# A highly efficient sublimation purification system using baffles with orifices

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**Abstract**

Here we report a highly efficient sublimation purification system using baffles with orifices in the sublimation tube. It is clearly demonstrated that the purity of materials is increased largely by introducing some pieces of baffles with orifices in the high-temperature region (sublimation region), which was confirmed by comparing the melting point ($T_m$) and the high-performance liquid chromatography (HPLC) purity with those of purified one by a conventional system. The driving voltages of electro-luminescence (EL) devices were also compared and showed the same tendency with the $T_m$ and HPLC purity data. Not only the purity but also the effective yield of purified materials was also increased by introducing baffles in low-temperature region. Some

expected mechanisms of improving the purification efficiency by introducing baffles were also discussed.

## 1. Introduction

With a significant progress in recent year in the fields of organic electronic devices such as organic light-emitting diodes (OLEDs), organic thin-film transistors (OTFTs), and organic solar cells (OSCs), the purity of the active materials became one of severe matters of concern [1-7]. Usually the impurities act as charge traps and significantly affect the charge transport in organic electronic devices [8,9]. Consequently, the impurities directly affect not only the performance but also the reliability of devices, which makes this impurity problem much more important in the commercialization of organic electronic devices [1-3,10-15].

For the purpose of elimination of impurities from target materials, several purification methods have been used such as zone refining from the melt, chromatography and train sublimation technique, and so on [2,10,16-19]. Gradient sublimation purification technique, especially, is considered to be the most common method for the purification of organic semiconductors because most of the organic semiconductors are not solved enough in common organic solvents and do not have a liquid phase at atmospheric pressure or below [2,7,16]. In this method, the source material is sublimed in a long glass tube which is in a vacuum state with or without an inert gas flow. The elimination of impurities from target material is obtained by separated deposition of them on detached region, which is derived by a constant temperature gradient along the long sublimation tube. Usually, the target material grows

on the inside wall of the tube in a short distance from the sublimation region (high-temperature region), while more volatile impurities are evacuated or grow far away from the sublimation region, and nonvolatile impurities usually remain in the source boat. Because the main – almost the only – driving force of the separation between impurities and target materials is the temperature gradient of the long sublimation tube, it is essential to control the temperature gradient of the long sublimation tube very carefully for an efficient purification process.

With this technique, however, usually one cannot get a sufficient purity through just one purification process, and needs a couple of purifying processes to get a sufficiently high purity of target materials. Consequently, it consumes long time and a lot of source materials inefficiently [16,20]. After a couple of sublimation purification, one can get only 50 % or less from the first source materials. These drawbacks become more serious problems in the view point of low cost devices which is one of the most important competitive merits of organic electronic devices. Therefore the improvement of the purifying efficiency is urgently needed for the realization of low-cost and high-performance organic electronic devices.

Our research group has already reported a modified sublimation purification system using arrays of partitions [21]. By installing arrays of partitions in the sub-limation tube, the HPLC purity of 1,3-bis[2-(2,2'-bipyridine-6yl)-1,2,4-oxadiazol-5yl] benzene (Bpy-OXD) was increased from 99.37% to 99.73%. This increase of purity resulted in lowering the driving voltage of EL device (for luminance of 1000 cd/$m^2$) as large as 1 V (from 4.7 V to 3.9 V), and increasing the lifetime of device 1.5 times longer (from 50 h to 79 h). In that system, however, some inherent problems exist and hinder us in commercializing as an efficient purification system. One is the difficulty of

extracting the purified materials from the array of partition. Although the final yield was almost the same with that of a conventional method, it is very difficult and time-consuming to extract the purified materials deposited on the array of partition, especially on the junction parts between partitions. Another problem is the existence of undivided region by partitions – the surface of glass tube – which is almost the same state with the conventional method.

In this paper, we report a highly efficient sublimation purification system using baffles with orifices to solve those problems mentioned above. The purity and the effective yield of purified materials were improved simultaneously by introducing baffles with orifices in the sublimation glass tube.

## 2. Experimental

### *2.1 New purification system*

The new sublimation purification system developed in this study was shown schematically in Fig. 1. There are two heaters; one is for the sublimation of materials and set on the high-temperature ($T_h$) region (Heater 1, 10 cm in length), and the other is for temperature gradient of long glass tube which is set on the low-temperature ($T_l$) region where purified materials are deposited (Heater 2, 20 cm in length). The sublimation tube is a 70 cm long quartz tube (40 mm in external diameter, 2 mm in thickness), and the pressure in the tube was controlled 1 Pa or 80 Pa with an Ar gas (99.9999%) flow.

Several pieces of baffles (32 mm in diameter) with orifices were inserted between

inner glass tubes (32 mm in diameter), and they were attached each other tightly enough to prevent leakage of purified materials through joint chinks between inner tubes and baffles. Two groups of baffles were introduced separately in $T_l$ region and $T_h$ region, respectively. The number of baffles, hence the interval between baffles, was changed from 0 to 2 or 3 (20 mm and 10 mm intervals, respectively) in $T_h$ region. The intervals between baffles in $T_l$ region were also changed from 20 mm to 50 mm. Baffles were installed very carefully not to align orifices straightly between neighbored ones. A photograph of Fig.1 (b) shows the set of 3 pieces of baffles in $T_h$ region and 50 mm interval in $T_l$ region.

We have used mainly two kinds of baffles with different orifices; one has two orifices (10 mm in diameter) and another four (7 mm in diameter), as shown in Fig. 1 (c). We have also used two kinds of materials for the baffles; stainless steel (SS) and quartz. The percentage of open areas (orifices) is about 25%, and the thickness is 2 mm for all kinds of baffles.

We have also modified the source boat to be a similar shape with the inner glass tube having a narrow orifice on the rear side to prevent a reverse flow of sublimed materials as shown in Fig.1 (a) and (b). Several pieces of glass tubes whose diameter is the same with the inner glass tube were installed on the rear of the source boat up to the gas inlet for the guidance of Ar gas into the source boat through a narrow orifice. Otherwise most of Ar gas flow outside of the source boat not into it because of a narrow orifice of the source boat, which resulted in 2 times longer sublimation time.

*2.2 Evaluation of purification efficiency*

For the evaluation of purification efficiency of a new purification system, we used three organic materials; bathocuproine (BCP, TCI, 97%), tris(8-hydroxyquinolinato) aluminum(III) ($Alq_3$, TCI, > 95%) and 1,3-bis[2-(2,2'-bipyridine-6yl)-1,2,4-oxadiazol-5yl]benzene (Bpy-OXD, Hodogaya Chemical Co., Ltd., > 99%), whose molecular structures are shown in Fig. 2. We have purified these materials under various conditions – mainly changing the interval between baffles inserted in $T_l$ region and the number of baffles inserted in $T_h$ region with various kinds of baffles described at the previous section –, and compared the purification efficiency with that of conventional method.

As the factors for purification efficiency, we have evaluated and compared the purity (for BCP and Bpy-OXD) and the yield (for $Alq_3$ and BCP) of purified materials. For the evaluation of the purity factor, we have measured the melting point ($T_m$) of purified materials with the differential scanning calorimetry (DSC, Seiko Instruments, DSC6200, 2˚C/min heating condition). We have also compared the driving voltages to get 10 mA/cm$^2$ ($V_{10J}$) and 100 mA/cm$^2$ ($V_{100J}$) of EL devices whose structure is shown in Fig. 2 (d) schematically; all of the materials used in this study are electron transport materials, and used as the electron transport layer (ETL) in the EL devices. In general, $T_m$ goes up and driving voltage of EL device goes down as the purity is increased [7,19, 22,23]. For Bpy-OXD, we have also checked the HPLC purity and compared with the results of $T_m$ and driving voltages. The measurement condition of HPLC is as follow: Column: Inertsil ODS-2 (5 μm, 4.6 × 250 mm), Carrier: $CH_3CN$/ 0.05% TFA = 4/6, Rate: 0.9 ~ 1.0 ml/min, Temp.: 40°C, Det.: 254 nm. For the evaluation of the yield factor of purified materials, we have extracted carefully all of materials deposited at $T_l$ region which is divided by a fixed length, and made it as the total yield. Among them,

we have made the yield from a fixed section (50 mm length from the start of $T_l$ region) as the effective yield. And then we have calculated the ratio of the effective yield ($R_{EY}$) by dividing the effective yield with the total yield.

## 3. Result and discussion

### *3.1 Yield*

For the understanding of the effect of introducing baffles on yield, we have compared the total yield and the effective yield of purified BCP under various purification conditions, and some representative results are shown in Fig. 3, and summarized in Table 1. When we compared the total yield, we cannot get any relation between the total yield and the purification condition. In some conditions the total yield was increased compared with the conventional method, and in another conditions the yield was decreased. However, when we compared the effective yield – yield from the first glass tube with 50 mm length where is considered to collect the highest purity materials – it was found that the effective yield was increased by introducing baffles in all conditions. These increases became clearer by comparing $R_{EY}$, as shown in Table 1. In a conventional method, $R_{EY}$ was about 73%, and it was increased up to about 78% by introducing baffles. If we consider that yields from the first baffle in $T_l$ region were about 8% which are not concluded in the effective yields, these increases are much more meaningful.

This result strongly suggests that the purified materials are deposited more concentrated region by introducing baffles, which means that purified materials can be

extracted from narrower region. This may be related not only to the efficiency of extraction but also to the purity of extracted materials since more pure materials can be deposited on narrower region.

To elucidate the effect of introducing baffles on the yield more clearly, we have changed the intervals between baffles in $T_l$ region, and investigated whether there are any relations with the effective yield. The results with $Alq_3$ are summarized in Fig. 4 and Table 2. The intervals were controlled to be from 50 mm to 20 mm (Fig. 4 (b) ~ (e)), and compared with a conventional method (Fig.4 (a)). At first, when we compare the effective yield from the marked region by two blue lines whose width is about 13 cm, it seems that there is not any relation between the intervals and the effective yield. However when we look at the $R_{EY}$, it is clear that the $R_{EY}$ is increased as the intervals are shortened. Considering 13 cm is quite broad region in this purification system, this clear relation between the intervals and the $R_{EY}$ affords proof of the effect of introducing baffles on the yield mentioned above. When we compare the width of region where 50 % yield was obtained, we can grasp this effect even more clearly. As shown in Fig. 4, yield 50 % lines were shifted to $T_h$ region as the intervals were shortened, which means that purified materials were deposited more compactly by introducing baffles and the deposition region was narrowed as the intervals was shortened.

In this section, it was clearly described that baffles introduced in $T_l$ region make purified materials deposited on more concentrated region which was revealed with increased $R_{EY}$ value.

*3.2 Purity*

To evaluate the effect of introducing baffles on the purity clearly, we have used Bpy-OXD which is relatively easy to get HPLC purity data and to compare another data such as $T_m$ and driving voltages of EL devices. It is also possible to compare this new purification system with the former one of our research group because it was also used in the former purification system.

All of results for Bpy-OXD were summarized in Table 3. We have used two kinds of baffles; QA has two orifices and QB four which are shown in Fig. 1 (C), and both of them are made of quartz. We have purified Bpy-OXD with introducing two or three baffles in $T_h$ region – totally four kinds of sets; QA2, QA3, QB2, QB3 – and compared the purity data of them with those of non-purified (Raw) one. We have also purified with a conventional method (without baffles, No or Conv.), and compared it with the above data. In all case, the purified materials were extracted from the first inner glass tube of $T_l$ region with a length of 50 mm. The intervals of baffles in $T_l$ region were also fixed as 50 mm. The yields of purified Bpy-OXD have shown the same tendency with those of mentioned in the former section, and are not mentioned in this section any more.

At first, we have checked the melting point ($T_m$) of purified materials with DSC, and the results were shown in Fig. 5. $T_m$ was measured from a point of intersection of two tangent lines of DSC curves, as shown in Fig. 5. The value of half width at half maximum (HWHM) of the peak was also calculated. The right half parts of all peaks are almost the same with each other, and we calculated only the left part of HWHM. In general, $T_m$ goes up and HWHM becomes narrow as the purity gets higher [22]. As summarized in Table 3, $T_m$ was increased abruptly and HWHM also got narrow after

purification. These behaviors show us that the material purity was increased by the purification process definitely. The most important thing is that all of the materials purified with introducing baffles have higher $T_m$ and smaller HWHM than those of material purified by a conventional method even though the differences are not so remarkable.

We have also made EL devices of purified Bpy-OXDs with a device structure shown in Fig. 2, and compared their driving voltages to get 10 mA/cm$^2$ ($V_{10J}$) and 100 mA/cm$^2$ ($V_{100J}$). As shown in Fig. 6 (a) together with $T_m$ graphically, $V_{10J}$ and $V_{100J}$ show almost the same tendencies with $T_m$. These changes of $V_{10J}$ and $V_{100J}$ show us another strong evidence of increased purity by introducing baffles in $T_h$ region.

Finally, we have measured HPLC purity of all purified Bpy-OXDs. The purity of the raw material before purification is 99.27%. After purification with a conventional method, the purity is increased to 99.80%. By introducing baffles, the purity is increased more largely upto 99.95% (QA2 and QB2). This purity increase comes to be more obvious when we compare the decrement of the impurities; percentage of the decrease of impurity content after the purification against the raw material. For a conventional method, the decrement is 72.6% (from 0.73% to 0.20%). For the new system, the decrement is increased up to 93.2% (from 0.73% to 0.05%). This is very striking value because we can get only 92.5% value at the best after twice purifications by a conventional method even when we apply the same decrement for the second purification cycle. Generally, it becomes more difficult to eliminate impurities from purer materials, and we can expect the decrement value of the second purification cycle to be smaller than that of the first cycle. Consequently, the decrement value of 93.8% is even more meaningful and cannot be easily attained even we make purification twice

with a conventional method. This value is also far better than that of the former purification system we have reported before although the purity of the starting material was somewhat different. The former system showed only 71.8% decrement (from 0.96% to 0.27%) [21]. This large difference can be a strong evidence that this new purification system has been improved greatly by solving the problems of the former system mentioned in section 1. The main solution may be the full separation of deposition area of purified materials by introducing baffles.

It is also valuable to mention that the tendency of $T_m$ (accordingly the driving voltage of EL devices) is almost the same with that of HPLC purity, as shown in Fig. 6 (b). This means that we can compare the purity of materials indirectly by comparing $T_m$ and/or the driving voltages of EL devices instead of HPLC measurement. Because most of organic electronic materials are not easily soluble in general organic solvents, it is difficult to measure the purity directly by HPLC. In that case, we can estimate the purity of purified materials indirectly by comparing the $T_m$ and/or the device performance made of it.

In this section, it was clearly described that the purity of purified materials was increased largely by introducing baffles in $T_h$ region. The impurity decrement becomes 93.2% value by introducing baffles which is expected to be better than that of twice purified ones by a conventional method.

*3.3 Comparison with a conventional method*

As described in the previous two sections, the yield and the purity of the new purification system are enhanced largely comparing with a conventional method. It

seems, however, that we need much more intuitive evidence for the enhancement of purification efficiency of this new system. For this purpose, we have repeated the purification of BCP three times with a conventional method, and compared its yield (from the first 50 mm glass tube) and purity with those of purified one just once by the new purification system (QB2 condition). The results are summarized in Table 4.

At first, the yield of purified BCP was decreased as the purification is repeated, and the final yield after repeating three times was 14.9%. This means that we can get just 0.15 g of purified BCP from 1 g source BCP after repeated purification three times. This result show us that how serious the wasting materials is in repeating purification. On the other hand, the yield of the new system was 64.5%, and is reasonable value considering only 0.5 g BCP set in the source boat.

We have checked the driving voltages of EL devices made of purified BCPs. Surprisingly, the driving voltage was increased after the $2^{nd}$ purification [24]. It was lowered again largely after the $3^{rd}$ purification, but it was still higher than the value for purified one by QB2 condition. This result means that the purity of BCP purified three times by a conventional method is still lower than that of BCP purified just once by the new system. When we consider the yield simultaneously, this result shows us very clearly and intuitively how efficient this new purification system is. We can get at least 4 times larger quantity of purified materials – even the purity is much higher – by using this new purification system instead of a conventional method.

*3.4 Dicussion*

It was clearly demonstrated that the purifying efficiency (both of the yield and the

purity) has been improved in the new sublimation purification system. This improvement is definitely due to introducing baffles in the sublimation tube. In this section, we want to discuss what kinds of mechanisms work to improve the purifying efficiency by just introducing baffles with orifices.

At first, the dominant mass transport mechanism is diffusion in this system because the pressure is controlled to be 1 Pa or 80 Pa with an Ar gas flow. In this pressure condition, the mean free path ($l$) of sublimed materials will be from a few millimeters to several tens of micrometers [25,26]. Because both of the diameter of orifices in baffles and the intervals between baffles are larger than $l$, we don't need consider the effusion process. Actually, it is still unclear for the present what the exact role of baffles is, but at least three kinds of mechanisms are under consideration and acceptable quite reasonable ones.

The first is that the collision of sublimed materials with baffles can enhance the collapse of clusters into individual molecules which can result in promotion of impurity separation from target materials. In principle, materials are sublimed and deposited in a molecular state in sublimation purification method. However, it is well known that materials are diffused not only in a molecular state but also in a cluster form in a real purification system. If there is an impurity molecule in the cluster, that impurity will be deposited on the same region with target materials. In this new purification system, clusters can undergo frequent collision with baffles and glass tubes, and be collapsed into smaller clusters or even into individual molecules. These collapses of clusters can promote the separation of impurities from the target material, and result in increase of the purity of deposited materials.

The second is that the travelling distance of sublimed materials unto deposition

points can be extended by introducing baffles. Sublimed materials which may be directly diffused unto deposition region without baffles can collide with baffles and change its diffusion direction and result in the increase of travelling distance. Because there are a few baffles at least and the orifices are not aligned straightly each other, the collision of sublimed materials with baffles can be occurred very often, and the travelling distance may be increased very largely. This increase of travelling distance can lead to the enhanced separation of impurities from target materials.

The third is that baffles installed in $T_l$ region can suppress the efflux of purified materials out of the extraction region. Some of purified target materials can be flowed out of the extraction region and grow far away from the sublimation region together with impurities, which is one of the serious causes of lowering the purification yield. Baffles installed in $T_l$ region can block such efflux of purified materials and return them into the extraction region, which can increase the effective yield. Such a role of baffles installed in $T_l$ region may be related not only to the effective yield but also to the purity of extracted materials as mentioned in section 3.1.

## 4. Summary

We have developed a highly efficient sublimation purification system using baffles with orifices in the sublimation tube. It was described that baffles introduced in $T_l$ region made purified materials deposited on more concentrated region which was revealed with increased $R_{EY}$ value. It was also clearly demonstrated that the purity of purified materials was increased largely by introducing baffles in $T_h$ region. The impurity decrement increased up to 93.2% by introducing baffles from 72.6% in a

conventional method, which is expected to be better than that of twice purified ones by a conventional method. From the results of multiple purification of BCP by a conventional method, it was also proved that one can get at least 4 times larger quantity of purified materials – even the purity is much higher – by using this new purification system instead of a conventional method. This improvement of purifying efficiency by introducing baffles in the sublimation tube was discussed briefly with three kinds of possible functions of baffles; collapsing clusters into individual molecules, extending travelling distance, and suppressing the efflux of purified materials.

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Table 1. Summary of the yield data of purified BCP under various conditions which are shown in Fig. 3.

| Condition | Total yield[1] (%) | Effective yield[2] (%) | $R_{EY}$[3] (%) |
|---|---|---|---|
| Conv. | 86.49 | **63.35** | **73.25** |
| A | 84.58 | **66.06** | **78.10** |
| B | 86.72 | **68.34** | **78.80** |
| C | 87.09 | **67.77** | **77.82** |

1. The quantity of BCP set in the source boat was 0.5 g.
2. A yield from the first glass tube with 50 mm length.
3. $R_{EY}$ = (Effective yield / total yield)×100

Table 2. Summary of the yield data of purified $Alq_3$ under various conditions with different intervals between baffles which are shown in Fig. 4.

| Interval (mm) | Total yield[1] (%) | Effective yield[2] (%) | $R_{EY}$[3] (%) |
|---|---|---|---|
| No | 74.88 | 71.92 | **96.05** |
| 50 | 73.43 | 70.65 | **96.21** |
| 40 | 72.33 | 69.90 | **96.64** |
| 30 | 77.88 | 75.48 | **96.91** |
| 20 | 74.64 | 72.73 | **97.44** |

1. The quantity of $Alq_3$ set in the source boat was 1.0 g.
2. A yield from the marked region of about 13 cm length.
3. $R_{EY}$ = (Effective yield / total yield)×100

Table 3. Summary of the purity data of various Bpy-OXDs. The relations between $T_m$ and the driving voltage, HPLC purity were also shown in Fig. 6 graphically.

| Baffles | # of baffles | $T_m$ (℃) | HWHM (℃) | $V_{10J}$ (V) | $V_{100J}$ (V) | HPLC Purity (%) |
|---|---|---|---|---|---|---|
| Raw | | **257.34** | 1.76 | **3.97** | **6.56** | **99.27** |
| No | | **261.83** | 1.32 | **3.71** | **6.00** | **99.80** |
| QA | 2 | **262.43** | 1.13 | **3.29** | **5.53** | **99.95** |
| | 3 | **262.14** | 1.22 | **3.41** | **5.67** | **99.81** |
| QB | 2 | **262.40** | 1.17 | **3.52** | **5.74** | **99.95** |
| | 3 | **262.39** | 1.25 | **3.59** | **5.71** | **99.93** |

Table 4. Summary of the yield and the purity data of multiple purified BCP with a conventional method, and purified BCP with the new system under QB2 condition.

| Condition | Yield (%) | Relative Yield[1] (%) | $V_{10J}$ (V) | $V_{100J}$ (V) |
|---|---|---|---|---|
| Raw | - | - | **8.97** | **12.49** |
| 1st | 70.8[2] | - | **7.65** | **11.50** |
| 2nd | 57.8 | 37.8 | **10.89** | **13.93** |
| 3rd | 47.9 | **14.9** | **7.59** | **11.52** |
| QB2 | **64.5**[3] | - | **7.45** | **11.03** |

1. Calculated against the BCP quantity set at the 1st cycle.
2. Yield from about 1.0 g.
3. Yield from about 0.5 g.

FIGURE CAPTIONS

Fig. 1. (a) A schematic illustration of the new sublimation purification system where baffles with orifices are inserted between inner glass tubes. (b) An example of set-up of the new purification system; 3 pieces of baffles in $T_h$ region and 50 mm interval in $T_l$ region. 90˚ twisted installing of baffles by turns not to align orifices straightly between neighbored ones is worthy of notice. (c) Representative two kinds of baffles with 2 and 4 orifices.

Fig. 2. Molecular structures of (a) bathocuproine (BCP), (b) tris(8-hydroxyquinolinato) aluminum(III) ($Alq_3$), and (c) 1,3-bis[2-(2,2'-bipyridine-6yl)-1,2,4-oxadiazol-5yl] benzene (Bpy-OXD). (d) EL device structure used in this study. All of purified materials were used to make the electron transport layer (ETL).

Fig. 3. Some representative results of purification of BCP under various purifying conditions; (a) a conventional method without introducing baffles, (b) introducing baffles only in $T_h$ region, (c) introducing baffles with four orifices in both of $T_h$ and $T_l$ regions, and (d) the same setting with (c) except the number of orifices of baffles (16 orifices).

Fig. 4. Results of purification of $Alq_3$ (a) with a conventional method (without baffles), and (b~e) with the new system under different intervals between baffles; (b) 50 mm, (c) 40 mm, (d) 30 mm, and (e) 20mm. The width of marked region by two blue lines is about 13 cm. Red lines represent the place to where 50 % yield was extracted from the

start.

Fig. 5. DSC curves of purified Bpy-OXDs with various purifying conditions which are defined by the color of line. The detailed conditions are explained in the text. Two tangent lines for the raw material and QA2 were also shown by dotted lines with the same colors with the main curves, which were drawn for measuring $T_m$.

Fig. 6. Graphical summaries of (a) $T_m$ and two driving voltages ($V_{10J}$ and $V_{100J}$), and (b) $T_m$ and HPLC purity. Note that the lines in graphics are just for visual guidance.

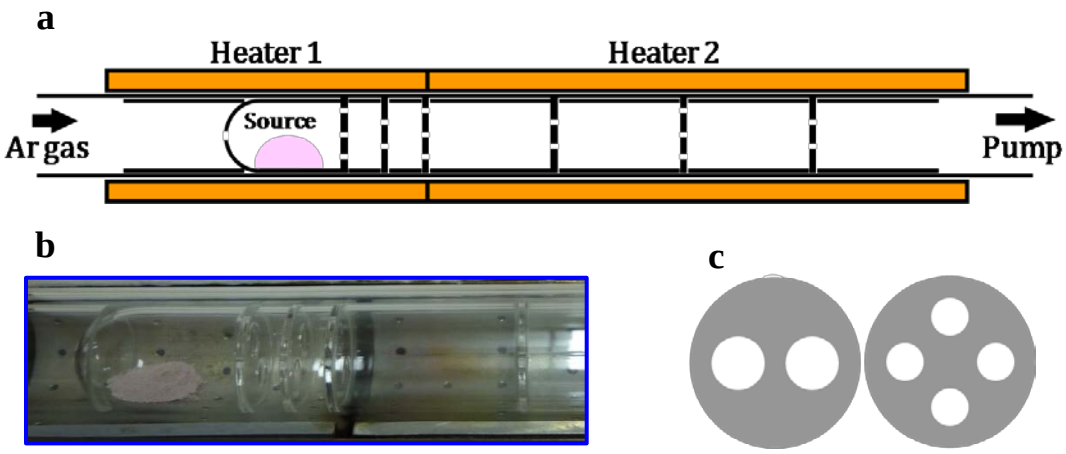
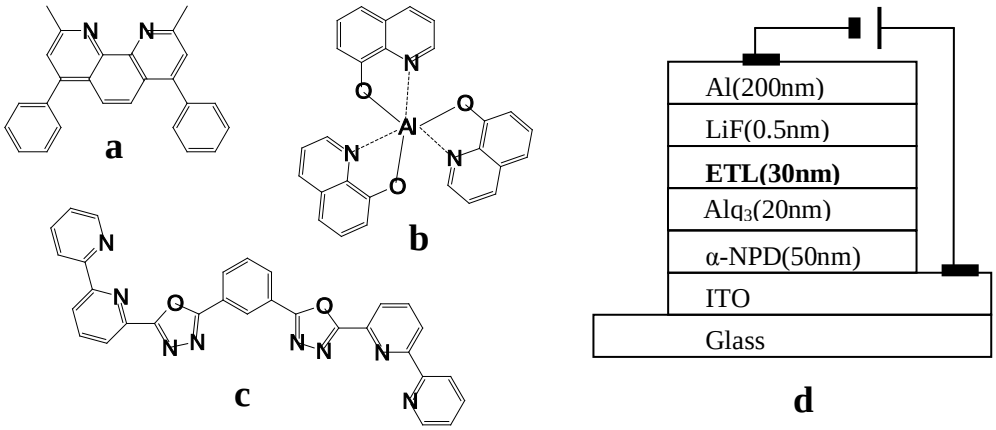



Fig. 1. (a) A schematic illustration of the new sublimation purification system where baffles with orifices are inserted between inner glass tubes. (b) An example of set-up of the new purification system; 3 pieces of baffles in $T_h$ region and 50 mm interval in $T_l$ region. 90˚ twisted installing of baffles by turns not to align orifices straightly between neighbored ones is worthy of notice. (c) Representative two kinds of baffles with 2 and 4 orifices.

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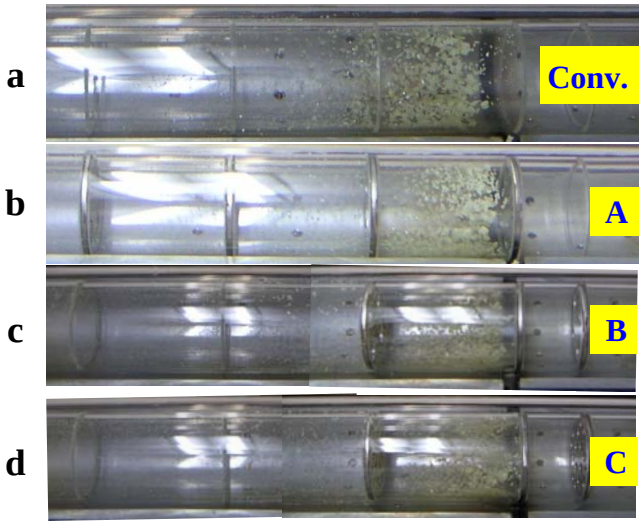


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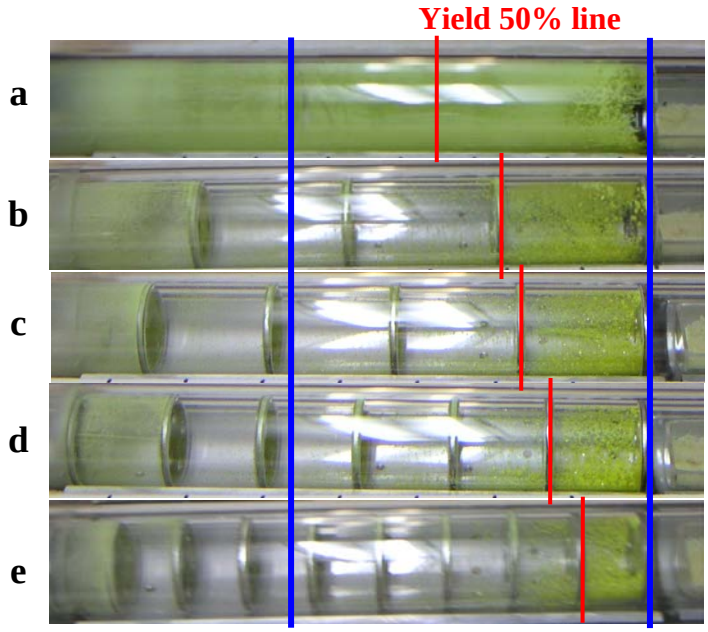


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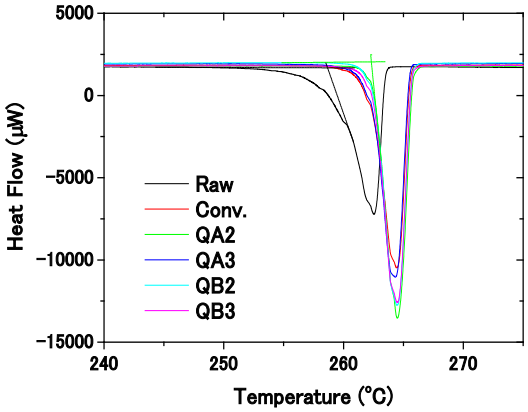


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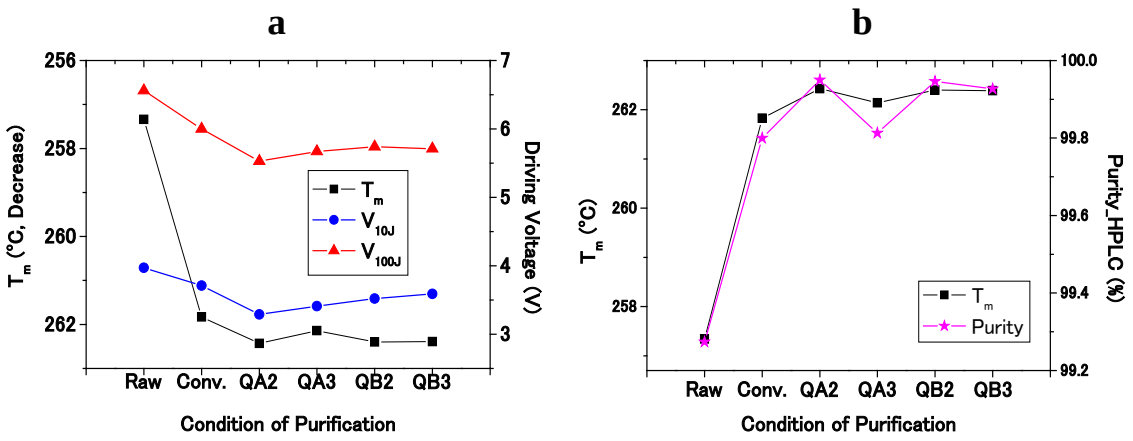


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