

## Preparation of Perovskite: Fullerene Bulk Heterojunction Using a Surfactant Free Microemulsion Scheme. Modeling, Simulation and Experimental Studies

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$\text{CH}_3\text{NH}_3\text{PbI}_3$  perovskite material has shown excellent optoelectronic properties for its use in solar cells. However, issues like stability and dissimilarity in charge carrier mobility limits its applicability in Bulk Heterojunction (BHJ) solar cells. Efforts have been made by incorporating suitable conjoining material in BHJ to increase stability and performance of solar cells. However, the solubility of BHJ components in one solution may pose problems in the single-step synthesis of BHJ. Here, we report our theoretical and experimental work on preparing perovskite: Indene  $\text{C}_{60}$ -Bisadduct (ICBA) BHJ using a Cyclohexane: Acetone: DMSO (CAD) Surfactant Free Microemulsion (SFME) scheme, which can solve the problem of the solubility of BHJ components in a single solution. A critical initial acetone volume fraction is essential to maintain the stability of the microemulsion depending on its composition. With the help of theoretical simulation, we studied evaporation dynamics of SFME with a range of initial acetone volume, which can take SFME from an unstable state to a stable one. It was observed that, depending on the initial acetone volume fraction and substrate temperature, the solidifying thin film of SFME on the substrate may transit through different states related to its stability. This can have marked effect on the structural and optoelectronic properties of BHJ. Experimental studies confirmed these predictions. This method can open a novel way of tailoring perovskite:organic BHJ for optimum performance in optoelectronic devices.

**Keywords:** Perovskite, Perovskite:ICBA bulk heterojunction (BHJ), Surfactant free microemulsion (SFME), Simulation, Morphology control through microemulsion composition.

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### 1. INTRODUCTION

Organic-inorganic lead halide perovskites (OILHPs) have been attracting great attention as promising PV materials due to their advantages such as high absorption coefficient, tunable band gap, long carrier diffusion length and solution processability. The performance of perovskite solar cells (PSCs) has been improved significantly and has achieved efficiency of 25.5 % [1]. OILHPs suffer from disadvantages like charge mobility mismatch and phase instability. It has been proposed that, incorporation of acceptor material like fullerene derivative, inorganic quantum dots [2, 3] in perovskite matrix will balance the charge extraction and additionally enhance the stability of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  perovskite phase. Single step synthesis of perovskite: acceptor bulk heterojunction is quite challenging due to several reasons, including the solubility limit of solutes in a single solvent and the deposition technique [2]. Many review studies on progress in PSCs have attracted attention of researchers worked in this field. Antonio reviewed on the recent progress in materials and device architectures for efficient and stable PSCs [4]. Likely Meidan Ye et al. gives brief information related to interfacial engineering of PSCs, they suggest strategies for the interfacial engineering of PSCs with probable benefits with enhanced light harvesting, improved charge separation and transport, and improved device stability [5]. Wenzhan Xu and co-workers reported a bulk heterojunction perovskite solar cell (BHJ PSC) by introducing  $\text{Zn}_2\text{SnO}_4$  nanoparticles into the active layer in order to address such unbalanced electron and hole diffusion lengths within perovskite materials, which

led to significantly suppressed photocurrent hysteresis, dramatically enhanced device stability, and reproducibility [6]. Fei Wu et al. demonstrated improved efficiency and simultaneously reduced hysteresis in  $\text{TiO}_2$ -based planar PSCs by directly dissolving ICBA into the perovskite precursor solution [7]. In preparation of BHJ PSC, fullerene derivative material has been introduced into it as an acceptor [8-10]. In single step synthesis of BHJ PSC, both donor and acceptor have the restriction of solubility in a single solvent. To overcome this problem, we have used a surfactant free microemulsion (SFME) for BHJ formation. Recently, we have reported for the first time the use of the SFME scheme in the fabrication of a perovskite:PCBM BHJ thin film using the slot-die coating technique [11].

In this paper, we report our theoretical and experimental studies on perovskite:ICBA BHJ using Cyclohexane:Acetone:DMSO (CAD) SFME scheme (see supplementary Fig. A1). The stability of the microemulsion during the thin film formation demands a critical volume of acetone in the solidifying film. With the help of theoretical simulation, we studied evaporation dynamics of SFME for two substrate temperatures. At given volume fractions of SFME constituents and the substrate temperature, the solidifying thin film of SFME on the substrate may transit through different states related to its stability. This can have marked effect on the structural and optoelectronic properties of BHJ formed. Experimental studies on perovskite:ICBA BHJ thin films prepared by slot-die method confirmed these predictions. This method can open a novel way of tailoring perovskite:organic BHJ for optimum performance in optoelectronic devices.

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## 2. MATERIALS AND METHODS

Methylammonium iodide was synthesized in our lab (see Fig. A2 in Appendix) and lead iodide ( $\text{PbI}_2$ ) was purchased from Sigma Aldrich. Dimethyl sulfoxide (DMSO), Cyclohexane and Acetone (AR-Grade) were also from Sigma Aldrich, as well as Indene- $\text{C}_{60}$  bisadduct (ICBA) fullerene derivative. Before deposition, glass films were cleaned with laboline (soap solution), water, acetone, and isopropyl alcohol in an ultrasonic bath for 10 min at each step. The pristine perovskite precursor solution and blend solution were prepared by the SFME scheme, see Fig. 1.

For MAI synthesis and thin film deposition method, see Appendix (Fig. A2).

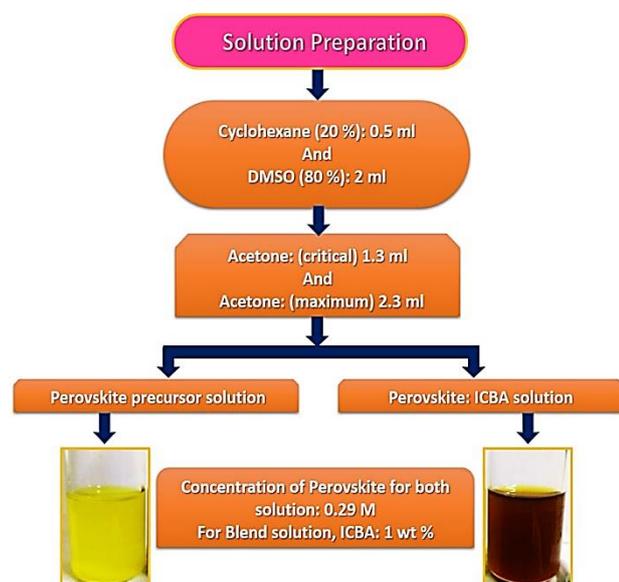


Fig. 1 – Steps of solution preparation

## 3. MODEL FOR SLOT-DIE COATING OF THIN FILMS USING MICROEMULSION

A microemulsion is a system of polar, nonpolar, amphiphilic solvents, which is a single, optically isotropic and thermodynamically stable liquid solution. There is another special type of microemulsion called surfactant free microemulsion (SFME), where a solvent is used which is soluble in both immiscible solvents. We employed SFME in our experiment to fabricate pristine perovskite as well as perovskite:fullerene derivative BHJ thin films by the slot-die method. A thin film of microemulsion was formed on a heated substrate and solidified. During solidification, the proportion of solvents in SFME varies as a function of time, depending on the evaporation dynamics of the respective solvents. Accordingly, the ‘state’ of microemulsion may change as a function of time. This will determine the morphology and hence the optoelectronic properties of the solidified thin film. The evaporation dynamics of the solvents at different temperatures was simulated. The volume of different solvents as a function of time was obtained using the following relation for the evaporation flux:

$$(E_r) = (4.161 \times 10^{-5})u^{0.75}T_f M (P_s/P_H) g/(cm^2)(s), \quad (1)$$

where  $E_r$  is the evaporation flux, which was calculated

using the United State Air Force Method (USAFM) described by Robert D. Morrison [12],  $u$  is the wind speed (m/s),  $T_f$  is the liquid temperature-correction factor,  $M$  is the pool liquid molecular weight (g/mol),  $P_s$  is the pooled liquid vapor pressure at ambient temperature (mm Hg),  $P_H$  is the vapor pressure of hydrazine at ambient temperature (mm Hg),  $T_P$  is the pooled liquid surface temperature ( $^{\circ}\text{C}$ ). If  $T_P = 0^{\circ}\text{C}$  or less,  $T_f = 1.0$ , otherwise  $T_f = 1.0 + 0.0043 T_P^2$ .

The hydrazine vapor pressure ( $P_H$ ) at absolute ambient temperature ( $T_A$  in K) can be obtained using the following relation:

$$(P_H) = 760 \exp \left[ 65.3319 - (7245.2 / T_A) - (8.22 \ln T_A) + (6.1557 \times 10^{-3}) T_A \right]. \quad (2)$$

During deposition, the distance between the substrate and the slot die tip was  $\sim 100 \mu\text{m}$ . Hence the thickness ( $Th$ ) of the settled liquid film was assumed to be  $\sim 100 \mu\text{m}$ .

## 4. RESULTS AND DISCUSSION

First, we studied the formation of a microemulsion of cyclohexane (pure solvent for the fullerene derivative (ICBA)) and dimethyl sulfoxide (pure solvent for the perovskite precursor) using acetone. For a fixed volume of the cyclohexane (C): dimethyl sulfoxide (D) mixed solvent system, we changed the relative proportion of the two solvents and examined the minimum volume of acetone required, called hereafter as the critical volume of acetone and indicated by  $V_c$ , to stabilize the microemulsion in each case. Fig. 2 shows the change in  $V_c$  as a function of D/C ratio.

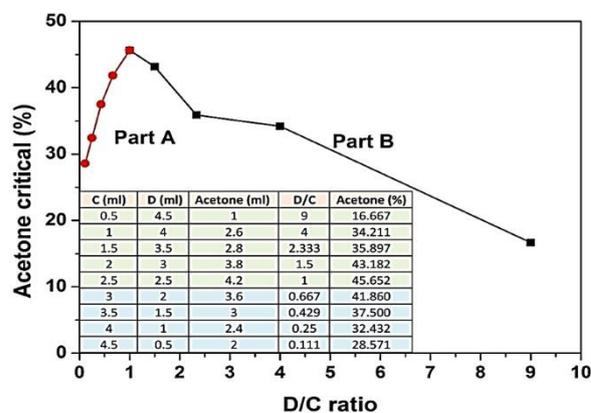
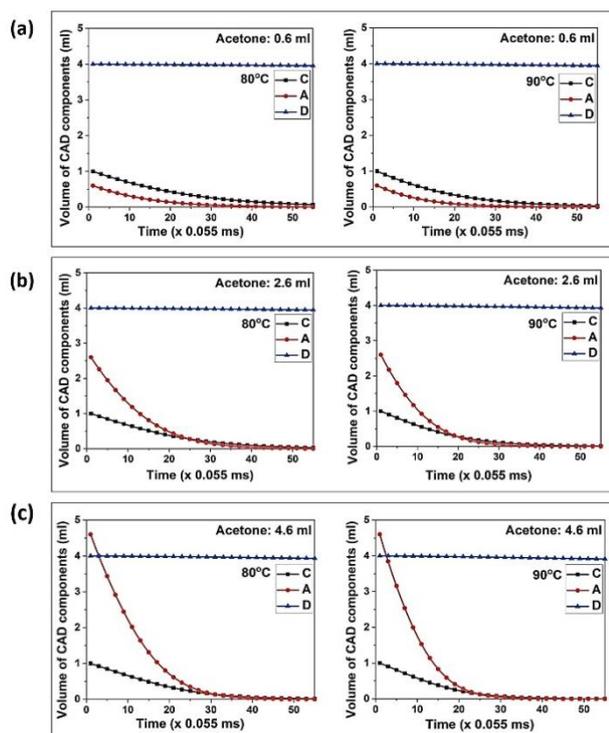


Fig. 2 – Variation in the critical volume of acetone as a function of DMSO/cyclohexane ratio

It is observed that as the D/C ratio increases up to 1,  $V_c$  also increases. Thereafter, as the D/C ratio rises beyond 1,  $V_c$  decreases. This determination of  $V_c$  as a function of D/C ratio helped us to predict the state of the microemulsion during solidification. For DMSO (4 ml) + cyclohexane (1 ml) mixed solvent system, we examined the variation in solvent volumes as a function of time, for three different volumes of acetone viz. acetone volume (0.6 ml) less than  $V_c$ , acetone volume (2.6 ml) equal to  $V_c$  and acetone volume (4.6 ml) greater than  $V_c$ . The results are shown in Fig. 3.

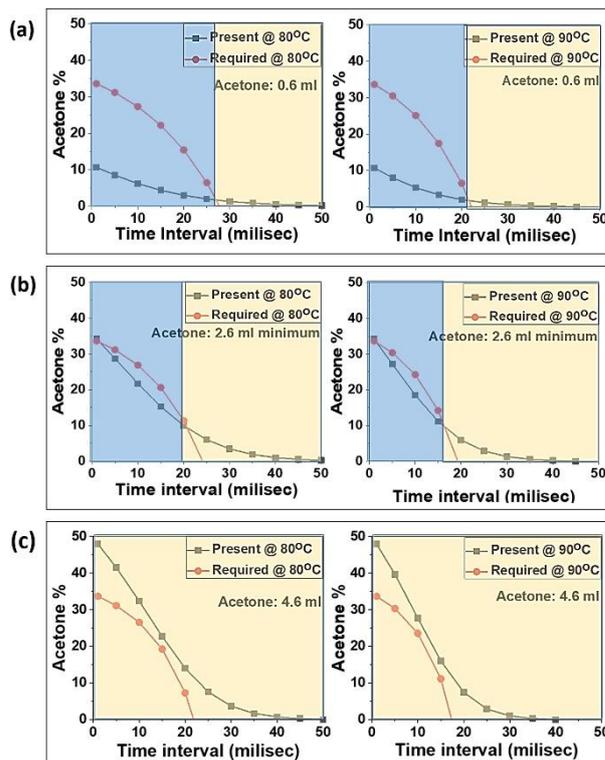


**Fig. 3** – Variation in the volume of solvents cyclohexane (C), DMSO (D), acetone (A) as a function of time for three different volumes of acetone viz. acetone volume: less than [Row a], equal to [Row b] and greater than [Row c] critical volume of acetone ( $V_c$ ), for two substrate temperatures in each case

It is clear that the D/C ratio, which demands a specific  $V_c$  for stability, is also a function of time during solidification. Therefore, the stability of the microemulsion at any instant will be determined by the D/C ratio and the acetone volume present at that instant in the solidifying film. At any instant, the acetone volume actually *present* (say,  $V_p$ ) in the solidifying film and the critical acetone volume *required* (based on D/C ratio) at that instant (say,  $V_r$ ) can be computed. If  $V_p > V_r$ , the microemulsion will be stable, otherwise it will be unstable. The variation of  $V_p$  and  $V_r$  as a function of time for three different cases and for two substrate temperatures in each case is shown in Fig. 4. During solidification, the timeslot during which the emulsion is stable is shown by yellow shading, and the timeslot in which the emulsion is unstable is shown by blue shading.

It can be observed that for a microemulsion with an initial acetone volume less than or equal to  $V_c$  (Fig. 4a and Fig. 4b), the microemulsion is unstable during the initial deposition time interval (whose extent is determined by the substrate temperature). However, it then becomes stable due to the change in the D/C ratio during solidification. For a microemulsion with an initial acetone volume much higher than  $V_c$  (Fig. 4c), the microemulsion is stable during the total solidification process. This microemulsion dynamics can have significant effect on the morphology and therefore on the optoelectronic properties of thin films deposited by this way.

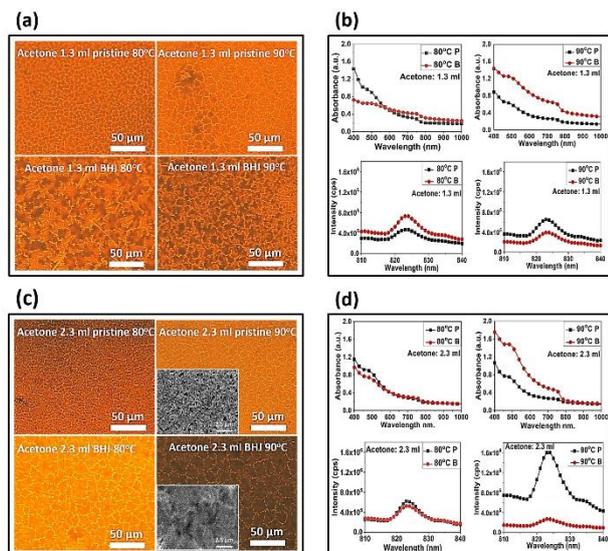
For acetone volume less than  $V_c$ , a stable microemulsion cannot be achieved. We, therefore, decided to focus our experimental study only on microemulsions with acetone volume equal to and greater than  $V_c$ .



**Fig. 4** – Variation of the acetone volume (%) actually present ( $V_p$ ) and the critical volume of acetone required (based on D/C ratio) at that instant ( $V_r$ ) as a function of time for three different cases and for two substrate temperatures

Thus, we performed experiments with an emulsion composition, in which in case (1) the acetone volume was equal to  $V_c$  (1.3 ml) and in case (2) the acetone volume was equal to that required to have a stable microemulsion till solidification (2.6 ml). Microemulsions were prepared for deposition of perovskite and perovskite-ICBA BHJ, and thin films were prepared in both cases using the slot-die method at two different substrate temperatures. In case (1), the fact that the microemulsion is unstable during the initial period and then achieves stability (as seen in Fig. 3b) leads to the formation of different morphology in BHJ compared to that in case (2), wherein the microemulsion is stable right from the disposal on the substrate to complete solidification. We expect to get its reflection in different structural and optoelectronic properties of thin films. The optical microscopic images, absorption and photoluminescence spectra are shown in Fig. 5. Optical microscope images in Fig. 5a for acetone volume of 1.3 ml and in Fig. 5c for acetone volume of 2.6 ml for two substrate temperatures in each case show the dependence of morphology on the microemulsion composition and substrate temperature. For films deposited with initial acetone volume exactly equal to  $V_c$ , the microstructure is observed to be dependent on the substrate temperature (Fig. 5a). Films formed at higher substrate temperatures show better absorption spectra. However, BHJ films deposited at both substrate temperatures do not show strong PL quenching (Fig. 5b). However, films deposited with initial acetone volume far greater than  $V_c$  to ensure the microemulsion stability throughout the solidification process (Fig. 5c) show encouraging

results. In this case, it is also observed that the microstructure is determined by the substrate temperature, and films formed at higher substrate temperatures show much better absorption spectra. Interestingly, BHJ films deposited at 90 °C substrate temperature show significant PL quenching (Fig. 5d), indicating the BHJ morphology formation for favorable charge transfer. SEM photographs of pristine and BHJ films deposited at these parameters are also shown in the inset in Fig. 5c. It shows the growth of a compact, pinhole free BHJ active layer compared to the pristine perovskite thin film. The band gap for all films was around 1.5 eV.



**Fig. 5** – (a) Microscopic images and (b) absorption and PL spectra: films deposited using a microemulsion with acetone volume equal to the critical volume ( $V_c$ ) of acetone. (c) Microscopic images and (d) absorption and PL spectra: films deposited using a microemulsion with acetone volume ensuring the microemulsion stability during complete solidification. The volumes of individual solvents were half of those taken in calculations used in Fig. 2

## 5. CONCLUSIONS

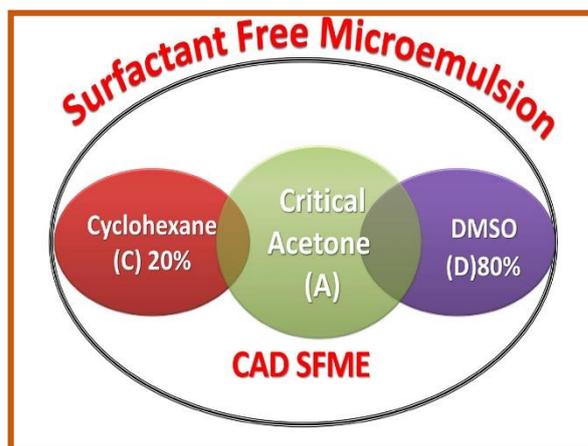
A model for the deposition of thin films using a microemulsion (specifically cyclohexane: acetone: DMSO) with the slot-die method is presented. The stability of the microemulsion needs a critical volume of acetone depending on the ratio of the other two solvents. The evaporation dynamics of the microemulsion simulated for different microemulsion compositions and substrate temperatures revealed the dynamics in ‘state of microemulsion’ during the solidification process. Its effect on the structural and optoelectronic properties of perovskite and perovskite:ICBA BHJ was also studied experimentally. Significant photoluminescence quenching was observed for a specific composition of the microemulsion with specific acetone fraction in it. This confirmed the BHJ morphology formation for favorable charge transfer. Thus, it can be concluded that the proper choice of the microemulsion composition, the acetone fraction in it and the substrate temperature in the slot-die method can lead to the desired BHJ morphology. Surfactant free microemulsion composition, leading to the active layer formation with

optimum performance, can be guessed based on the method presented in this article. The results indicate that this method can open a novel way of tailoring perovskite: organic BHJ for optimum performance in optoelectronic devices.

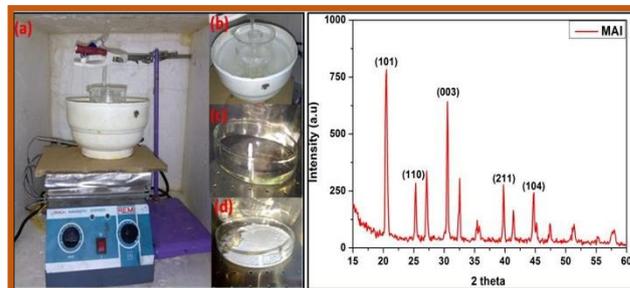
## ACKNOWLEDGEMENTS

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## APPENDIX



**Fig. A1** – CAD SFME System



**Fig. A2** – Experimental setup of MAI synthesis with the XRD spectrum for confirmation

## MAI Preparation and Thin Film Deposition

For the synthesis of methylammonium iodide (MAI) we used a methylamine (MA) solution (33 wt. % in absolute ethanol purchased from sigma Aldrich) and hydroiodic acid (57 wt. % in water purchased from Sigma Aldrich). 20 ml of HI was taken in conical flask and 18 ml of MA was slowly added in HI with the solution flow rate of 72 ml/h at 0 °C (maintained by ice bath) with the continuous stirring and under dark condition. The experimental setup is as shown in Fig. A2a and Fig. A2b. After 2 hours of continuous stirring, the reacted solution was poured in a cleaned Petri dish to obtain the white crystalline powder (Fig. A2c), which was then transferred into the vacuum oven maintained at 100 °C with 450 mbar pressure. The obtained white crystalline powder of MAI is shown in Fig. A2d. The XRD spectrum of the  $\text{CH}_3\text{NH}_3\text{I}$  powder is as shown,

which confirms the formation of pure  $\text{CH}_3\text{NH}_3\text{I}$ .

The pristine perovskite and perovskite-ICBA BHJ thin films were deposited by using the indigenously developed slot-die deposition method. For film deposition, the solution was supplied to the slot-die nozzle through a syringe pump with 5 ml/h solution flow rate

at the 5 l/min air flow rate.

The deposition was taken on the glass substrate to optimize the substrate temperature with constant deposition speed 1 mm/s at different substrate temperature ranging from 80 °C to 95 °C and ~ 10 % atmospheric humidity for different values of acetone.

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## Приготування об'ємного гетеропереходу перовскіт : фулерен з використанням схеми мікроемульсії без поверхнево-активної речовини. Моделювання, симуляція та експериментальні дослідження

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Перовскітний матеріал  $\text{CH}_3\text{NH}_3\text{PbI}_3$  продемонстрував відмінні оптоелектронні властивості для використання в сонячних елементах. Однак такі проблеми, як стабільність і несхожість у мобільності носіїв заряду, обмежують його застосування в сонячних елементах з об'ємним гетеропереходом (BHJ). Для підвищення стабільності та продуктивності сонячних елементів було докладено зусиль шляхом включення відповідного сполучного матеріалу в BHJ. Однак розчинність компонентів BHJ в одному розчині може створити проблеми при одностадійному синтезі BHJ. Тут ми звітуємо про нашу теоретичну та експериментальну роботу з отримання BHJ перовскіт : Indene  $\text{C}_{60}$ -Bisadduct (ICBA) з використанням схеми мікроемульсії без поверхнево-активної речовини (SFME) циклогексан:ацетон:DMSO (CAD), яка може вирішити проблему розчинності компонентів BHJ в одному розчині. Критична початкова об'ємна частка ацетону є важливою для підтримки стабільності мікроемульсії залежно від її складу. За допомогою теоретичного моделювання ми вивчили динаміку випаровування SFME з діапазоном початкового об'єму ацетону, який може перевести SFME із нестабільного стану в стабільний. Було помічено, що залежно від початкової об'ємної частки ацетону та температури підкладки тонка плівка SFME на підкладці, що твердіє, може переходити через різні стани, пов'язані з її стабільністю. Це може мати помітний вплив на структурні та оптоелектронні властивості BHJ. Експериментальні дослідження підтвердили ці прогнози. Даний метод може відкрити новий шлях виготовлення BHJ перовскіт : органічний для оптимальної роботи в оптоелектронних пристроях.

**Ключові слова:** Перовскіт, Об'ємний гетероперехід (BHJ) перовскіт:ICBA (BHJ), Мікроемульсія без поверхнево-активної речовини (SFME), Моделювання, Контроль морфології через склад мікроемульсії.