DOI: 10.1002/((please add manuscript number))

Article type: Full Paper

Delicate Morphology Control Triggers 14.7% Efficiency All-Small-Molecule Organic Solar Cells

Hua Tang, Haiyan Chen, Cenqi Yan *, Jiaming Huang, Patrick W. K. Fong, Jie Lv, Dingqin Hu, Ranbir Singh, Manish Kumar, Zeyun Xiao, Zhipeng Kan, Shirong Lu * & Gang Li *

H. Tang, H. Chen, J. Lv, D. Hu, Prof. Z. Xiao, Prof. Z. Kan, Prof. S. Lu

Organic Semiconductor Research Center,

Chongqing Institute of Green and Intelligent Technology

Chinese Academy of Sciences, Chongqing, 400714, P. R. China

E-mail: lushirong@cigit.ac.cn

H. Tang, Dr. C. Yan, J. Huang, Dr. P. Fong, Prof. G. Li

Department of Electronic and Information Engineering, The Hong Kong Polytechnic University, Hung Hum, Kowloon, Hong Kong SAR, P. R. China.

E-mail: cenqi.cq.yan@polyu.edu.hk, gang.w.li@polyu.edu.hk

H. Tang, J. Lv

University of Chinese Academy of Sciences

This is the author manuscript accepted for publication and has undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the [Version of Record](#). Please cite this article as [doi: 10.1002/aenm.202001076](https://doi.org/10.1002/aenm.202001076).

This article is protected by copyright. All rights reserved.

Beijing 100049, P. R. China

Dr. R. Singh

Department of Energy & Materials Engineering, Dongguk University, Seoul 04620, Republic of Korea

Dr. M. Kumar

Pohang Accelerator Laboratory, Pohang University of Science and Technology, Pohang 37673, Republic of Korea.

Abstract

Morphology is a critical factor to determine the photovoltaic performance of organic solar cells (OSCs). However, delicately fine-tuning the morphology involving only small molecules is an extremely challenging task. Herein, we demonstrate a simple, generic, and effective concentration induced morphology manipulation approach to prompt both the state-of-the-art thin-film BTR-Cl:Y6 and thick-film BTR:PC₇₁BM all-small-molecule (ASM) OSCs to a record level. The morphology is delicately controlled by subtly altering the prepared solution concentration but maintaining the identical active layer thickness. The remarkable performance enhancement achieved by this approach mainly results from the enhanced absorption, reduced trap-assistant recombination, increased crystallinity, and optimized phase-separated network. These findings demonstrate that concentration induced morphology manipulation strategy can further propel the reported best-performing ASM OSCs to a brand-new level, and provide a promising way to precisely control the morphology towards high-performance ASM OSCs.

1. Introduction

Solution-processed bulk-heterojunction (BHJ) organic solar cells (OSCs) have emerged as a promising rival for next-generation photovoltaic technology by virtue of their short energy payback time, low carbon footprint, and easy fabrication into flexible, light-weight, and semitransparent devices.¹⁻⁴ All-small-molecule (ASM) OSCs, in particular, have arisen as a preferred candidate

This article is protected by copyright. All rights reserved.

attracting academics and industries, due to the unique superiorities of small molecules, such as well-defined chemical structures, easy purification, excellent batch-to-batch reproducibility, and thus splendid scalability.⁵⁻⁷ Unfortunately, in terms of power conversion efficiency (PCE), ASM OSCs still lag far behind polymer solar cells (PSCs) that have achieved 17% efficiency breakthrough recently.⁸⁻¹² Thus, further prompting the PCE of ASM OSCs is of significance to facilitate the industrialization of organic photovoltaics.

Morphology is a critical factor to determine the performance of OSCs.^{1, 6, 7, 13-16} Hence, manipulating the morphology of active layer is as important as the design of active layer materials and modification of interfaces, and has become one of the research hotspots of ASM OSCs.¹⁷⁻²¹ A number of device engineering techniques are effective in controlling the dynamics of solvent evaporation towards ideal morphology during or behind the film formation of OSCs, such as thermal annealing (TA), solvent vapor annealing (SVA) and solvent additives.^{6, 22-27} However, the active layer morphology involving only small molecules is very sensitive to the aforementioned strategies, which generally alter the morphology significantly on the phase separation, molecular packing, crystallinity, and domain size.^{19, 20, 28-31} For instance, small molecule donor H11 exhibits a preferential edge-on orientation, and small molecule acceptor IDIC displays a preferential face-on orientation. When the H11 is blended with IDIC, the as-cast blend film demonstrates a random orientation with disordered microstructural features, whereas the blend film after thermal annealing presents a 3D charge pathway, which provides charge transport channels both vertically and horizontally, and finally results in a better photovoltaic performance than the as-cast device.³² The technique of delicately optimizing the ASM active layer has been rarely investigated and requires further study.

The BHJ blend concentration is an important while much less studied parameter in OSC research. It has been shown that concentration directly affects the polymer aggregation states in solution, which can be utilized to achieve high-efficiency OSC.³³ The Diluting Concentrated Solution (DCS) technique has shown the effectiveness in fine-tuning morphology of PSCs.³⁴ Polymers can contact and entangle in high-concentration solution, and such aggregation state in the solution can be reserved during dilution since the diffusion of solvent molecules into polymers is much faster than the diffusion of polymer into solvent molecules. Eventually, this novel approach enabled polymer-based binary (PTB7:PC₇₁BM, PBDTTT-C-T:PC₇₁BM and PBDTTT-C-T:PPDIOT) and ternary OSCs

(PTB7:ICBA:PC₇₁BM) with 6-37% enhancement of efficiency relative to those directly using the reported optimal concentration.³⁴

Since the morphological factor is the key to obtain efficient ASM OSCs and the concentration control technique is a promising solution, however, similar PSC-fitted morphology manipulation approach has never been demonstrated in solution-processed ASM OSCs. Herein, a simple, generic, and effective approach is introduced to further refine the active layer on almost faultless morphology of the state-of-the-art ASM OSCs (BTR-Cl:Y6 OSCs with extraordinary 3D transport texture and BTR:PC₇₁BM OSCs with nanofibrillar network) towards top-performing ASM OSCs.^{28, 29} Based on the reported optimal solution concentration for thin-film BTR-Cl:Y6 (16 mg ml⁻¹) and thick-film BTR:PC₇₁BM (40 mg ml⁻¹) ASM OSCs, we alter the concentration but maintain the identical thickness of the photoactive layer.^{28, 29} Eventually, we demonstrate that the slightly higher concentration of 18 mg ml⁻¹ for thin-film ASM OSC presents the champion PCE of 14.7%, which exceeds that of 16 mg ml⁻¹ (12.9%) and 20 mg ml⁻¹ (13.6%). Likewise, for the BTR:PC₇₁BM thick-film (*ca.* 300nm) ASM OSC, efficiency for 44 mg ml⁻¹ (10.2%) outperforms those for the reported optimal concentration of 40 mg ml⁻¹ (9.2%) and excessively higher concentration of 48 mg ml⁻¹ (9.6%). Note, the 14.7% efficiency of BTR-Cl:Y6 system and 10.2% of BTR:PC₇₁BM stands the champion photovoltaic efficiency of thin-film and thick-film ASM OSCs respectively (**Figure 2a**).^{19, 29, 32, 35-40} These performance enhancements are mainly ascribed to the precise morphology control, leading to the enhanced absorption, the improved crystallinity, the reduced trap-assistant recombination and the suppressed energetic disorder. In addition, the dramatic fill factor change of BTR-Cl:Y6 thin film devices (from 68.3% to 74.7%) and BTR:PC₇₁BM thick film devices (from 71.6% to 74.7%) soundly proves the effectiveness of this approach on precise morphology manipulation, which also provides an alternative avenue to further boosting the photovoltaic performance of ASM OSCs.

Figure 1 (a) Molecular structures of BTR-Cl and Y6. (b) The schematic of morphology evolution from a prepared solution with different concentrations to blend film with the same thickness of active layers. Normalized UV-vis absorption spectra of (c) BTR-Cl and Y6 in solution and as thin film and (d) BTR-Cl:Y6 blend in solution and as thin film. (e) The absorption coefficient spectra of blend film (after TA for 0s and 20s) processed with different concentrations. Time-resolved in situ UV-Vis absorption

spectra of optimized blend film of (f) Low, (g) Medium, and (h) High concentration under TA (120°C). (g) Energy level diagram of BTR-Cl and Y6. 2D GIWAXS patterns of (j) BTR-Cl and (k) Y6.

2. Results and discussion

In this work, BTR-Cl:Y6 system is carefully selected as the first research group. **Figure 1a** depicts the molecular structures of BTR-Cl and Y6. **Figure 1b** shows the schematic of the morphology evolution from prepared solution with varied concentration (Low: 16 mg ml⁻¹; Medium: 18 mg ml⁻¹; High: 20 mg ml⁻¹. The same as below) to blend film of the same thickness. **Figure 1c** presents normalized UV-vis absorption spectra of BTR-Cl and Y6 in solution and as pristine films. The absorption maxima of BTR-Cl and Y6 films are at 580 and 836 nm, which are redshifted by 62 and 104 nm relative to the corresponding solutions, respectively, implying the existence of strong intermolecular interactions in both solid films. The extra shoulder peak of BTR-Cl film at 626 nm unveils BTR-Cl's strong crystallinity. BTR-Cl and Y6 film exhibit absorption onsets of 698 and 931 nm, respectively, which account for the respective optical bandgaps of 1.77 and 1.33 eV. **Figure 1d** demonstrates the normalized UV-vis absorption spectra of BTR-Cl:Y6 blend in solution and as thin film. The absorption maximum of blend solution appears on the identical peak of Y6, whereas the absorption maximum of the blend film is located at the wavelength of the peak of BTR-Cl, implying the synergistic effect of the blend character and the dynamics of solvent evaporation during film formation can alter the absorption behavior.

In-situ UV-vis absorption measurements (**Figure 1f-h**) are carried out to investigate the absorption transformation under the optimized posttreatment technique (TA 120°C for 10 min) for the BTR-Cl:Y6 system. We have shown that, at the as-cast state, the medium concentration BHJ blend film possesses the best absorption capability. In addition, the absorption of all the three concentration systems are observed to get saturated with nearly the same time duration (*ca.* 7s. **Figure 1f-h**), and the medium concentration maintains the best absorption then. It is inferred that the concentration induced approach does not change the solidification process, but significantly alters the absorption capability of the blend films, among which the medium concentration film shows the best performance. The corresponding absorption spectra under TA of 0 and 20s are

shown in **Figure 1e**. The TA process optimizes the absorption of the blend films in two aspects, that is, enhancing the BTR-Cl peak and red-shifting the Y6 peak, together contributing to the remarkably improved blend absorption. **Figure 1i** displays the energy level diagram of BTR-Cl and Y6. BTR-Cl possesses the lowest unoccupied molecular orbital (LUMO) level of -3.70 eV and the highest occupied molecular orbital (HOMO) level of -5.46 eV, which match well with Y6 (-4.10 eV/ -5.65 eV).^{29, 41} As shown in Figure 1j and 1k, BTR-Cl and Y6 demonstrated “edge-on” and “face-on” orientation, respectively, which are in accordance with our previous work.

Table 1. Photovoltaic performance of optimized OSCs based on BTR-Cl:Y6 and BTR:PC₇₁BM under simulated AM1.5G illumination (100 mW cm⁻²).

Active layer	Concentration n [mg ml ⁻¹]	Thickness ^a [nm]	V_{OC} [V]	J_{SC} [mA cm ⁻²]	Calc. J_{SC} [mA cm ⁻²]	FF [%]	Ave. PCE ^b [%]	Max. PCE ^c [%]
BTR-Cl:Y6	16	ca. 110	0.86	24.17	23.22	65.5	13.3	13.6 ^d
	16		0.83	22.80	22.33	68.3	12.6	12.9
	18		0.83	23.66	23.44	74.7	14.2	14.7
	20		0.84	22.62	22.05	71.8	13.3	13.6
BTR:PC ₇₁ BM	40	ca. 300	0.93	13.95	13.69	69.6	8.9	9.1 ^e
	40		0.93	13.88	13.42	71.6	9.0	9.2
	44		0.94	14.57	14.05	74.7	9.9	10.2
	48		0.93	14.27	13.89	72.1	9.4	9.6

^a The thickness of the ASM OSC active layer.

^b The average values obtained from 20 devices.

^c Values are for the champion PCE device.

^{d,e} Values are obtained from the literature.^{28, 29}

BHJ ASM OSCs in this work were fabricated with the conventional device architecture of ITO/poly (3,4-ethylenedioxythiophene):poly (styrene sulfonate) (PEDOT:PSS)/active layer/phenyl(2-naphthyl) diphenylphosphine oxide (Phen-NaDPO)/Ag. The BHJ devices were optimized by tuning the solution concentration and varying the posttreatment techniques. **Table 1** summarizes the figures of merit of the best-performing ASM OSCs under simulated AM1.5G irradiation (100 mW cm^{-2}). **Figure 2a** summarizes the reported work with the champion PCE of thin-film/thick-film ASM OSCs in the recent five years. To our best knowledge, this concentration induced approach elevates both of thin-film and thick-film ASM OSCs to a record level.

Figure 2 (a) Summary of the reported work with the best PCE of the binary thin-/thick-film ASM OSCs in the recent 5 years, (b) J-V characteristics, (c) EQE spectra (Δ EQE of low and medium

concentration relative to high concentration), and (d) photocurrent density (J_{ph}) as a function of the effective voltage (V_{eff}) of the optimized ASM OSCs.

Figure 2b depicts the current density–voltage (J – V) characteristics of the optimized ASM OSCs. The 16 mg ml⁻¹ (low concentration) device shows a high PCE of 12.9% with a V_{oc} of 0.83 V, a J_{sc} of 22.80 mA cm⁻², and an FF of 68.3%. The FF is dramatically enhanced from 68.3% to 74.7%, and the J_{sc} is slightly improved from 22.80 to 23.66 mA cm⁻², which lead to the excellent PCE of 14.7% when the prepared solution concentration reaches 18 mg ml⁻¹ (medium concentration) and the final active layer thickness retains 110 nm. However, when the solution concentration is further elevated to 20 mg ml⁻¹ (high concentration), the efficiency of the device drops to 13.6% with reduced FF of 71.8% and decreased J_{sc} of 22.05 mA cm⁻². These results demonstrate that optimal concentration can result in the best photovoltaic performance. In addition, we also tested another state-of-the-art thick-film BTR:PC₇₁BM ASM OSCs and obtained similar results that medium concentration of 44 mg ml⁻¹ gained 10.2% efficiency, higher than those of low and high concentration (9.2% and 9.6%). (**Table 1**) It is worth mentioning that the champion PCE of 14.7% represents an ~14% enhancement compared with the PCE of the low concentration control device and is the top value of ASM OSCs to our knowledge.

Figure 2c shows the external quantum efficiency (EQE) spectra of the optimized devices based on the prepared solution with different concentrations. The EQE curves of all the three devices are very similar in shape, but the medium concentration exhibits a stronger photoresponse than that of the low and high concentration device in the range of 380–420 and 480–840 nm, which contributes to the increased J_{sc} ; the EQE maximum of the medium concentration device is 80.7%, obviously higher than the low concentration of 75.5% and high concentration of 74.6%. The J_{sc} values of the low, medium, and high concentration of BHJ devices integrated from the EQE spectra are 22.33, 23.44, and 22.05 mA cm⁻², respectively, consistent with the J_{sc} values measured from the solar simulator (within a 2.5% error, **Table 1**).

In addition to the slightly improved J_{sc} , another remarkably enhanced parameter is the FF, which contributes to the most enhancement of performance. Recent studies also have

demonstrated that the FF is largely correlated with the competition between charge recombination and extraction, both of which have a nonlinear incremental relationship with the charge carrier mobility. The concentration induced strategy in this work significantly enhances the FF; and thus it is important to closely check this key parameter by examining the transport, collection, and recombination behavior of photogenerated charge carriers.

The photocurrent density (J_{ph}) as a function of the effective voltage (V_{eff}) was plotted to investigate the charge generation and extraction properties (**Figure 2d**). $J_{ph} = J_L - J_D$, in which J_L is the current density under illumination and J_D is that in the dark. $V_{eff} = V_0 - V_A$, where V_0 is the voltage when J_{ph} is equal to 0, and V_A is the applied bias voltage. At a high V_{eff} of 2.5 V, the gross photogenerated excitons are assumed to be dissociated into free charge carriers and then collected by electrodes. The medium concentration BHJ device exhibits a saturated current density (J_{sat}) of 23.77 mA cm⁻², higher than the low concentration (23.50 mA cm⁻²) and high concentration BHJ devices (22.97 mA cm⁻²), which is in line with the better photon harvest of the medium concentration blend. The exciton dissociation efficiency ($\eta_{diss} = J_{SC}/J_{sat}$) and charge collection efficiency ($\eta_{coll} = J_{max\ power}/J_{sat}$) were calculated under the short-circuit and maximum power output conditions, respectively. The medium concentration device presents a η_{diss} of 99.53% and a η_{coll} of 88.20%, higher than the low concentration device (η_{diss} of 97.00% and η_{coll} of 83.10%) and high concentration device (η_{diss} of 98.46% and η_{coll} of 87.48%), indicating this concentration induced strategy facilitates exciton dissociation as well as charge collection.

Figure 3 (a) J_{sc} versus P_{light} and (b) V_{oc} versus P_{light} of the optimized devices. (c) TPV and (d) TPC of the optimized devices. (e) zero-field hole mobility $\mu_{0,h}$, and (f) electron mobility $\mu_{0,e}$ versus $(1000/T)^2$.

To explore the behavior of the free charge carriers in the devices, J-V curves under various incident light intensities and the transient photovoltage/photocurrent (TPV/TPC) were performed. Previous researches have reported that the bimolecular recombination losses could be quantified by employing the power-law relation of $J \propto I^\alpha$ to fit J_{sc} as a function of the incident light intensity. In short, a value of α equal to unity reflects the extreme case where all the free carriers are swept out and collected at the electrodes before recombination. From **Figure 3a**, α values of 0.969, 0.974, and 0.972 were obtained for low, medium, and high concentration BHJ devices, respectively, which are indicative of negligible bimolecular recombination losses for all these systems. The low bimolecular recombination losses guided us to analyze another loss mechanism: trap-assisted Shockley-Read-Hall (SRH) recombination. In this case, V_{oc} was plotted as a function of the incident light intensity (**Figure 3b**). The data were fitted according to the expression $V_{oc} \propto nkT/q \ln(I)$, where k , T , and q are the Boltzmann constant, the temperature in Kelvin, and elementary charge, respectively. Any deviation from 1 (trap-free condition) indicates the presence of trap-assisted recombination. The fitted data shown in **Figure 3b** displayed n values of 1.33, 1.05, and 1.22 for low, medium, and high concentration BHJ devices, implying that the medium concentration BHJ device suffers from less

trap-assisted recombination than the others. These results reveal that concentration control of the prepared solution can significantly reduce the density of the trap-assisted recombination center, which accounts for the performance improvement of the medium concentration BHJ device.

Further insights into the charge recombination dynamics and extraction across BHJ active layers in devices were analyzed by TPV and TPC measurements. The carrier lifetimes (τ) under open-circuit conditions (**Figure 3c**) were extracted from the TPV decay dynamics employing monoexponential fits under a 1 sun bias.^{13, 42-44} The medium concentration BHJ device exhibits a τ value of 3.76 μs , longer than the low and high concentration counterparts (3.25 and 3.56 μs), in line with the weaker recombination in medium concentration blend. In addition to charge transport, charge extraction properties also matter. The competition between carrier sweep-out and recombination during the operation was obtained through the TPC test (**Figure 3d**). The photocurrent decay time under short-circuit conditions is 0.37 μs for the medium concentration BHJ device, smaller than that for the low (0.41 μs) and high concentration device (0.40 μs), illustrating that this concentration induced approach can effectively facilitate charge carrier extraction, which is in agreement with the aforementioned higher charge collection efficiency of 88.20% in the medium concentration BHJ device (**Figure 2d**).

To investigate the charge transport process, both hole and electron carrier mobilities were quantified by the space-charge-limited-current (SCLC) model.⁴⁵⁻⁴⁷ Hole-only devices were fabricated with the structure of ITO/PEDOT:PSS/active layer/ MoO_3 /Ag and electron-only devices with ITO/ ZnO /Phen-NaDPO /Active layer/ Phen-NaDPO /Ag. The medium concentration device presents the hole mobilities of $8.51 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and electron mobilities of $2.51 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, higher than those of the low concentration (6.32×10^{-5} and $2.26 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and the high concentration (8.29×10^{-5} and $2.47 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). In addition, the more balanced charge mobilities ($\mu_e/\mu_h = 2.95$) result in the higher FF of 74.7% in the medium concentration BHJ devices.

The hole and electron energy disorder (σ_h and σ_e) was also evaluated by temperature-dependent electron transport measurements using the Gauss disorder model (GDM):

$$\mu_0 = \mu_{\infty} \exp \left[- \left(\frac{4}{9} \right) \left(\frac{\sigma}{kT} \right)^2 \right]$$

where k is the Boltzmann constant, T is the temperature, μ_0 is the zero-field mobility, and μ_∞ is the mobility at infinite temperature. **Figure 3e, f** depicts the zero-field hole and electron mobilities of the low, medium, and high concentration ASM OSCs as a function of $1/T^2$. The medium concentration ASM OSC exhibits σ_h value of 22.1 meV, and σ_e value of 15.4 meV. Both the low and high concentration counterparts demonstrate slightly higher values ($\sigma_h = 27.2$ meV, $\sigma_e = 15.9$ meV for low concentration and $\sigma_h = 24.4$ meV, $\sigma_e = 15.6$ meV for high concentration), indicating this concentration control strategy is capable of suppressing both hole and electron energetic disorder in the active layer, thereby improving the J_{SC} and FFs in the corresponding devices, also confirming the reduced trap-assisted recombination in the medium concentration BHJ devices.

Figure 4 2D GIWAXS patterns of films based on BTR-Cl:Y6 blend of (a) low concentration, (b) medium concentration, and (c) high concentration. The schematic morphology based on BTR-Cl:Y6 blend films of (d) low concentration, (e) medium concentration, and (f) high concentration. AFM phase images with height images inset of BTR-Cl:Y6 blend film of (g) low concentration, (h) medium concentration, and (i) high concentration. (j) Corresponding GIWAXS intensity profiles along the in-plane (purple lines) and out-of-plane (red lines) directions.

Grazing-incidence wide-angle X-ray scattering (GIWAXS) was performed to investigate the molecular packing and orientation in the thin films, and the corresponding GIWAXS parameters are summarized in **Table S5-6**. As **Figure 1j** presents, BTR-Cl exhibits a preferential edge-on orientation, whereas Y6 demonstrates a preferential face-on orientation (**Figure 1k**), in agreement with previously reported work.^{29, 41} For the blend films processed by prepared solution with various concentrations, all the BHJ blend films demonstrate similar molecule orientation which contains both edge-on and face-on orientations. Such coexistence of edge-on and face-on orientations is capable of potentially forming a 3D charge transport pathway.^{1, 18, 19, 32, 48}

The medium concentration BHJ film exhibits (100) lamellar peaks at $q_{xy} \approx 0.34 \text{ \AA}^{-1}$ (coherence length (CCL) = 14.13 nm) and $q_z \approx 0.28 \text{ \AA}^{-1}$ (CCL = 9.12 nm) (**Figure 4b and j**). In comparison, its low-concentration counterpart displays (100) lamellar peaks at $q_{xy} \approx 0.34 \text{ \AA}^{-1}$ (CCL = 13.46 nm) and $q_z \approx 0.28 \text{ \AA}^{-1}$ (CCL = 8.07 nm; and the high-concentration counterpart has $q_{xy} \approx 0.34 \text{ \AA}^{-1}$ (CCL = 13.79 nm) and $q_z \approx 0.28 \text{ \AA}^{-1}$ (CCL = 8.31 nm), which demonstrate the slightly stronger crystallinity of medium concentration blend. The (010) π - π stacking shows the same tendency. (**Figure 4a, c, and j**) The medium concentration BHJ film exhibits (010) π - π peaks at $q_{xy} \approx 1.73 \text{ \AA}^{-1}$ with CCL = 4.42 nm and $q_z \approx 1.68 \text{ \AA}^{-1}$ with CCL = 4.22 nm, whereas its low-concentration analog presents $q_{xy} \approx 1.73 \text{ \AA}^{-1}$ with CCL = 3.53 nm and $q_z \approx 1.68 \text{ \AA}^{-1}$ with CCL = 3.47 nm, and the high-concentration analog displays $q_{xy} \approx 1.73 \text{ \AA}^{-1}$ with CCL = 4.38 nm and $q_z \approx 1.68 \text{ \AA}^{-1}$ with CCL = 3.21 nm. **Figure 4 d-f** presents the schematic morphology of the BTR-Cl:Y6 blend processed from the prepared solution of low, medium, and high concentration, where the blue and red refer to BTR-Cl and Y6 respectively. The identical molecule orientation and the largest CCL of both lamellar and π - π peak in the medium concentration BHJ film soundly prove that the concentration induced morphology manipulation strategy endows the resulting medium concentration blend film with pronounced crystallinity, which are beneficial for charge transport and in turn accounts for its enhanced μ_h and μ_e , as well as the reduced charge recombination, in accordance with the TPV results.

The donor/acceptor phase separation in the active layer was studied by atomic force microscopy (AFM) (**Figure 4g-i**) and transmission electron microscopy (TEM) (**Figure S4a-c**). As the AFM height images show, the medium concentration BHJ films have a root mean square roughness

(R_q) values of 0.89 nm (**Figure 4h (inset)**), which is larger than its counterparts of low (**Figure 4g (inset)**, R_q = 0.81 nm), and high concentration BHJ film (**Figure 4i (inset)**, R_q = 0.87 nm), implying that concentration induced approach influences the molecular aggregation, which is in conformity with the change of crystallinity of the optimized films ascertained by GIWAXS characterization. (**Figure 4a-c, and j**) As the AFM phase images indicate, relative to the low and high concentration BHJ films, the medium concentration film presents a more uniform network (**Figure 4g-i**), which is beneficial for charge separation and transport.^{6, 31, 44, 49-51} As shown in the TEM images, the medium concentration BHJ film displays a pronounced and clear phase separation and donor/acceptor interpenetrating network compared to the low and high concentration BHJ films, which is advantageous for charge transport.^{18, 42, 52} These morphology data are in accord with the information from $J_{ph} - V_{eff}$ and mobility measurement.

As the GIWAXS, AFM, and TEM results together demonstrate, concentration induced approach delicately tunes the morphology, which is reflected in the stronger crystallinity and more obvious and uniformed phase separation of the medium concentration blend and leads to the improvement of charge separation and transport in the corresponding BHJ device.

3. Conclusion

In summary, we reported a simple, generic, and effective approach to delicately manipulate the morphology induced by varying the prepared solution concentration and prompts both the thin (BTR-Cl:Y6) and thick film (BTR:PC₇₁BM) ASM OSCs to record value. We found that the concentration induced morphological changes leads to 1) the enhanced absorption, which contributed to the J_{sc} ; 2) the reduced trap-assistant SRH recombination, and therefore prolonged the carrier lifetime, suppressed the energetic disorder as well as facilitated the charge extraction; 3) the increased crystallinity and more uniform charge separation network, and thereby contributed to the significantly improved FF. Our findings demonstrated that this concentration induced strategy paves an avenue to further intricately fine-tune the morphology towards high-performance ASM OSCs.

Methods

This article is protected by copyright. All rights reserved.

Materials: BTR-Cl was synthesized by H. C (detailed information can be found from our previous work)²⁹, BTR was purchased from 1 Material Tech Inc., PC₇₁BM was purchased from lumatech Inc., and Y6 was purchased from Solarmer Material Inc. The chloroform (CF) and solvent additives 1,8-diiodooctane (DIO) were purchased from Sigma Aldrich.

Device Fabrication: The all-small-molecule organic solar cells were prepared on glass substrates with tin-doped indium oxide (ITO, 15 Ω /sq) patterned on the surface (device area: 0.08 cm²). Substrates were prewashed with isopropanol to remove organic residues before immersing in an ultrasonic bath of soap for 15 min. Samples were rinsed in flowing deionized water for 5 min before being sonicated for 15 min each in successive baths of deionized water, acetone, and isopropanol. Next, the samples were dried with pressurized nitrogen before being exposed to a UV-ozone plasma for 20 min. A thin layer of PEDOT:PSS (~30nm) (Clevios AL4083) was spin-coated onto the UV-treated substrates, the PEDOT-coated substrates were subsequently annealed on a hot plate at 150 °C for 20 min, and the substrates were then transferred into the glovebox for active layer deposition.

All solutions were prepared in the glovebox. The optimized thin film devices were obtained by dissolving BTR-Cl:Y6 in chloroform (CF) with extra 0.3% DIO using a D/A ratio of 1.6:1 (wt/wt), the total concentration of low (16 mg ml⁻¹), medium (18 mg ml⁻¹) and high (20 mg ml⁻¹). Note: The as-prepared solutions were stirred overnight at room temperature before being spin coat on the PEDOT:PSS substrates. The active layers were dynamically spin-coated employing prepared solution with different concentration and maintain the final thickness of the active layer around 110 nm. The active layers were thermal annealed with 120°C for 10 min and followed by evacuating in the transition chamber of glovebox for 1 hour. For BTR:PC₇₁BM thick film, the optimized thick film devices were obtained by dissolving BTR:PC₇₁BM in chloroform (CF) using a D/A ratio of 1:1 (wt/wt), the total concentration of low (40 mg ml⁻¹), medium (44 mg ml⁻¹) and high (48 mg ml⁻¹). Note: The as-prepared solutions were stirred overnight at room temperature before being spin coat on the PEDOT:PSS substrates. The active layers were spin-coated employing prepared solutions with different concentrations and maintain the final thickness of the active layer around 300 nm. The active layers were then exposed to solvent vapor annealing (SVA) with Dichloromethane (DCM) vapors for 10-55s.

Then, a ~10nm-thin layer of Phen-NaDPO was coated on top as the electron transport layer. The samples were then dried at room temperature for 1 hour. Next, the samples were placed in a thermal evaporator for evaporation of a 90 nm-thick layer of Silver (Ag) evaporated at $1.5 \text{ \AA s}^{-1}$; the pressure of less than 2×10^{-6} Torr. Following electrode deposition, samples underwent J - V testing.

The current density-voltage (J - V) curves of devices were measured using a Keithley 2400 Source Meter in a glove box under AM 1.5G (100 mW cm^{-2}) using an Enlitech solar simulator. A $2 \times 2 \text{ cm}^2$ monocrystalline silicon reference cell with a KG5 filter (purchased from Enli Tech. Co., Ltd., Taiwan). The EQE spectra were measured using a Solar Cell Spectral Response Measurement System QE-R3011 (Enlitech Co., Ltd.). The light intensity at each wavelength was calibrated using a standard monocrystalline Si photovoltaic cell.

Transient photovoltage (TPV). The measurement was conducted under 1 sun conditions by illuminating the device with a white light-emitting diode. The solar cell device was set under open-circuit conditions. The charge carrier could not be extracted but was recombined. Accordingly, the transient decay represented the charge carrier lifetime.

Transient photocurrent (TPC). The measurement was conducted under 1 sun conditions by illuminating the device with a white light-emitting diode. The solar cell device was set under the short-circuit condition.

Atomic Force Microscopy (AFM) Imaging. A Dimension Icon atomic force microscope (AFM) from Bruker was used to image the active layers in tapping mode (heights and phase images are represented below).

Grazing-incidence wide-angle X-ray scattering (GIWAXS). Silicon substrates for GIWAXS test were sonicated for 15 min each in successive baths of detergent, DI water, acetone, and isopropanol. The substrates were then dried with pressurized nitrogen before being exposed to the UV-ozone plasma for 20 min. The BHJ layers were prepared following methods described in Section of Device Fabrication. GIWAXS measurements were carried out at the 5A beamline of the Pohang Light Source II (PLS-II) in South Korea. The GIWAX images were recorded at a 0.13° incidence angle with X-rays of 11.57 keV ($\lambda = 1.0716 \text{ \AA}$) and MAR345 image plate detector.

Coherence length (CCL) calculation. The CCL is calculated based on the equation: $CCL = 1.8\pi/FWHM$. Where the FWHM is the full width at half-maximum. In this manuscript, the values of FWHM and CCL for low, medium, and high systems are summarized in Table S5 and S6.

Acknowledgments

H. Tang and H. Chen contributed equally to this work. S. Lu thanks the support from research grants from the National Youth Thousand Program Project (R52A199Z11), the National Special Funds for Repairing, and Purchasing Scientific Institutions (Y72Z090Q10) and the “Artificial Intelligence” Key Project of Chongqing (No. cstc2017rgzn-zdyfX0030). G. Li and C. Yan thank the support from Research Grants Council of Hong Kong (Project Nos 15218517, C5037-18G), Shenzhen Science and Technology Innovation Commission (Project No. JCYJ20170413154602102), the funding for Project of Strategic Importance (Project Code: 1-ZE29), and Postdoctoral Fellowships Scheme (PDFS. Code: YW3Y) provided by the Hong Kong Polytechnic University. Z. Kan thanks the support from the CAS Pioneer Hundred Talents Program (Y82A060Q10, Y92A160Q10) and National Natural Science Foundation of China (No. 61805245). H. Chen thanks the Natural Science Foundation of Chongqing (cstc2019jcyj-msxmX0400) and Youth Innovation Promotion Association Chinese Academy of Sciences (2020379).

References

- [1] C. Yan, S. Barlow, Z. Wang, H. Yan, A. K. Y. Jen, S. R. Marder and X. Zhan, *Nat. Rev. Mater.*, **2018**, 3, 18003.
- [2] G. Li, W.-H. Chang and Y. Yang, *Nat. Rev. Mater.*, **2017**, 2, 17043.
- [3] G. Li, R. Zhu and Y. Yang, *Nat. Photon.*, **2012**, 6, 153-161.

- [4] P. Cheng, G. Li, X. Zhan and Y. Yang, *Nat. Photon.*, **2018**, 12, 131-142.
- [5] T. Duan, H. Tang, R.-Z. Liang, J. Lv, Z. Kan, R. Singh, M. Kumar, Z. Xiao, S. Lu and F. Laquai, *J. Mater. Chem. A*, **2019**, 7, 2541-2546.
- [6] S. D. Collins, N. A. Ran, M. C. Heiber and T.-Q. Nguyen, *Adv. Energy Mater.*, **2017**, 7, 1602242.
- [7] Y. Huo, H.-L. Zhang and X. Zhan, *ACS Energy Lett.*, **2019**, 4, 1241-1250.
- [8] Q. Liu, Y. Jiang, K. Jin, J. Qin, J. Xu, W. Li, J. Xiong, J. Liu, Z. Xiao, K. Sun, S. Yang, X. Zhang and L. Ding, *Science Bulletin*, **2020**,
- [9] L. Zhan, S. Li, T.-K. Lau, Y. Cui, X. Lu, M. Shi, C.-Z. Li, H. Li, J. Hou and H. Chen, *Energy & Environ. Sci.*, **2020**, 13, 635-645.
- [10] Y. Lin, Y. Firdaus, M. I. Nugraha, F. Liu, S. Karuthedath, A. H. Emwas, W. Zhang, A. Seikhan, M. Neophytou, H. Faber, E. Yengel, I. McCulloch, L. Tsetseris, F. Laquai and T. D. Anthopoulos, *Adv. Sci.*, **2020**, 7, 1903419.
- [11] Y. Lin, B. Adilbekova, Y. Firdaus, E. Yengel, H. Faber, M. Sajjad, X. Zheng, E. Yarali, A. Seikhan, O. M. Bakr, A. El - Labban, U. Schwingenschlögl, V. Tung, I. McCulloch, F. Laquai and T. D. Anthopoulos, *Adv. Mater.*, **2019**, 31, 1902965.
- [12] R. Ma, T. Liu, Z. Luo, Q. Guo, Y. Xiao, Y. Chen, X. Li, S. Luo, X. Lu, M. Zhang, Y. Li and H. Yan, *Sci. China Chem.*, **2020**, 63, 325-330.
- [13] R.-Z. Liang, Y. Zhang, V. Savikhin, M. Babics, Z. Kan, M. Wohlfahrt, N. Wehbe, S. Liu, T. Duan, M. F. Toney, F. Laquai and P. M. Beaujuge, *Adv. Energy Mater.*, **2019**, 9, 1802836.
- [14] G. Li, V. Shrotriya, J. Huang, Y. Yao, T. Moriarty, K. Emery and Y. Yang, *Nat. Mater.*, **2005**, 4, 864-868.
- [15] H. Sun, T. Liu, J. Yu, T.-K. Lau, G. Zhang, Y. Zhang, M. Su, Y. Tang, R. Ma, B. Liu, J. Liang, K. Feng, X. Lu, X. Guo, F. Gao and H. Yan, *Energy & Environ. Sci.*, **2019**, 12, 3328-3337.

- [16] H. Sun, Y. Tang, C. W. Koh, S. Ling, R. Wang, K. Yang, J. Yu, Y. Shi, Y. Wang, H. Y. Woo and X. Guo, *Adv. Mater.*, **2019**, 31,
- [17] T. Liu, Z. Luo, Q. Fan, G. Zhang, L. Zhang, W. Gao, X. Guo, W. Ma, M. Zhang, C. Yang, Y. Li and H. Yan, *Energy & Environ. Sci.*, **2018**, 11, 3275-3282.
- [18] T. Liu, Z. Luo, Y. Chen, T. Yang, Y. Xiao, G. Zhang, R. Ma, X. Lu, C. Zhan, M. Zhang, C. Yang, Y. Li, J. Yao and H. Yan, *Energy & Environ. Sci.*, **2019**, 12, 2529--2536.
- [19] H. Tang, T. Xu, C. Yan, J. Gao, H. Yin, J. Lv, R. Singh, M. Kumar, T. Duan, Z. Kan, S. Lu and G. Li, *Adv. Sci.*, **2019**, 6, 1901613.
- [20] T. Liu, D. Meng, Y. Cai, X. Sun, Y. Li, L. Huo, F. Liu, Z. Wang, T. P. Russell and Y. Sun, *Adv. Sci.*, **2016**, 3, 1600117.
- [21] H. Yin, C. Zhang, H. Hu, S. Karuthedath, Y. Gao, H. Tang, C. Yan, L. Cui, P. W. K. Fong, Z. Zhang, Y. Gao, J. Yang, Z. Xiao, L. Ding, F. Laquai, S. K. So and G. Li, *ACS Appl. Mater. Interfaces*, **2019**, 11, 48095-48102.
- [22] M. T. Dang, L. Hirsch, G. Wantz and J. D. Wuest, *Chem. Rev.*, **2013**, 113, 3734-3765.
- [23] G. Zhang, J. Zhao, P. C. Y. Chow, K. Jiang, J. Zhang, Z. Zhu, J. Zhang, F. Huang and H. Yan, *Chem. Rev.*, **2018**, 118, 3447-3507.
- [24] Z. Zhou, S. Xu, J. Song, Y. Jin, Q. Yue, Y. Qian, F. Liu, F. Zhang and X. Zhu, *Nat. Energy*, **2018**, 3, 952-959.
- [25] Y. Yang, W. Chen, L. Dou, W.-H. Chang, H.-S. Duan, B. Bob, G. Li and Y. Yang, *Nat. Photon.*, **2015**, 9, 190-198.
- [26] D. Baran, R. S. Ashraf, D. A. Hanifi, M. Abdelsamie, N. Gasparini, J. A. Rohr, S. Holliday, A. Wadsworth, S. Lockett, M. Neophytou, C. J. Emmott, J. Nelson, C. J. Brabec, A. Amassian, A. Salleo, T. Kirchartz, J. R. Durrant and I. McCulloch, *Nat. Mater.*, **2017**, 16, 363-369.

- [27] N. Gasparini, X. Jiao, T. Heumueller, D. Baran, G. J. Matt, S. Fladischer, E. Spiecker, H. Ade, C. J. Brabec and T. Ameri, *Nat. Energy*, **2016**, 1,
- [28] K. Sun, Z. Xiao, S. Lu, W. Zajaczkowski, W. Pisula, E. Hanssen, J. M. White, R. M. Williamson, J. Subbiah, J. Ouyang, A. B. Holmes, W. W. Wong and D. J. Jones, *Nat. Commun.*, **2015**, 6, 6013.
- [29] H. Chen, D. Hu, Q. Yang, J. Gao, J. Fu, K. Yang, H. He, S. Chen, Z. Kan, T. Duan, C. Yang, J. Ouyang, Z. Xiao, K. Sun and S. Lu, *Joule*, **2019**, 3, 3034-3047.
- [30] I. A. Howard, R. Mauer, M. Meister and F. Laquai, *J. Am. Chem. Soc.*, **2010**, 132, 14866–14876.
- [31] T. Liu, L. Huo, S. Chandrabose, K. Chen, G. Han, F. Qi, X. Meng, D. Xie, W. Ma, Y. Yi, J. M. Hodgkiss, F. Liu, J. Wang, C. Yang and Y. Sun, *Adv. Mater.*, **2018**, 30, 1707353.
- [32] H. Bin, Y. Yang, Z. G. Zhang, L. Ye, M. Ghasemi, S. Chen, Y. Zhang, C. Zhang, C. Sun, L. Xue, C. Yang, H. Ade and Y. Li, *J. Am. Chem. Soc.*, **2017**, 139, 5085-5094.
- [33] J. Gao, W. Chen, L. Dou, C.-C. Chen, W.-H. Chang, Y. Liu, G. Li and Y. Yang, *Adv. Mater.*, **2014**, 26, 3142–3147.
- [34] P. Cheng, C. Yan, Y. Li, W. Ma and X. Zhan, *Energy & Environ. Sci.*, **2015**, 8, 2357-2364.
- [35] Q. Fan, T. Liu, M. Zhang, W. Su, U. A. Méndez - Romero, T. Yang, X. Geng, L. Hou, D. Yu, F. Liu, H. Yan and E. Wang, *Small Methods*, **2020**,
- [36] R. Zhou, Z. Jiang, C. Yang, J. Yu, J. Feng, M. A. Adil, D. Deng, W. Zou, J. Zhang, K. Lu, W. Ma, F. Gao and Z. Wei, *Nat. Commun.*, **2019**, 10, 5393.
- [37] D. Deng, Y. Zhang, J. Zhang, Z. Wang, L. Zhu, J. Fang, B. Xia, Z. Wang, K. Lu, W. Ma and Z. Wei, *Nat. Commun.*, **2016**, 7, 13740.
- [38] J. Ge, L. Xie, R. Peng, B. Fanady, J. Huang, W. Song, T. Yan, W. Zhang and Z. Ge, *Angew. Chem. Int. Ed.*, **2020**, 59, 2808-2815.
- [39] Q. Yue, H. Wu, Z. Zhou, M. Zhang, F. Liu and X. Zhu, *Adv. Mater.*, **2019**, 31, 1904283.

- [40] M. Zhang, J. Wang, F. Zhang, Y. Mi, Q. An, W. Wang, X. Ma, J. Zhang and X. Liu, *Nano Energy*, **2017**, 39, 571-581.
- [41] J. Yuan, Y. Zhang, L. Zhou, G. Zhang, H.-L. Yip, T.-K. Lau, X. Lu, C. Zhu, H. Peng, P. A. Johnson, M. Leclerc, Y. Cao, J. Ulanski, Y. Li and Y. Zou, *Joule*, **2019**, 3, 1140-1151.
- [42] H. Tang, C. Yan, S. Karuthedath, H. Yin, Y. Gao, J. Gao, L. Zhang, J. Huang, S. K. So, Z. Kan, F. Laquai, G. Li and S. Lu, *Sol. RRL*, **2020**, 4, 1900528.
- [43] R.-Z. Liang, M. Babics, A. Seitkhan, K. Wang, P. B. Geraghty, S. Lopatin, F. Cruciani, Y. Firdaus, M. Caporuscio, D. J. Jones and P. M. Beaujuge, *Adv. Func. Mater.*, **2018**, 28, 1705464.
- [44] C. Yan, T. Yang, W. Gao, Y. Xiao, Y. Li, X. Lu, C. Yang and G. Li, *Sol. RRL*, **2019**, 3, 1900262.
- [45] D. Bartesaghi, C. Perez Idel, J. Kniepert, S. Roland, M. Turbiez, D. Neher and L. J. Koster, *Nat Commun*, **2015**, 6, 7083.
- [46] H. Yin, L. K. Ma, Y. Wang, J. Huang, H. Yu, J. Zhang, P. C. Y. Chow, W. Ma, S. K. So and H. Yan, *Adv. Mater.*, **2019**, 30, 1903998.
- [47] K. Gao, S. B. Jo, X. Shi, L. Nian, M. Zhang, Y. Kan, F. Lin, B. Kan, B. Xu, Q. Rong, L. Shui, F. Liu, X. Peng, G. Zhou, Y. Cao and A. K. Y. Jen, *Adv. Mater.*, **2019**, 31, 1807842.
- [48] Y. Chang, Y. Chang, X. Zhu, X. Zhou, C. Yang, J. Zhang, K. Lu, X. Sun and Z. Wei, *Adv. Energy Mater.*, **2019**, 9, 1900190.
- [49] C. Yan, T. Liu, Y. Chen, R. Ma, H. Tang, G. Li, T. Li, Y. Xiao, T. Yang, X. Lu, X. Zhan, H. Yan, G. Li and B. Tang, *Sol. RRL*, **2019**, 3, 201900377.
- [50] T. Liu, W. Gao, Y. Wang, T. Yang, R. Ma, G. Zhang, C. Zhong, W. Ma, H. Yan and C. Yang, *Adv. Func. Mater.*, **2019**, 29, 1902155.
- [51] C. Yan, W. Wang, T.-K. Lau, K. Li, J. Wang, K. Liu, X. Lu and X. Zhan, *J. Mater. Chem. A*, **2018**, 6, 16638-16644.

[52] J. Huang, L. Xie, L. Hong, L. Wu, Y. Han, T. Yan, J. Zhang, L. Zhu, Z. Wei and Z. Ge, Mater. Chem. Front., **2019**, 3, 1244-1252.

A simple, generic, and effective concentration induced morphology manipulation approach is demonstrated to prompt the state-of-the-art all-small-molecule (ASM) BTR-Cl:Y6 and BTR:PC₇₁BM organic solar cells (OSCs) to a record level. This approach provides a promising way to delicately control the morphology towards high-performance ASM OSCs.

Table of Contents

This article is protected by copyright. All rights reserved.

Author Manuscript

Minerva Access is the Institutional Repository of The University of Melbourne

Author/s:

Tang, H;Chen, H;Yan, C;Huang, J;Fong, PWK;Lv, J;Hu, D;Singh, R;Kumar, M;Xiao, Z;Kan, Z;Lu, S;Li, G

Title:

Delicate Morphology Control Triggers 14.7% Efficiency All-Small-Molecule Organic Solar Cells

Date:

2020-06-05

Citation:

Tang, H., Chen, H., Yan, C., Huang, J., Fong, P. W. K., Lv, J., Hu, D., Singh, R., Kumar, M., Xiao, Z., Kan, Z., Lu, S. & Li, G. (2020). Delicate Morphology Control Triggers 14.7% Efficiency All-Small-Molecule Organic Solar Cells. *ADVANCED ENERGY MATERIALS*, 10 (27), <https://doi.org/10.1002/aenm.202001076>.

Persistent Link:

<http://hdl.handle.net/11343/275868>