 43.3 kDa as revealed by the GPC trace (Supplementary Fig. 49)”.

2. What concentration/dosage of SDS was used during nanoparticle synthesis? Residual SDS inside active films acts as insulating impurity and deteriorates charge transport. The authors should characterize residual SDS content and systematically discuss its negative impacts on device performance.

Reply: We thank the reviewer for raising this important point. The initial SDS concentration in the aqueous phase was 10 mg mL⁻¹. During nanoparticle-synthesis, 6 mL of the SDS solution was used, corresponding to a total SDS dosage of 60 mg.

After chloroform evaporation and nanoparticle formation, the dispersions were subjected to five centrifugation-wash cycles to remove free and loosely associated SDS. To evaluate the residual surfactant, we collected and dried solids from the unwashed dispersion and from the dispersion after five washing cycles and compared their FTIR spectra. The Y6 C≡N stretching band at approximately 2216 cm⁻¹ was used as an internal reference, and the integrated SDS-associated bands near 592 and 1220 cm⁻¹ were analyzed independently (Figure R12). The residual fraction was calculated from the change in the SDS-to-Y6 integrated-area ratio before and after washing. Both SDS-associated bands decreased substantially after washing. The two independent spectral markers yielded a residual SDS fraction of approximately 3-10% relative to the

unwashed sample. When referenced to the initial aqueous-phase volume, this corresponds to an equivalent SDS concentration of approximately 0.30-0.95 mg mL⁻¹. Because the analysis is based on FTIR band-area ratios in a multicomponent solid matrix, this value can be considered as a semi-quantitative estimate of residual SDS content.

SDS is required during miniemulsion formation to stabilize the aqueous nanoparticle dispersion, but residual surfactant can become detrimental after film deposition. Previous studies of water-processed nanoparticle photovoltaics have shown that residual surfactants can disrupt molecular ordering and particle-to-particle electronic connectivity, thereby limiting charge-carrier mobility and increasing recombination (Nat. Commun. 2018, 9, 5335). Ionic surfactants can also generate mobile-ion-induced capacitance and interfacial dipole layers at the device contacts, which may restrict charge extraction (ACS Appl. Mater. Interfaces 2019, 11, 10074). In this study, all control, 1-PN and DPE dispersions were subjected to the same centrifugation-washing protocol to minimize processing-related variation. We therefore identify residual SDS as a likely common limitation of the devices and we agree that more effective removal of SDS remains an important route for further improving device performance.

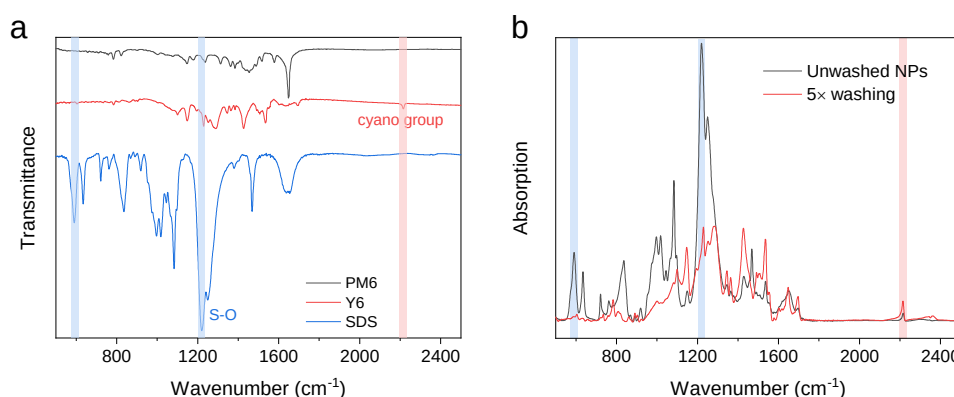


Figure R12. Fourier-transform infrared spectra of neat PM6, neat Y6, and neat SDS (a) and PM6:Y6·NPs before and after washing process (b).

Our modification to the manuscript:

On page 12-13, please read “FTIR analysis using the Y6 C≡N stretching band as an internal reference estimated that approximately 3-10% of the initial SDS remained in the concentrated NP inks (Supplementary Fig. 38 and Supplementary Note 3). Although present at a substantially reduced level, the residual SDS may disrupt particle-to-particle electronic connectivity and introduce mobile-ion effects in film state, thereby potentially limiting charge transport.”

On page 6-7 in Supporting Information, please read “For residual-SDS analysis, solids were collected from the unpurified dispersion and from the dispersion after five

centrifugation-washing cycles and dried under identical conditions. FTIR spectra were recorded in KBr transmission mode. The C≡N stretching band of Y6 at approximately 2216 cm⁻¹ was used as an internal reference. Two SDS-associated bands near 592 and 1220 cm⁻¹ were analyzed independently. The former was treated as an empirical SDS fingerprint with relatively limited interference from PM6 and Y6, whereas the latter was attributed predominantly to sulfate-headgroup-related S-O vibrations.

The transmittance spectra were first converted to absorbance according to $A(\lambda) = -\log_{10}(T)$, where $A(\lambda)$ is the absorbance at a certain wavelength λ and T is the corresponding transmittance. Then, local linear baselines were constructed over the Y6 C≡N region and the two SDS-associated regions for a calculation of integrated areas of the bands near 2216, 592 and 1220 cm⁻¹ (denoted as S_{2216} , S_{592} , and S_{1220} , respectively). For each SDS-associated band, a normalized response was calculated using

$$R_{\text{SDS}} = \frac{S_{\text{SDS}}}{S_{2216}}$$

Assuming that the integrated absorbance ratio is proportional to the SDS-to-Y6 mass ratio and the mass loss of Y6 before and after centrifugation is negligible, an equivalent residual SDS concentration referenced to the initial aqueous-phase volume was estimated as

$$C_{\text{SDS},5} = 10 \frac{R_{\text{SDS},5}}{R_{\text{SDS},0}} \text{ mg mL}^{-1}$$

For the unwashed and 5-times-washing samples, the S_{2216} values were 0.24 and 0.78, respectively. The corresponding S_{592} values were 4.33 and 0.40, giving normalized responses of 18.04 and 0.513. The residual fraction estimated from the 592 cm⁻¹ band was therefore 2.84%, corresponding to an equivalent SDS concentration of about 0.28 mg mL⁻¹. For the band near 1220 cm⁻¹, the integrated areas were 19.88 and 6.06 for the unwashed and 5-times-washing samples, respectively. This indicates a residual fraction of 9.38% and an equivalent SDS concentration of approximately 0.94 mg mL⁻¹.

The two independent SDS-associated bands therefore indicate that approximately 3-10% of the initial SDS remained associated with the washed nanoparticle solids after five centrifugation cycles. Because this analysis relies on FTIR band-area ratios in a multicomponent solid matrix and may be affected by peak overlap, these values give a semi-quantitative estimation of resident SDS. Nevertheless, both spectral markers consistently show that the washing procedure removed most of the SDS, while a small residual fraction remained.”

3. Which preparation parameters (e.g., organic solution concentration, SDS loading, ultrasonic power, processing temperature) exert dominant effects on nanoparticle size

and microphase separation? Corresponding control experiments are suggested to clarify the influence law.

Reply: We thank the reviewer for this important suggestion. To clarify how the preparation parameters influence nanoparticle size and microphase separation, we performed a series of control experiments by independently varying the chloroform concentration, SDS concentration, ultrasonication power and evaporation temperature around the reference condition of 16 mg/mL PM6:Y6, 10 mg/mL SDS, 200 W and 40 °C. The resulting particle sizes were directly measured by DLS (Figure R13). Absorption-corrected PL measurements were performed to evaluate changes in the donor-acceptor interaction (Figure R14-15), and selected samples prepared at different evaporation temperatures were examined by cryo-TEM (Figure R16).

The particle size was most affected by the organic-phase concentration and SDS concentration within the ranges examined. Increasing the PM6:Y6 concentration from 10 to 18 mg/mL increased the DLS size from approximately 65 to 105 nm. This trend is consistent with an increase in the semiconductor mass contained in each emulsion droplet (ACS Appl. Mater. Interfaces 2018, 10, 44116; ACS Appl. Mater. Interfaces 2018, 10, 23225). By contrast, increasing the SDS concentration from 5 to 15 mg/mL reduced the particle size from approximately 103 to 59 nm, consistent with more effective stabilization of the newly generated oil-water interface and suppression of droplet growth after breakup (ACS Appl. Mater. Interfaces 2017, 9, 13380). The effect of ultrasonication was non-monotonic. Increasing the ultrasonic power from 100 to 200 W reduced the particle size from approximately 107 to 78 nm, whereas a further increase to 300 W produced particles of approximately 110 nm. These results identify an intermediate processing window near 200 W under the present ultrasonic condition. Evaporation temperature had a comparatively small influence on particle size between 25 and 40 °C, for which diameters of approximately 80 nm were obtained, but the particles increased to approximately 89 and 107 nm at 50 and 65 °C, respectively. Cryo-TEM provided direct evidence that temperature also altered the internal radial structure. Based on an equivalent spherical core-shell like geometry, the estimated shell-like outer-region thickness increased from approximately 7 nm (25 °C) and 7.5 nm (40 °C) to 12.5 nm (50 °C) and 14.5 nm (65 °C), respectively (Figure R16). Thus, accelerated solvent removal at higher temperature not only increased the final particle size but also promoted greater radial structural differentiation during solidification.

The absorption-corrected PL results exhibited corresponding but parameter-dependent changes. Increasing the organic-phase concentration or evaporation temperature generally increased the Y6-dominated PL intensity, whereas increasing the SDS concentration to 15 mg/mL reduced it. These trends are consistent with changes in the

efficiency of donor-acceptor exciton quenching. However, since PL intensity is also affected by particle size and non-radiative decay, we therefore used PL as a basis for verifying the Y6 exciton quenching environment and, based on this, infer changes in phase separation. The non-monotonic PL response to ultrasonication, in particular, the absence of a simple correlation between particle size and PL for this series indicates that ultrasonication affects both particle size and exciton-quenching environment.

Within the parameter ranges studied, the organic-phase concentration and SDS concentration produced the larger changes in particle size, while ultrasonication exhibited an optimum range. Evaporation temperature provided a clear control over the internal organization, as supported by cryo-TEM. For the comparison central to this work, the control, 1-PN and DPE nanoparticles were all prepared using identical PM6:Y6 concentration, SDS loading, ultrasonication and evaporation conditions. The observed differences in particle size, interfacial organization and internal ordering can be primarily attributed to additive-regulated interfacial and aggregation kinetics.

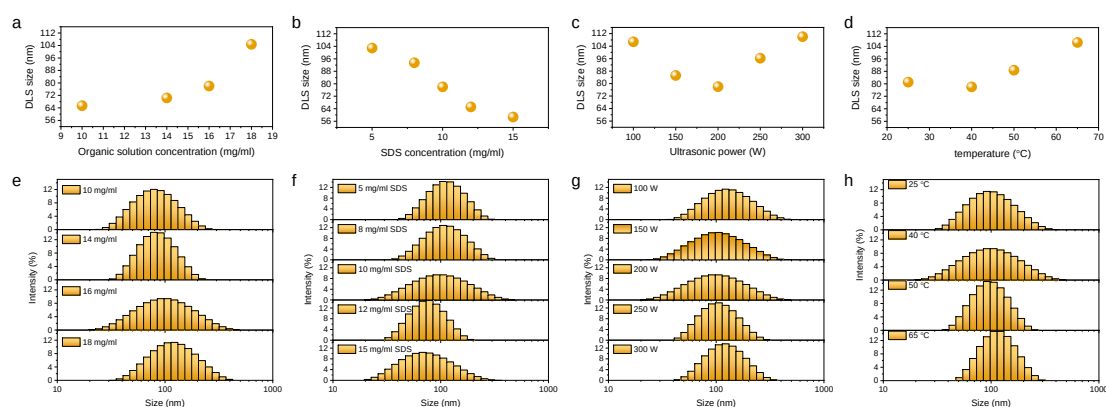


Figure R13. Comparison of DLS size of aqueous PM6:Y6 NPs prepared under different conditions of organic solution concentration (a), SDS concentration (b), ultrasonic power (c), and evaporation temperature (d) and the corresponding DLS size distribution (e-h).

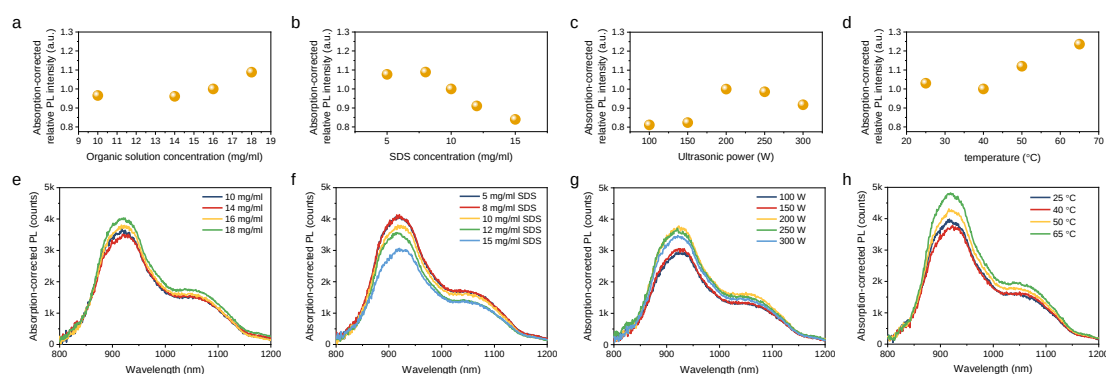


Figure R14. Absorption corrected relative PL intensity of PM6:Y6 NP dispersions prepared under different conditions of organic solution concentration (a), SDS concentration (b), ultrasonic power (c), and evaporation temperature (d) and the

corresponding absorption corrected PL spectra under 780 nm excitation (e-h).

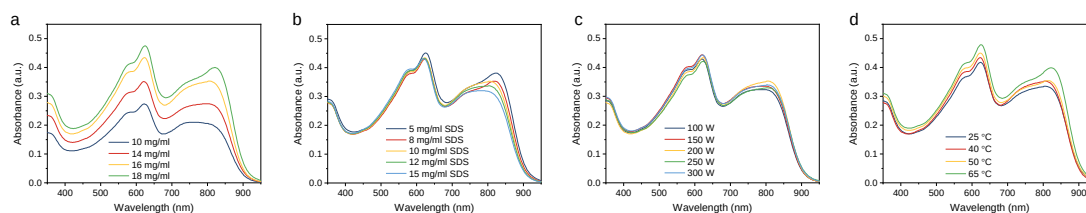


Figure R15. Absorption spectra of PM6:Y6 NP dispersions prepared under different conditions of organic solution concentration (a), SDS concentration (b), ultrasonic power (c), and evaporation temperature (d).

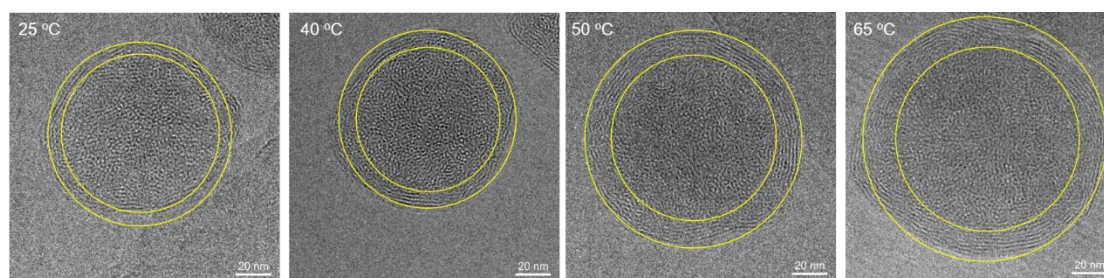


Figure R16. High resolution cryo-TEM images of PM6:Y6 NPs prepared at different evaporation temperatures (25 °C, 40 °C, 50 °C, and 65 °C). Geometric estimation for the shell thickness was conducted by the yellow circular curve.

4. Will DPE and 1-PN additives remain inside the active layer after spin-coating and thermal annealing?

Reply: We thank the reviewer for raising this important question. To examine whether DPE and 1-PN remain in the films after deposition and thermal annealing, we performed ^1H NMR measurements on redissolved nanoparticle films. To reduce the signal interference of broad aromatic resonances of PM6, neat Y6 nanoparticle films prepared with and without the additives were used as model samples to estimate the additive content. The Y6, Y6 1-PN, and Y6 DPE samples were examined in three states: the initial CF solutions used for nanoparticle preparation, the as-cast nanoparticle films redissolved in CDCl_3 and the redissolved films after thermal annealing at 200 °C for 10 min. In the initial solutions, the Y6 1-PN and Y6 DPE samples exhibited clearly additive-associated resonances within 7.3-8.0 ppm and 6.8-7.5 ppm, respectively, which were absent from the neat Y6 control spectrum (Figure R17). These signals were substantially reduced in the spectra of the as-cast films, indicating that most of the initially introduced additive was removed during nanoparticle formation, centrifugation and spin-coating.

To estimate the retained fractions of additives, Y6 and additive resonances were integrated and the additive-to-Y6 ratios were then compared between the initial

solutions and the redissolved films. For the Y6 1-PN sample, the corrected Y6:1-PN ratio changed from approximately 1:5.5 in the initial solution to 1:0.20 in the as-cast film, corresponding to retention of approximately 3.64% of the initially added 1-PN. For the Y6 DPE sample, the corresponding ratio changed from approximately 1:11 to 1:0.35, corresponding to retention of approximately 3.18% of the initially added DPE. These percentages describe the fractions retained relative to the initial additive loading. After thermal annealing, the characteristic 1-PN and DPE resonances were no longer detectable under the present NMR acquisition conditions. We therefore conclude that a small fraction of each additive remains in the as-cast model films, whereas the residual contents after thermal annealing are below the detection limit of the present ^1H NMR measurements. This result indicates that the additives were almost completely removed after annealing.

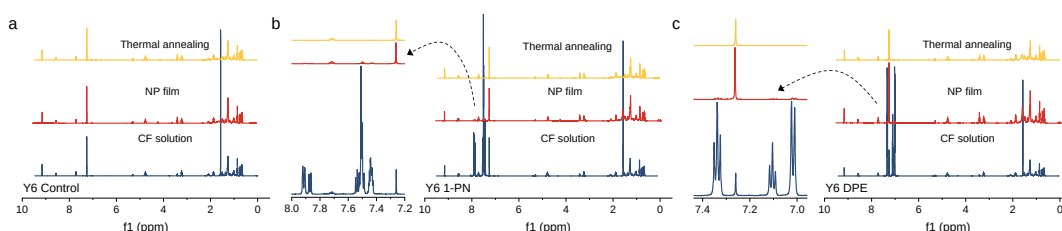


Figure R17. NMR ^1H spectra of Y6 samples without and with additives in CDCl_3 .

Our modification to the manuscript:

On page 12-13, please read “Semi-quantitative ^1H NMR analysis of redissolved Y6-only model NP films further showed that approximately 3.18% of the initially added DPE and 3.64% of the initially added 1-PN were retained after spin-coating, whereas the characteristic additive resonances were no longer detectable after thermal annealing (Supplementary Fig. 37).”

5. How do chloroform evaporation rate and temperature regulate nanoparticle size, internal component distribution and phase-separated nanostructure during miniemulsion preparation? The underlying kinetic mechanism needs further elaboration.

Reply: We thank the reviewer for the valuable suggestion. In response, we prepared PM6:Y6 nanoparticles at evaporation temperatures of 25, 40, 50 and 65 $^{\circ}\text{C}$ and characterized their size, internal structure and in situ PL evolution. Here, evaporation temperature was used as a practical means of modulating the chloroform evaporation, while direct thermal effects were difficult to independently decoupled. DLS measurements (Figure R13) showed that the hydrodynamic diameter remained

approximately 80 nm at 25 and 40 °C, indicating that moderate changes in evaporation temperature had little influence on the particle size. The diameter subsequently increased to approximately 89 nm at 50 °C and 107 nm at 65 °C. A similar increase in particle size with solvent-evaporation temperature has been reported for aqueous conjugated-polymer colloids (Colloids Surf. A 2020, 594, 124633). However, there is currently a difference of opinion regarding whether the increase in particle size stems from changes in the droplets or from partial coalescence of the particles (ACS Nano 2014, 8, 4313; Langmuir 2020, 36, 10811-10821; Colloids Surf., A 2020, 594, 124633). We have therefore unable assigning the size increase to a specific mechanism in this study.

Cryo-TEM provided direct evidence that evaporation temperature altered the radial nanoparticle structure. All four samples exhibited a core-shell-like morphology, but the equivalent thickness of the shell-like outer layer increased from approximately 7 nm (25 °C) and 7.5 nm (40 °C) to 12.5 nm (50 °C) and 14.5 nm (65 °C), respectively (Figure R16). Based on the compositional and structural assignment established for the control nanoparticles, the outer layer is predominantly associated with PM6-dominated region. The results therefore indicate that accelerated solvent removal at higher temperatures promotes stronger radial component differentiation and leads to a thicker PM6-dominated outer region. Besides, the local fringe periodicities in both the outer region and the particle interior shifted toward larger values at higher temperatures. The outer-region periodicity changed from approximately 2.02 nm at 25-40 °C to 2.05 nm at 50 °C and 2.19 nm at 65 °C, whereas the corresponding interior periodicities changed from approximately 1.90-1.95 nm to 2.02 and 2.25 nm (Figure R18). These changes indicate expanded local molecular packing. This may relate to the faster precipitation process induced by the higher solvent evaporation, resulting in molecules lacking a sufficient time window to form a tighter packing.

In situ PL measurements further showed that nanoparticle formation proceeds through solvent volatilization, solidification and final-state regimes (Figure R19). Increasing the evaporation temperature systematically shortened the first two regimes and accelerated the PL-intensity and spectral evolution. We interpret this behavior as a more rapid increase in the PM6:Y6 concentration within the droplets, followed by earlier nanoparticle densification. The faster PL decay therefore reflects the accelerated development of the exciton-quenching environment. The relatively blue-shifted emission at higher temperatures corresponds to the locally loosened Y6 stacking observed by cryo-TEM.

Taken together, these results support a kinetic competition between chloroform removal and molecular assembly. At 25-40 °C, the slower solvent-removal process provides a

longer time window for molecule assembly before vitrification. At 50-65 °C, solvent evaporation becomes more rapid and leads to the PM6-favoured interfacial distribution to be arrested before component redistribution. This produces a thicker PM6-dominated outer layer and a less compact local packing environment. Evaporation-rate-dependent control of particle-surface organization and internal morphology has also been observed in other polymer-containing emulsion systems (ACS Nano 2017, 11, 2133-2142), suggesting its importance to manipulate particle morphology. It should be noted that, although additives extended the solidification duration from 55 min (control) to 70 min (1-PN) and 65 min (DPE). DPE also slightly reduced particle size, while 1-PN increased it; and long-range ordered structures appeared within the additive-treated particles. This finding, when compared with samples from different evaporation temperatures, suggests the different mechanism of additives in regulating particle structure.

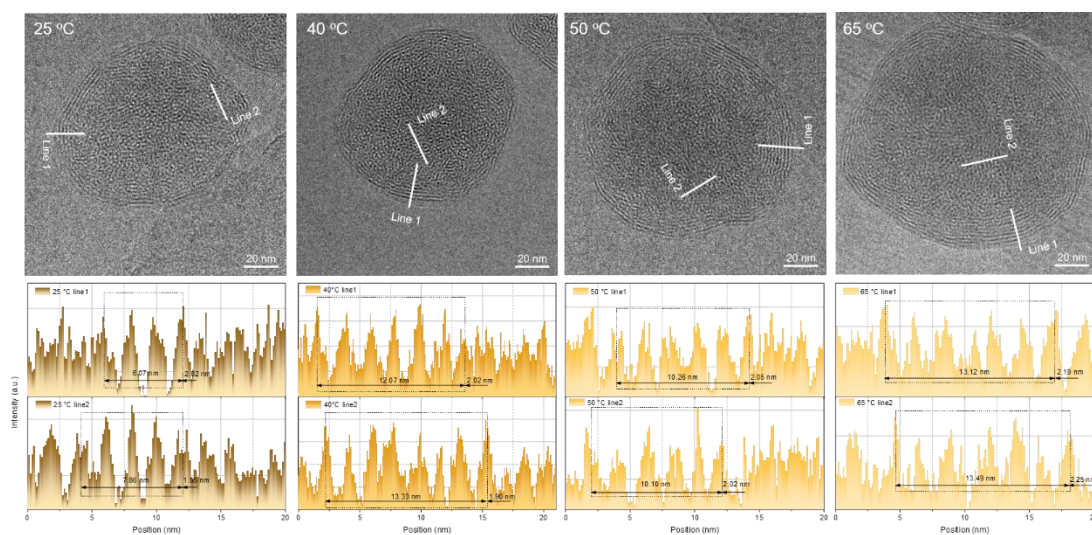


Figure R18. High resolution cryo-TEM images of PM6:Y6 NPs prepared at different evaporation temperatures (25 °C, 40 °C, 50 °C, and 65 °C). Intensity profiles along the marked lines and the corresponding lattice spacings are shown.

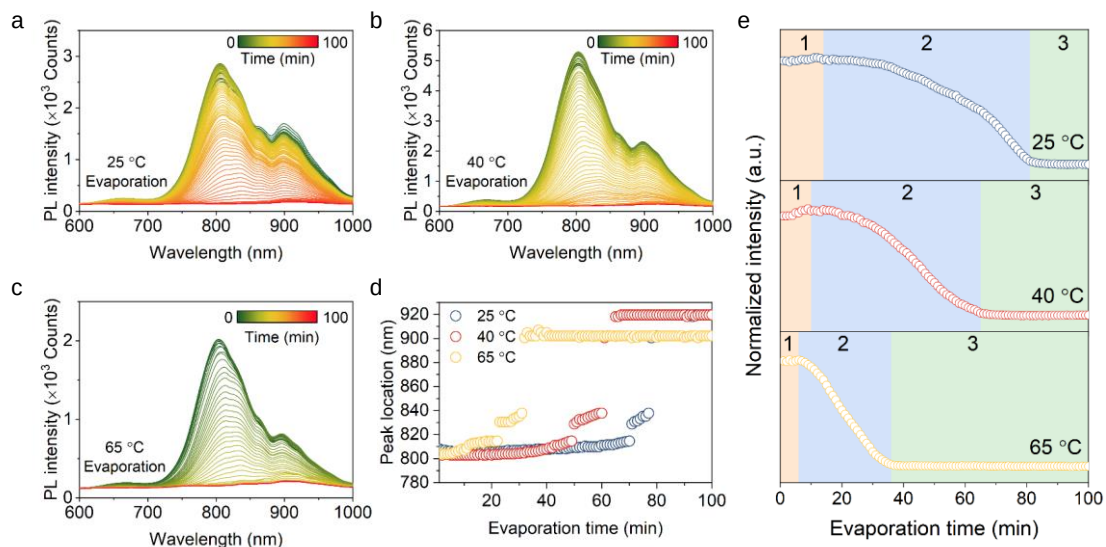


Figure R19. (a-c) Time-resolved PL spectra during evaporation for PM6:Y6 dispersions with different evaporation temperature. Time evolution of PL peak position (d) and PL peak intensity (e) for PM6:Y6 dispersions prepared at different evaporation temperature.

Our modification to the manuscript:

On page 10, please read “In addition, control experiments varying the evaporation temperature show that delayed solvent removal alone cannot reproduce the additive-dependent structural trends (Supplementary Figs. 24-25). Temperature-dependent solvent removal primarily alters the particle size and the thickness of the PM6-dominated outer layer, whereas the additives produce distinct size changes while enhancing internal ordering. Thus, the prolonged solidification window contributes to, but does not solely account for, the additive-induced structural regulation.”