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Single crystal growth, structural analysis and electronic band structure of a nitrogen-containing polyacene Benzo[*i*]benzo[6',7']quinoxalino[2',3':9,10]phenanthro[4,5-*abc*]phenazine

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We synthesized a nitrogen-containing polyacene Benzo[*i*]benzo[6',7']quinoxalino[2',3':9,10]phenanthro[4,5-*abc*]phenazine (BBQPP) and a prepared single crystal for X-ray diffraction. Because BBQPP was insoluble to ordinary organic solvents, we used a new “flux evaporation method” to obtain the single crystals. The crystal structure of BBQPP was determined. Its band structure was calculated by density functional theory and the one-dimensional character of the band dispersion was revealed. © 2019 The Japan Society of Applied Physics

1. Introduction

Organic semiconductors are now used in organic LEDs for displays,¹⁾ and are actively studied aiming at thin-film transistors,^{2,3)} solar cells^{4–6)} and wearable electronic devices.⁷⁾ Carrier mobility is one of the most important parameters of semiconductors. Despite the continuous efforts to develop new semiconductor molecules, no molecules are reported to exceed the single crystalline rubrene ($\sim 40 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$).⁸⁾ Combination of structural analysis using single crystal X-ray diffraction and band calculation is one of the ways for screening organic semiconductors with high carrier mobility.

Nitrogen-containing polyacenes have been gathering attention because they are easily synthesized, chemically stable⁹⁾ and can be used as building blocks of two-dimensional covalent organic frameworks.¹⁰⁾ When seen as organic semiconductors, it is of interest whether they exhibit high carrier mobility or not, because from a naive view, the π - π interaction will become greater if the molecule becomes larger.^{11–13)} The physical properties of organic semiconductors are strongly influenced by their crystal structures. In order to investigate the crystal structure precisely, we need a single crystal. Here we encounter a problem: the solubility becomes drastically lower as the molecule becomes larger. It hinders synthesis and obtaining single crystals, which is important for the investigation of fundamental properties. Usually the *tert*-butyl group and/or long alkyl group are introduced to increase the solubility. Unfortunately, the substituent group disturbs the π - π interaction between the molecules. In fact, the reported mobility of acenes with side chains is 10^{-4} – $10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.¹⁴⁾

In this paper, we have studied a nitrogen-containing polyacene molecule benzo[*i*]benzo[6',7']quinoxalino [2',3':9,10]phenanthro[4,5-*abc*]-phenazine (BBQPP).^{9,15)} Although the synthesis of this molecule has already been reported, electronic properties as a semiconductor were not studied partly because it was impossible to grow single crystals. BBQPP is insoluble to ordinary solvent and synthesized as precipitate after the synthetic reaction. We developed a new “flux evaporation method” for the crystal growth of BBQPP and obtained single crystals with a size of $\sim 3 \text{ mm}$. We have briefly reported its crystal structure determined by X-ray diffraction.¹⁶⁾ In this

paper, we explain the experimental detail and use this crystal structure for density functional theory (DFT) calculations to obtain band dispersion.

2. Methods

2.1. Synthesis

BBQPP was synthesized by dehydration condensation reaction between carboxy and amino group by modifying the synthesis in the literature^{9,15)} (Fig. 1). Pyrene-4,5,9,10-tetraone (0.1 mmol) and 2,3-Diaminonaphthalene (0.2 mmol) was dissolved in 15 ml mixed solvent (*o*-dichlorobenzene: 2-methoxyethanol = 4:1). The mixture was heated to 150 °C and stirred for 6 h. The orange reaction products were obtained as precipitate and were collected by suction filtration and washed by ethanol. The product was characterized by ¹H-NMR (JEOL ECS400B) as a dilute solution in deuterized trifluoroacetic acid and matrix-assisted laser deposited ionization time of flight mass spectroscopy (MALDI-TOF-MS; Bruker).

2.2. Single crystal growth

BBQPP cannot be recrystallized from ordinary solvent such as *o*-dichlorobenzene due to the poor solubility. Hence, BBQPP was recrystallized by a new method which we call “flux evaporation method” (Fig. 2). 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.

2.3. DFT band calculation

The calculation was carried out using the Vienna Ab initio simulation package¹⁷⁾ which is based on DFT, plane waves and pseudopotentials. Our calculation was performed with the projector augmented wave method and the exchange–correlation energy treated using the Perdew–Burke–Ernzerhof functional¹⁸⁾ based on the generalized gradient approximation. The cutoff energy was 400 eV.

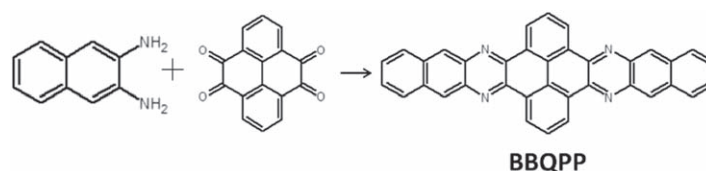


Fig. 1. Synthesis of BBQPP.

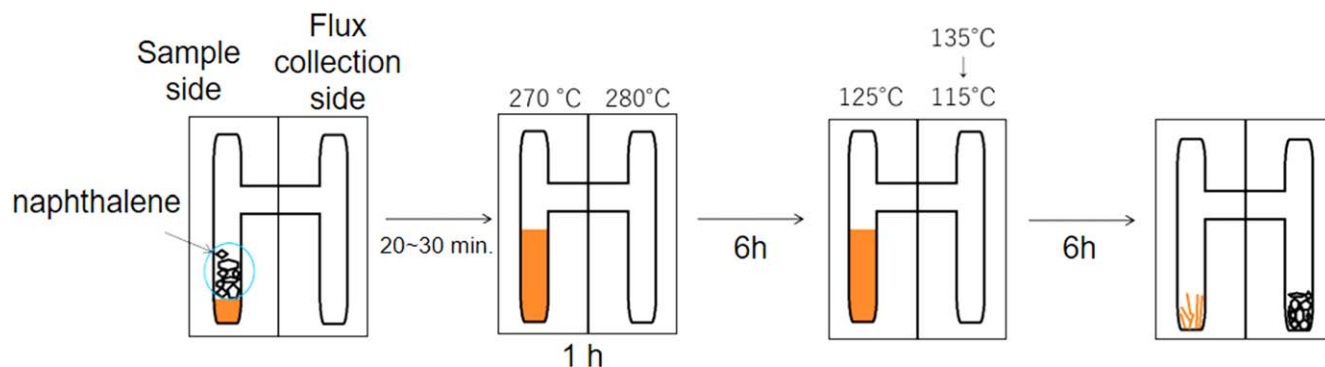


Fig. 2. (Color online) Schematic of the “flux evaporation method”.

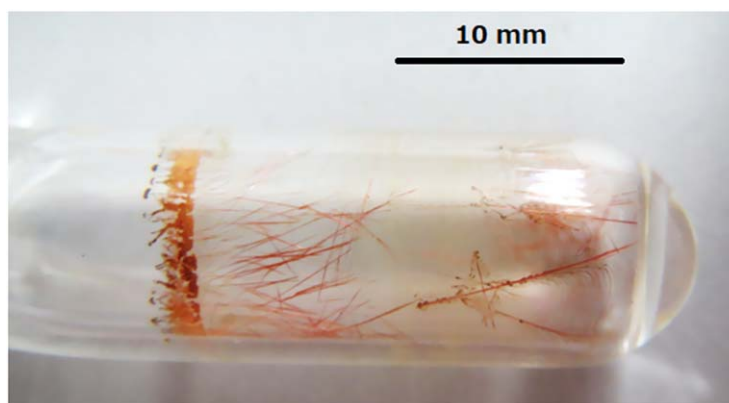


Fig. 3. (Color online) Single crystal of BBQPP grown by the flux evaporation method.

3. Results

3.1. Characterization of the synthesized product by ^1H -NMR and MALDI-TOF-MS

In ^1H -NMR using dilute solution in deuterized trifluoroacetic acid, all peaks were consistent with previous reports.^{9,15)} Molecular weight by MALDI-TOF-MS was mostly equal to the theoretical values (calculated 506.55, found 506.74). We concluded that all molecules were successfully synthesized.

3.2. Result of flux evaporation experiment

By flux evaporation method, we successfully obtained BBQPP single crystal as orange needle-like crystals (Fig. 3). It was also proved that naphthalene is a good solvent.

3.3. Single crystal X-ray diffraction

The crystal structure of BBQPP is shown in Fig. 4. System: monoclinic/Space group: $C 2/c$. The lattice constants were $a = 26.76$, $b = 3.76$, $c = 23.84(\text{\AA})$ $\alpha = \gamma = 90^\circ$, $\beta = 111.9^\circ$. The molecules stack in columns with different inclination angles in each columns. Since the inclination angles are not too small, it is difficult to judge the magnitude of inter-columnar electronic interaction.

3.4. Band dispersion

Figure 5 shows the band dispersion and the Brillouin zone of a monoclinic crystal. It is noticed that the dispersion is

observed along Γ -Z and A-X directions, which is parallel to the column direction. The bandwidths are 0.4 eV and 0.5 eV for HOMO and LUMO bands, respectively. Inter-columnar interaction seems less than 0.1 eV from X-H-H1-Y- Γ region of the band diagram.

4. Discussion

First we discuss the crystal growth of BBQPP. We tried many solvents but it was impossible to grow single crystal using ordinary solvents. Since BBQPP could not be sublimed easily by heating, it is impossible to make single crystals by physical vapor transport.^{19,20)} There are some reports on the use of unusual solvents for crystal growth of organic semiconductors, e.g., trichlorobenzene for pentacene²¹⁾ and poly(3-hexyl)thiophene (P3HT).²²⁾ However, trichlorobenzene did not work for BBQPP and hence we devised the present technique using naphthalene as a solvent. As for the mechanism of the growth, we currently speculate that high concentration of BBQPP in naphthalene than in other solvents are the key factor, which was made possible by the similarity in the structure with high population of aromatic rings in the molecules and the high temperature attained by lower vapor pressure of naphthalene compared with ordinary solvents. Templating effect^{23,24)} can also

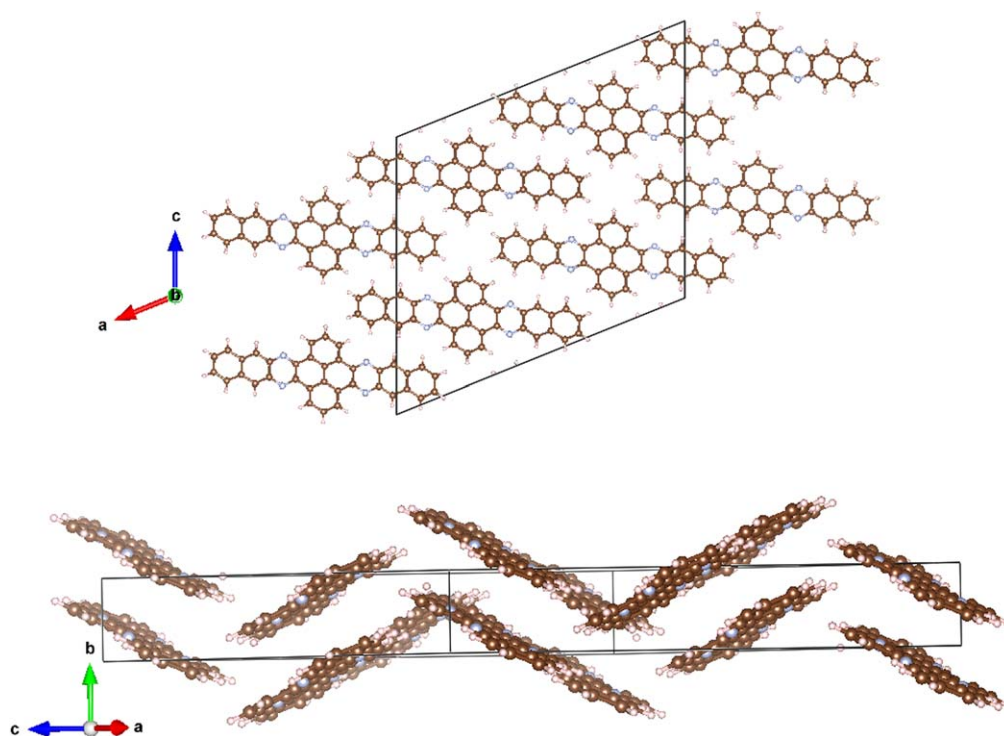


Fig. 4. (Color online) Crystal structure of BBQPP.

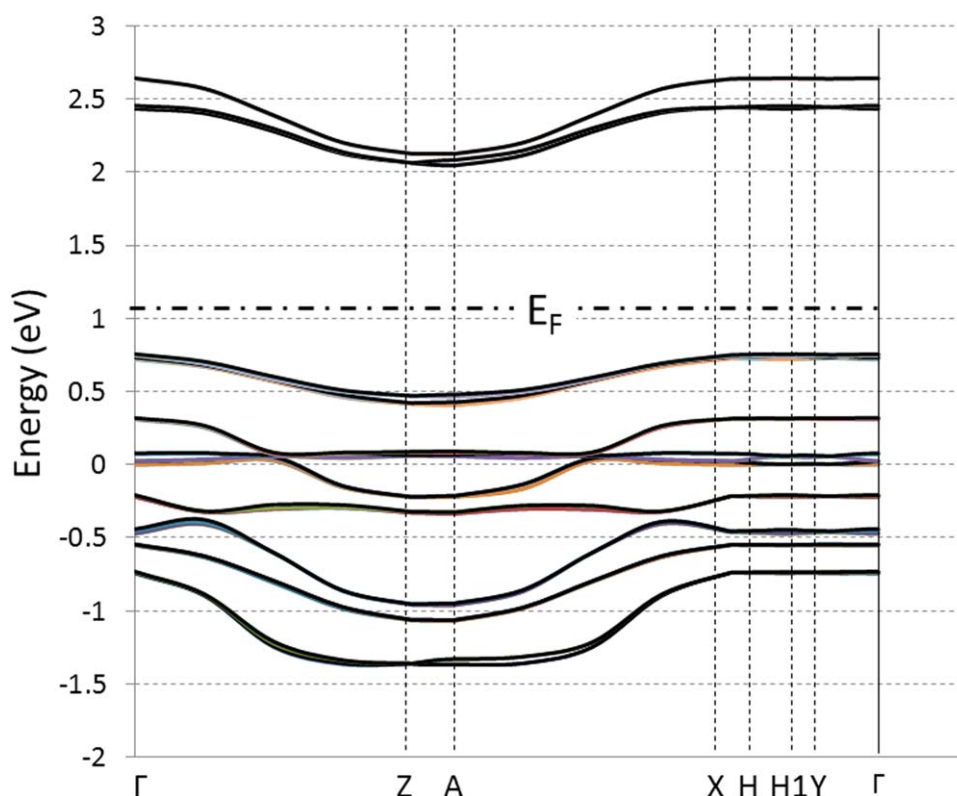


Fig. 5. (Color online) Band structure of BBQPP.

contribute in principle, but it requires confirmation in the future. The present method will be used for the growth of organic semiconductors and polymers that are insoluble to ordinary solvents. Application of naphthalene to “solvent-vapor annealing” technique^{25,26} is also promising.

Next we compare the structure of BBQPP to the categorized types of crystal structure of planar molecules. Reference 27 famous classification of polycyclic aromatic hydrocarbons

have four types: herringbone, sandwich herringbone, γ and β . Recently a new group “ β -herringbone” was proposed.²⁸ This classification can be used in the discussions of crystal structure of organic semiconductors.²⁹ In the sandwich herringbone, two parallel dimers are arranged in a herringbone structure. γ is a “flattened herringbone.” β is for “layered packing” which is characterized by a shortest crystal axis shorter than ~ 4 Å. “ β -herringbone” is intermediate of β and

herringbone. From the b axis (3.76 \AA) well below the criteria, It seems that structure of BBQPP is β type.

Finally we discuss the electronic structure of the BBQPP crystal. From the crystal structure shown in Fig. 4, it is obvious that BBQPP does not have herringbone structure. It seems to have columnar structure with oblique stacking of molecules within the column. The interaction between columns will determine whether the electronic structure is one-dimensional or two/three dimensional. It was evaluated by the band calculation shown in Fig. 5. The inter-column interaction ($X-H-H1-Y-\Gamma$) is less than 0.1 eV and is much smaller than that along column direction ($0.4\text{--}0.5 \text{ eV}$ in $\Gamma\text{--}Z$ and $A\text{--}X$). One-dimensional structure is usually not promising as high performance transistor devices because it is weak to defects.^{30–32} A modification of molecular structure from BBQPP is necessary to make two/three-dimensional structure.

5. Conclusion

In this study, we synthesized a nitrogen-containing polyacene BBQPP and successfully made its single crystals by a new method we developed. Energy band structure was calculated by DFT using the crystal structure and one-dimensional character was observed. We expect that this flux evaporation method can be used to make single crystals of large aromatic molecules. Thus strong one-dimensional conduction is expected in BBQPP, which usually is not promising as high performance transistor devices because it is weak to defects.

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- 1) C. W. Tang and S. A. V. Slyke, *Appl. Phys. Lett.* **51**, 913 (1987).
- 2) X. Z. Peng, G. Horowitz, D. Fichou, and F. Garnier, *Appl. Phys. Lett.* **57**, 1062 (1990).

- 3) T. Sumitomo, K. Hiraga, S. Kunisuyoshi, K. Kudo, and K. Tanaka, *Mol. Cryst. Liq. Cryst. A* **294**, 193 (1997).
- 4) C. W. Tang, *Appl. Phys. Lett.* **48**, 183 (1986).
- 5) M. Hiramoto, H. Fujiwara, and M. Yokoyama, *Appl. Phys. Lett.* **58**, 1062 (1991).
- 6) G. Li, V. Shrotriya, J. S. Huang, Y. Yao, T. Moriarty, K. Emery, and Y. Yang, *Nat. Mater.* **4**, 864 (2005).
- 7) T. Someya, T. Sekitani, S. Iba, Y. Kato, H. Kawaguchi, and T. Sakurai, *Proc. Natl. Acad. Sci. USA* **101**, 9966 (2004).
- 8) J. Takeya, M. Yamagishi, Y. Tominari, R. Hirahara, Y. Nakazawa, T. Nishikawa, T. Kawase, T. Shimoda, and S. Ogawa, *Appl. Phys. Lett.* **90**, 102120 (2007).
- 9) A. Mateo-Alonso, N. Kukisic, G. Valenti, M. Marcaccio, F. Paolucci, and M. Prato, *Chem. Asian J.* **5**, 482 (2010).
- 10) W. Liu et al., *Nat. Chem.* **9**, 563 (2017).
- 11) M. M. Payne, S. R. Parkin, and J. E. Anthony, *J. Am. Chem. Soc.* **127**, 8028 (2005).
- 12) D. Chun, Y. Cheng, and F. Wudl, *Angew. Chem. Int. Ed.* **47**, 8380 (2008).
- 13) I. Kaur, N. N. Stein, R. P. Kopreski, and G. P. Miller, *J. Am. Chem. Soc.* **131**, 3424 (2009).
- 14) P.-Y. Gu, Z. Wang, G. Liu, H. Yao, Z. Wang, Y. Li, J. Zhu, S. Li, and Q. Zhang, *Chem. Mater.* **29**, 4172 (2017).
- 15) P. K. Sahoo, C. Giri, T. S. Haldar, R. Puttreddy, K. Rissanen, and P. Mal, *Eur. J. Org. Chem.* **2016**, 1283 (2016).
- 16) N. Sakai, T. Yanase, T. Nagahama, and T. Shimada, Ext. Abst. SSDM, 2018, p. K-8-03.
- 17) G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).
- 18) J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- 19) R. A. Laudise, Ch. Kloc, P. G. Simpkins, and T. Siegrist, *J. Cryst. Growth* **187**, 449 (1998).
- 20) S. Miyamoto, T. Shimada, M. Ohtomo, A. Chikamatsu, and T. Hasegawa, *Jpn. J. Appl. Phys.* **48**, 118003 (2009).
- 21) T. Minakata and Y. Natsume, *Synth. Met.* **153**, 1 (2005).
- 22) M. Brinkmann and J. C. Wittmann, *Adv. Mater.* **18**, 860 (2006).
- 23) M. Brinkmann, L. Hartmann, L. Biniek, K. Tremel, and N. Kayunkid, *Macromol. Rapid Commun.* **35**, 9 (2014).
- 24) M. Ohtomo, Y. Tsuchida, N. Muraya, T. Yanase, S. Sakai, T. Yonezawa, T. Nagahama, T. Hasegawa, and T. Shimada, *J. Phys. Chem. C* **117**, 11555 (2013).
- 25) K. C. Dickey, J. E. Anthony, and Y. L. Loo, *Adv. Mater.* **18**, 1721 (2006).
- 26) T. Shimada, *Thin Solid Films* **515**, 1568 (2006).
- 27) G. R. Desiraju and A. Gavezzotti, *Acta Crystallogr., Sect. B* **45**, 473 (1989).
- 28) B. Schatschneider, J. Phelps, and S. Jezowski, *CrystEngComm* **13**, 7216 (2011).
- 29) M. Klues and G. Witte, *CrystEngComm* **20**, 63 (2018).
- 30) M. E. Gershenson, V. Podzorov, and A. F. Morpurgo, *Rev. Mod. Phys.* **78**, 973 (2006).
- 31) Z. Bao, A. J. Lovinger, and A. Dodabalapur, *Appl. Phys. Lett.* **69**, 3066 (1996).
- 32) A. Yamamoto, Y. Murata, C. Mitsui, H. Ishii, M. Yamagishi, M. Yano, H. Sato, A. Yamano, J. Takeya, and T. Okamoto, *Adv. Sci.* **5**, 1700317 (2018).