

Optically pumped lasing of cyano-substituted thiophene/phenylene co-oligomers microcrystals fabricated by the slide boat method

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Abstract

Optically pumped lasing is observed in cyano-substituted thiophene/phenylene (TPCO) microcrystals fabricated by the slide boat method. Dot-shaped crystals with approximately 10 μm size are obtained. Needle- and platelet-like crystals are also obtained in other TPCO derivatives. The needle and platelet crystals show lower lasing threshold than that of the dot-shaped crystals with clear multi-mode lasing spectra.

1. Introduction

Thiophene/phenylene co-oligomers (TPCOs) are attracting organic semiconductor materials for photonic devices, because of their good performances of optical and transport properties [1]. In the TPCO systems, dual phenyl-capped co-oligomers, biphenyl-n-thiophene (BPnT) have been commercially available and their researches extend widely. Recently, the precursor phenomena of current-injected lasing have been observed in TPCO single crystals [2-4] and actually current injected gain-narrowed emissions have been reported [5]. These reports indicate that TPCO materials are good candidate for organic laser materials for current injected lasers, but all results have been observed in the discrete single crystal devices. In order to fabricate laminated thin film devices, we have developed a slide boat method to obtain the double heterostructures of TPCO crystalline films [6]. The method has been used in III-V inorganic semiconductor LED and lasers as one of the industrial fabrication method. In this report, we adopted the method to cyano-substituted TPCO materials, which showed rather blight electroluminescence (EL) in pn junction of TPCO systems [7].

2. Sample preparations

Here, we used 2,5-bis(4-cyanobiphenyl-4-yl)thiophene (BP1T-CN) and 5,5'-bis(4'-cyanobiphenyl-4-yl)-2,2'-bithiophene (BP2T-CN) were used. Both TPCO materials are n-type. Molecular structures of these co-oligomers are shown in the upper part of Fig. 1. The middle part of Fig. 1 shows schematic drawing of slide boat apparatus. It has independent temperature controllable 3 pots and a boat setting the substrate. The temperature of the substrate on the boat under the 3 pots were set at 240 $^{\circ}\text{C}$. TPCO materials heated in the pots are leaked as a gas or liquid phase from the slits at the bot-

tom of pots which are approached to the heated substrates. The substrates on the boat is slid slowly and films were formed on the substrates. We used SiO_2 , SiO_2/ITO , and $\text{Si}/\text{SiO}_2/\text{ITO}$ substrates. The TPCO layers fabrication was carried out in a globe box filled with nitrogen. The oxygen density was less than 500 ppm.

The bottom part of Fig. 1 shows melting point of three TPCO molecules and actual setting temperature for crystals growth. In the case of BP1T, the setting temperature of the pot was lower than the melting point. In the case of BP1T-CN, it was comparable to the melting point. In BP2T-CN case, it was higher than the melting point. The microscope images of three cases are shown in Fig. 2. In the case of BP1T, platelet crystals with the size of several tens of micrometer form film-like structures. On the other hand, in the case of BP2T-CN, dot-shaped microcrystals with the size of approximately 10 μm were grown on the substrate. These results indicate that the film formation of BP1T occurs from vaporized. On the other hand, the growth of BP2T-CN occurs from liquid phase and their droplets solidify to form many dot-shaped microcrystals. Growth temperature of the BP1T-CN case is almost the same as the melting point, so that its film morphology is mixed with that of vapor phase and liquid phase growths, as shown in the middle part of the BP1T-CN image. Not only the platelet crystals but also the dot-shaped crystals can lase by the optical pulse excitation. Details are described in the next section.

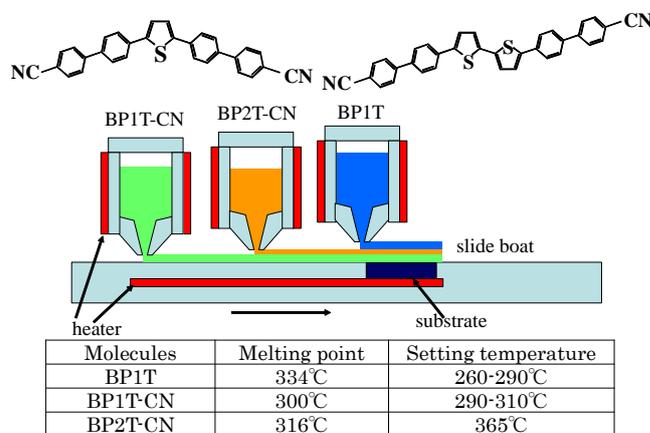


Fig. 1 Molecular structures of BP1T-CN and BP2T-CN and schematic view of the slide boat equipment.

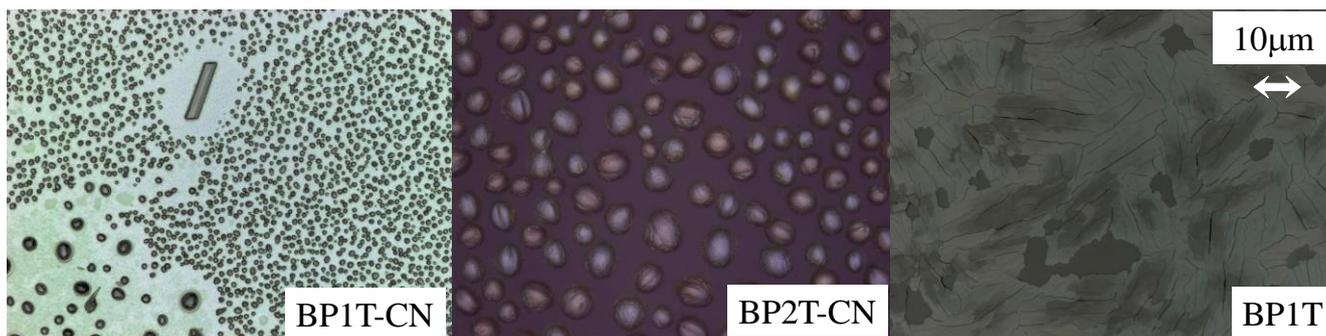


Fig. 2 Microscope images of three TPCOs fabricated by the slide boat method. Scales of 3 images are same as shown by the white arrow on the right upper part.

3. Optical-pumping experiments

We have carried out optical pumping experiments for three TPCO materials at RT in ambient air. The excitation photon energy, pulse width and repetition rate were 3.12 eV, 200-300 fs and 1 kHz, respectively. The top and middle parts of Fig. 3 show the fluorescence images of BP1T-CN microcrystals before and after the lasing, respectively. The excitation spot size was approximately 100 μm , so that some microdot crystals were excited simultaneously. However, only one dot indicated by the red arrow had strong emissions, indicating that only this dot lased. The situation was similar to the BP2T-CN case, so that the yield of the lasing crystals was not good in the case of dot-shaped microcrystals. On the other hand, platelet microcrystals as shown in the middle part of BP1T-CN images in Fig. 2, lased easily and showed microcavity mode spectra, as reported previously, where the microcrystals were fabricated by the gas phase crystallization and/or the mask shadowing deposition methods [8, 9]. Therefore, the slide boat method enable us to fabricate not only microcrystals but also crystalline films for organic lasing media by further control of preparation conditions. Details including the microcavity lasing-modes will be presented in the conference.

Acknowledgements

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References

- [1] S. Hotta, T. Yamao, S. Z. Bisri, T. Takenobu, and Y. Iwasa, *J. Mater. Chem.*, C2, 965 (2014) and references there in.
- [2] S. Z. Bisri, T. Takenobu, Y. Yomogida, H. Shimotani, T. Yamao, S. Hotta, and Y. Iwasa, *Adv. Funct. Mater.* 19, 1728 (2009).
- [3] T. Yamao, K. Terasaki, Y. Shimizu, and S. Hotta, *J. Nanosci. Nanotechnol.* 10, 1017 (2010).
- [4] S. Z. Bisri, K. Sawabe, M. Imakawa, K. Maruyama, T. Yamao, S. Hotta, Y. Iwasa, and T. Takenobu, *Sci. Rep.*, 2, 985 (2012).
- [5] H. Shimotani, T. Kanagasekaran, K. Kasai, S. Onuki and K. Tanigaki, *The 78th JSAP Autumn Meeting*, 7a-A203-1 (2017).
- [6] F. Sasaki, H. Mochizuki, H. Yanagi, and S. Hotta, *Reports on the 468th Topical Meeting of the Laser Society of Japan*, No.RTM-14-48 (2014) [In Japanese].
- [7] S. Dokiya, F. Sasaki, S. Hotta, and H. Yanagi, *Jpn. J. Appl. Phys.* 55, 03DC13 (2016).

- [8] H. Mizuno, T. Maeda, H. Yanagi, H. Katsuki, M. Aresti, F. Quochi, M. Saba, A. Mura, G. Bongiovanni, F. Sasaki, and S. Hotta, *Adv. Opt. Mater.* 2, 529 (2014).
- [9] K. Torii, T. Higuchi, K. Mizuno, K. Bando, K. Yamashita, F. Sasaki, and H. Yanagi, *ChemNanoMat*, 3, 625 (2017).

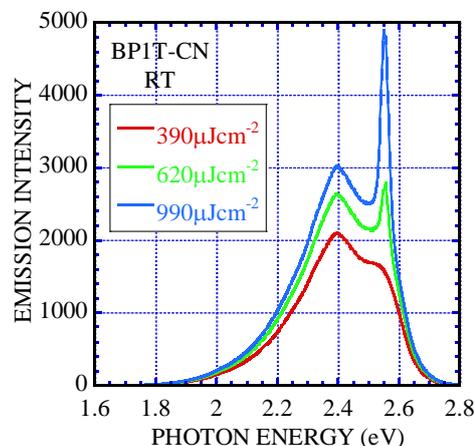
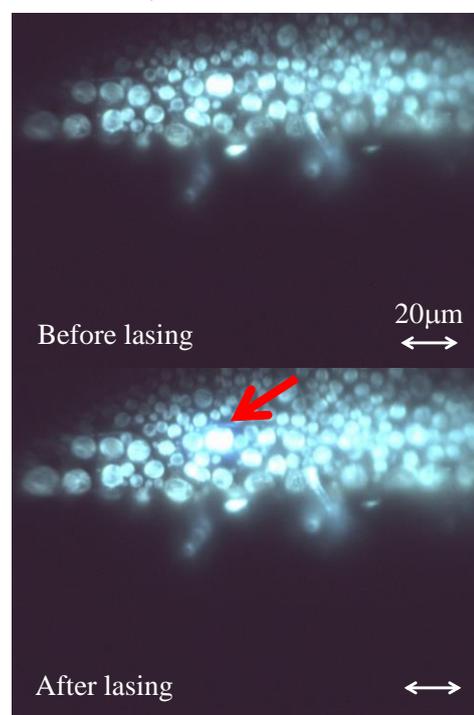


Fig. 3 Fluorescence images of BP1T-CN crystals under the optical pumping and spectra.