# Crystallisation of Organic Molecules with Remarkably Suppressed Coffee-

# ring Effect by Drop-drying Process Using Binary Solvent Core-shell

## **Droplets**

Yoolim Ahn,<sup>1,2</sup> Yohwan Park,<sup>1,2</sup> Jin Young Koo,<sup>1</sup> and Hee Cheul Choi\*<sup>1,2</sup>

1 Center for Artificial Low Dimensional Electronic Systems, Institute for Basic Science (IBS), Pohang 37673, Republic of Korea

2 Department of Chemistry, Pohang University of Science and Technology (POSTECH), Pohang 37673, Republic of Korea.

## **Table of Contents**

1.	Experimental Procedures	3
2.	Supporting Figures	
2.1	Phase separation of methanol/mesitylene binary solvent in vial system (Fig. S1-S3)	4
2.2	Covering mesitylene on MB/methanol droplet (Fig. S4)	7
2.3	Quality of crystals synthesized from different solvent mixture (Fig. S5)	8
2.4	Versatility test of the core-shell drop-drying (CSDD) method (Fig. S6-S7)	9
2.5	UV-VIS Absorption Spectra of solutions at different V <sub>mesitylene/MeOH</sub> (Fig. S8)	.11
2.6	Additional information of crystals synthesized at different C <sub>MB</sub> (Fig. S9-S10)	.12
2.7	Crystal growth direction control during <b>CSDD</b> process (Fig. S11)	.14
2.8	Low magnification SEM image of MB crystals obtained at $C_{MB}=2$ mg/mL (Fig. S12)	.15
3. I	References	.16

### **1. Experimental Procedures**

purchased without All chemicals were used as further purification. 3.7bis(dimethylamino)phenothiazin-5-ium chloride (methylene blue, MB) powder (2 mg, Sigma Aldrich, dye content≥82 %) was dissolved in a mixture of methanol (2 mL, JT Baker, HPLC) and mesitylene (2 mL, Sigma Aldrich, 98%), then ultrasonicated for 10 minutes to make a homogeneous solution. The drop-drying crystallisation was performed by dropping 8 µL of the MB/methanol/mesitylene solution was on a target solid substrate, such as Si or SiO<sub>2</sub>/Si wafer, which was then allowed to dry completely, which takes about 8 minutes. Irregular precipitates were formed when the solution composed of MB (2 mg) and methanol (4 mL) are drop-dried on a Si or SiO<sub>2</sub>/Si wafer. For control experiments, the drop-drying crystallisation was attempted at various solute conditions: (1) to examine the solute effect, the concentration of MB was varied from 0.5 mg/mL to 1 and 2 mg/mL, and (2) to examine the solvent effect, the volume ratio of methanol and mesitylene (V<sub>mesitylene/MeOH</sub>) was changed from 1 to 0, 0.25, 0.67, 1, 1.5 and 4. To characterize the morphology of the crystals, SEM images were obtained using a JEOL, JSM-7410F instrument. Each crystal was coated by Pith platinum for 20 seconds in 40 mA current to prevent the damage of crystals by electron beam. To examine the crystal structure, powder X-ray diffraction data were obtained using synchrotron radiation ( $\lambda = 1.23984$ Å) at the 5D beamline in Pohang Accelerator Laboratory (PAL). All obtained data were converted to Cu K $\alpha$  ( $\lambda$ = 1.54056 Å) radiation for better comparison with the reference. All UV-VIS spectra were obtained using a spectrophotometer (Shimadzu 2600). <sup>1</sup>H NMR spectra were collected using a 500 MHz NMR spectrometer (Bruker Avance III Ascend 500).

### 2. Supporting Figures



#### 2.1 Phase separation of methanol/mesitylene binary solvent in vial system

**Figure S1.** Evaporation-induced solution phase separation in a vial system. (a) Photographs of the solutions in vial. Homogeneous MB/methanol/mesitylene solution in a vial with a cap closed (left), and the same solution in a vial open to air (right). After keeping at room temperature for 6 hours, the solution was separated into two phases only in the opened vial where solvent could evaporate, but the homogeneous solution was maintained in the closed vial. (b) Photographs of immiscible layers before and after mixing by hand shaking



**Figure S2.** Evaporation-induced solution phase separation in a vial system. (a-b) Photographs of the MB/methanol/mesitylene solutions in (a) opened and closed vial and (b) them after 6 hours (c-e) <sup>1</sup>H-NMR spectra of (c) the original MB/methanol/mesitylene solution, and (d, e) upper and lower part of the phase-separated MB/methanol/mesitylene solution, respectively. Each solution was diluted by CD<sub>3</sub>CN. The orange and yellow circles indicate hydrogens in mesitylene and green circles indicate hydrogens of methanol. From these spectra, the solvent composition in each phase was calculated. The upper part had a solvent composition of mesitylene:methanol=0.107:0.893, and in the lower part it was 0.904:0.096.



**Figure S3**. Photograph of the MB/methanol/mesitylene solution that were kept at different temperature (14°C: left, 25°C: middle, 65°C: right) for 24 hours. At all temperature, one vial was kept opened and the other was kept closed. For all the temperature cases, results were same; solution was separated in open systems but, not in close systems. The only difference that temperature change makes is the solution separation rate; at higher temperature (65°C), the solution separation rate was faster than at lower temperatures due to the high evaporation rate at high temperature.

## **2.2** Covering mesitylene on the MB/methanol droplet



**Figure S4**. Schematic illustration and optical microscopic images of covering mesitylene on top of the MB/methanol droplet. (1) Dropping a droplet of MB/methanol solution on a substrate, (2, 3) Covering the droplet with an extra mesitylene solvent. (4) After complete dry of the solution.

#### 2.3 Quality of crystals synthesized from different solvent mixture



**Figure S5**. PXRD patterns of the crystals obtained from methanol/mesitylene solvent mixture (black), IPA/mesitylene solvent mixture (red) and methylene blue powder (blue). Simulated PXRD pattern of previously reported crystal<sup>1</sup> is represented by dark cyan color.

#### 2.3 Versatility test of the CSDD method

In order to test the generality of the binary solvent composed of methanol and mesitylene, we tried other solutes than MB. Several dye solutes, such as methyl orange, methyl red and phthalocyanine were examined. Phenothiazine, a well-known p-type semiconductor<sup>2</sup>, but lacks a solution-based method for growing them into morphologically well-defined crystals, was also examined, and the crystals were successfully grown into parallelepiped shape with well-defined facets from the core solvent, while shapeless crystals were grown from the shell solvent region (Fig. S6). We believe that it was resulted by the dissolved phenothiazine molecules in the shell, which enabled crystal growth even if the core is shrunk and the seed of the crystal is out of the core. In the case of methyl orange, crystals were grown, but in the cases of methyl red and phthalocyanine, crystals were not formed, instead they appeared like films on the substrate (Fig. S6, S7). The same solvent composition was used so the core-shell solvent separation occurred in all cases. However, the concentration in each solvent was quite different. For methyl orange, the concentration in the core solvent was higher than that of shell solvent as it can be assured from deeper colours in Fig. S6. In this case, diffusion of core solvent to shell solvent enable the molecules to reach supersaturation state so the crystals grew as same as methylene blue case. In contrast, for phthalocyanine dye and methyl red, the concentration of core and shell solvent did not show significant difference. If there is no significant difference in concentration or if it is more soluble in shell solvent, no supersaturation state is formed in the core solvent even after completely dissolving of core solvent to shell solvent. Taken together, it is necessary to have high solubility difference between core and shell solvent, which is high in core solvent and low in shell solvent.



**Figure S6**. Other examples of crystallisation by **CSDD** method: methyl orange (top row) and phenothiazine (bottom row). The methyl orange crystals were grown into a square plate shape in the core solvent similarly to the case of methylene blue, while no meaningful crystallisation was observed in the shell solvent region. The phenothiazine crystals were grown into a parallelepiped shape with well-defined facets in the core solvent, while shapeless crystals were grown in the shell solvent region. The scale bars in all images indicate 100 µm



**Figure S7**. Examples of unsuccessful crystallisation by **CSDD** method: 2,9,16,23-tetrakis(phenylthio)-29H,31H-phthalocyanine (phthalocyanine dye) and methyl red (scale bar: 100  $\mu$ m). Different from MB case, core and shell did not show a significant colour difference, which indicates that there was no solubility difference between core and shell.



2.4 UV-VIS Absorption Spectra of solutions at different  $V_{mesitylene/MeOH}$ 

**Figure S8**. UV-VIS absorption spectra of the MB/methanol/mesitylene solutions that have different methanol/mesitylene volume ratios. The inset indicates the peak of  $\pi$ - $\pi$ \* transition.

## 2.5 Additional information of crystals synthesized at different $C_{\text{MB}}$

The crystallographic orientation of lateral-grown MB crystal was determined by face indexing of the single crystal using a Bruker APEX II QUAZER instrument in house (Figure S9). Crystal dimension was confirmed by optical microscopy.



Figure S9. Face indexing of the lateral-grown MB single crystal.



**Figure S10**. PXRD patterns of the crystals synthesized from 0.5 (black), 1 (red), 2 (blue) and 4 (dark cyan) mg/mL of MB/methanol/mesitylene solutions. For comparison, precursor MB powder (magenta) and calculated pattern from the reference<sup>1</sup> (dark yellow) are also shown. The numbers under the peaks indicate corresponding planes that are calculated from the reference structure of MB.

#### 2.6 Crystal growth direction control during CSDD process

In order to confirm that the concentration change could induce significant difference on the surface tension, MB/methanol solutions with the concentration of 5 mg/mL and 40 mg/mL were dropped on the hydrophobic CYTOP substrate, which was designed to mimic the environment of the hydrophilic core covered by hydrophobic shell. As a result, the contact angle was increased when the MB concentration was increased, which means high surface tension. Since MB is an ionic salt, its high concentration leads the difference in surface tension<sup>3</sup> and it induces the difference in Marangoni flow, which consequentially changes the environment of core droplets. At low concentration dominates the Marangoni flow that is responsible for the force inducing crystal growth in a lateral direction dominates the Marangoni flow that is responsible for the vertical force inducing crystals. At high concentration of solute, on the other hand, the situation becomes completely opposite, that is Marangoni flow dominates over capillary flow, resulting in high yield vertically grown crystals<sup>4</sup>.



**Figure S11**. (a) Schematic illustration of the determining preferred growth direction and (b) optical images of the droplet of MB/methanol solution with different concentration (5 mg/mL, 40 mg/mL) on a hydrophobic CYTOP substrate.

2.7 Low magnification SEM image of MB crystals obtained at C<sub>MB</sub>=2 mg/mL



**Figure S12.** (a) Low magnification SEM image of MB crystals synthesized from 2 mg/mL MB/methanol/mesitylene solution. (b) Schematic illustration of the environment for the vertical growth of MB crystals. Crystal growth is restricted by the boundary of core droplets, which supports the role of reaction vessel.

### 3. Reference

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