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Synthesis of N-doped Polyacenes and Single Crystal Growth by Flux Evaporation Method

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Abstract

We synthesized N-doped polyacenes TQPP, DDQP and BBQPP and their single crystals were prepared for structure determination and possible device applications. TQPP and DDQP can be synthesized and crystallized using *o*-dichlorobenzene as a solvent. Because BBQPP was insoluble in ordinary organic solvents, we have developed a new "Flux Evaporation Method" to obtain its single crystals. The crystal structure was determined by single crystal X-ray diffraction.

1. Introduction

Organic semiconductors gather much attention due to the practical applications such as thin-film transistors, solar cells and wearable electronic devices. Mobility is the one of the most important parameters of semiconductors. Desipte the continuous efforts to develop new semiconductor molecules, no molecules are reported to exceed the single crystalline Rubrene (~40 cm^2/Vs[1]).

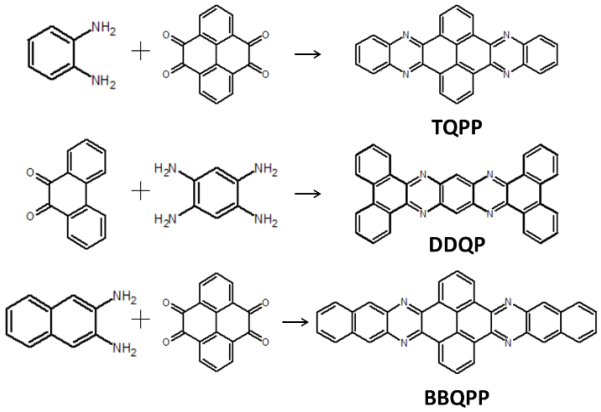
It is expected that the mobility become greater when the π-conjugated molecules (such as polyacene) become longer due to the enhancement of π-π interaction. However, a polyacene that is larger than hexacene is unstable in air. One of the strategies to stabilize polyacenes is introducing the pyrene structure and nitrogen (N) atoms. The problem of this method is that solubility becomes drastically lower as the molecule becomes larger. Many researchers introduced *tert*-butyl group and/or long alkyl group to increase the solubility. Unfortunately, substituent group disturb the π-π interaction between the molecules. In fact, the reported mobility of acenes with side chains is 10^{-4}~10^{-5} cm^2/Vs.[2]

In this study, we developed a new method "flux evaporation" to obtain single crystalline polyacenes without side chains. By using the newly designed equipment, BBQPP was successfully crystallized with a size of ~3 mm. Its crystal structure was determined by X-ray diffraction.

2. Experiment

Synthesis

We synthesized three N-doped acenes according to Scheme. 1 following literature.[2-4] TQPP and DDQP were recrystallized from *o*-dichlorobenzene, however, BBQPP cannot be recrystallized from *o*-dichlorobenzene due to the poor solubility. Hence, BBQPP was recrystallized from naphthalene as explained below.



Scheme. 1. Synthesis of acenes

Flux evaporation method

This method uses flux, which works as a solvent at elevated temperature but solid at room temperature. Here we used naphthalene as the flux. We prepared a H-shaped glass tube with an opening at one side. Then, BBQPP and naphthalene were put into one side (called sample side) of the tube. The tube was sealed under vacuum. The temperatures of the sample side and the other side (called flux collection side) were increased to 270°C and 280°C, respectively. When the BBQPP was completely dissolved in liquid naphthalene, the temperatures of the sample side and naphthalene side were slowly decreased to 125°C and 115°C, respectively.

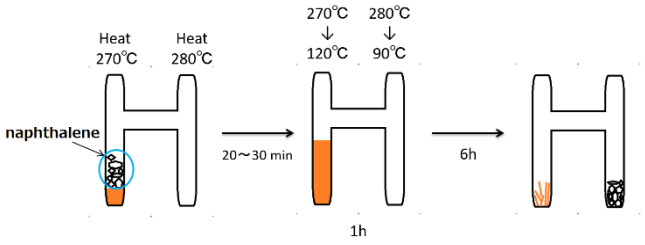


Fig. 1 Schematic of "Flux Evaporation Method"

3. Results and discussion

The synthesized TQPP, DDQP and BBQPP were characterized by NMR, FTIR and MALDI-TOF-MS. In NMR charts, all peaks were identical with the positions of the reported values[2-4]. C=O stretching vibrational mode in FTIR was disappear after the reaction. Molecular weights by MALDI-TOF-MS were mostly equal to the theoretical values. Therefore, we concluded that all molecules were successfully synthesized.

As seen in Fig. 2, TQPP, DDQP, BBQPP were obtained as yellow, red, and orange crystal, respectively, which indicates the difference of band gap values among molecules. They are all crystallized as needle-like crystals.

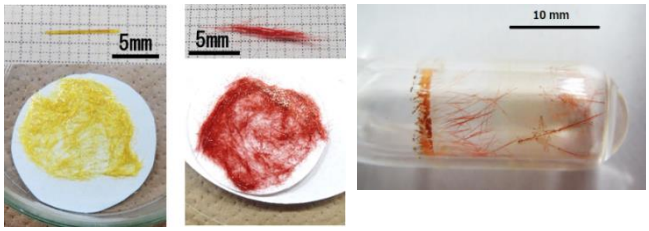


Fig. 2 Single crystals of TQPP, DDQP and BBQPP

Crystal structures of all molecules were determined by single crystal X-ray diffraction. The space group and lattice parameters were summarized in Table 1. Crystal structures of TQPP and DDQP were consistent with those of the previous reports.[3][4] Crystal structure of BBQPP was successfully identified as shown in Fig. 3. The space group of BBQPP is different from that of TQPP and DDQP. This result shows that stacking conformation changes when the molecular structure slightly changes. Their influences to the mobility are expected.

Table 1 Summary of crystal parameters

Molecule	Space Group	a/ Å	b/ Å	c/ Å	β
TQPP	$P2_1/c$	3.851	21.61	10.70	97.97°
DDQP	$P2_1/c$	3.781	16.63	17.08	95.34°
BBQPP	C2/c	26.76	3.760	23.84	111.9°

4. Conclusion

In this study, we synthesized three kinds of N-doped acene molecules. While TQPP and DDQP can be recrystallized from *o*-dichlorobenzene BBQPP cannot be dissolved in *o*-dichlorobenzene. Therefore, we invented new flux evaporation method called naphthalene method to obtain large single crystalline BBQPP. Then, we finally determined the crystal structure of BBQPP. We believe that the naphthalene method can be widely used for preparing large π-conjugated molecules such as acene.

References

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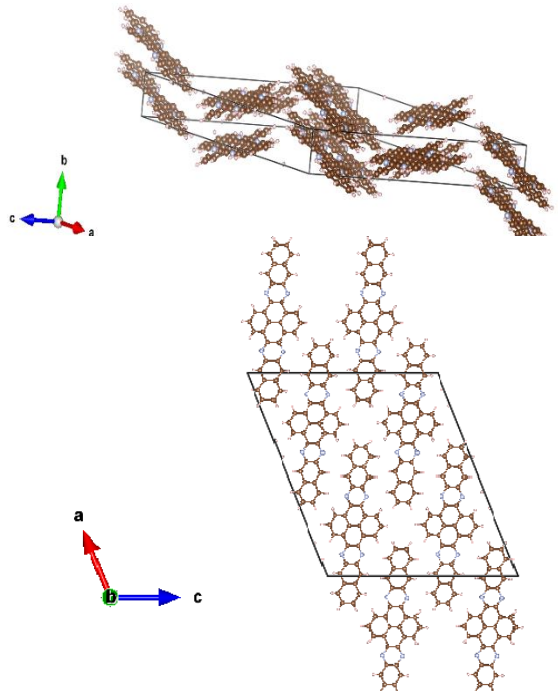

Fig. 3 Crystal structure of BBQPP