

Comparative Study of Single and Dual Gain-Narrowed Emission in Thiophene/Furan/Phenylene Co-Oligomer Single Crystals

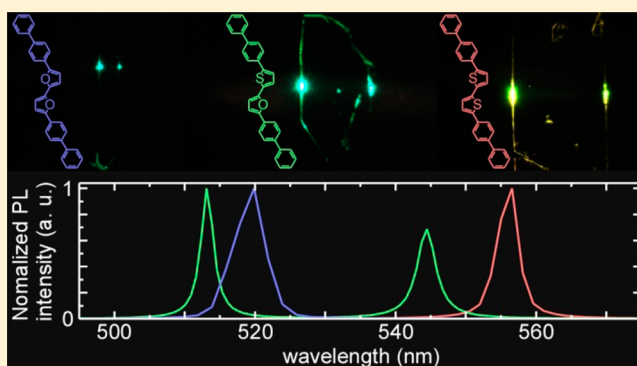
Hui Shang,[†] Hidekazu Shimotani,^{*,†} Susumu Ikeda,[‡] Thangavel Kanagasekaran,[‡] Kazuaki Oniwa,[‡] Tienan Jin,[‡] Naoki Asao,[‡] Yoshinori Yamamoto,[‡] Hiroyuki Tamura,[‡] Kenta Abe,[†] Miyuki Kanno,[†] Masayuki Yoshizawa,[†] and Katsumi Tanigaki^{*,‡}

[†]Department of Physics, Tohoku University, 6-3, Aramaki Aza-Aoba, Aoba-ku, Sendai 980-8578, Japan

[‡]WPI-Advanced Institute for Materials Research (WPI-AIMR), Tohoku University, 2-2-1 Katahira, Aoba-ku, Sendai 980-8577, Japan

Supporting Information

ABSTRACT: Three organic semiconductors consisting of thiophene, furan, and phenylene groups showed either one or two gain-narrowed emission peaks by excitation with a laser pulse. The two gain-narrowed emission peaks are optically studied and assigned to $0 \rightarrow 1$ and $0 \rightarrow 2$ vibronic transitions. The number of gain-narrowed emission peaks is determined by a degree of overlap of the vibronic emissions with ground-state and excited-state absorption of the material. Dependence of the gained emission intensity both on the total input energy and the density of the excited states shows that the two gain-narrowed peaks are attributed to two different decay processes: amplified spontaneous emission (ASE) and superfluorescence (SF). The input energy to be conserved in total is distributed between ASE and SF processes strongly dependent on the transition probability and the self-absorption of organic semiconductors as a gain media.



INTRODUCTION

Various attempts have been carried out for realizing organic semiconductor lasers from the standpoints of material and device structure,¹ because organic lasers have various advantages, such as low cost, feasibility in a fabrication process, and wide range tunability in wavelength compared with inorganic lasers.^{2–4} Optically pumped organic lasers have been known for almost 20 years,^{5–7} and thiophene/phenylene organic semiconductors are recognized as one of the most promising effective gain media.^{8–10} However, no one has yet succeeded in realizing electrically driven organic semiconductor lasers.^{11,12} Because the most essential component of lasers is a gain medium, detailed understanding of the gain properties of organic semiconductors accompanied by emission band narrowing is crucial.

Among numerous experiments reported so far on the photoluminescence (PL) properties of organic semiconductors, some materials show dual gain-narrowed emission peaks. Although the dual gain-narrowed emission had been intensively investigated in the past, their mechanism still remains unclear.^{13–18} Therefore, it is needed to elucidate differences between the materials showing single and dual gain-narrowed emission peaks.

Recently, we found that a series of semiconducting thiophene/furan/phenylene co-oligomers, which are BP2T, BPFT, and BP2F shown in Figure 1a–c, respectively, have

considerably different optical properties despite the similarity in molecular structure.^{19,20} Therefore, it is expected that their comparative studies provide new insight into dual gain-narrowed emission phenomena. Here, we report that dual gain-narrowed emissions are only observed for BPFT among the three semiconductors, and give reasonable interpretation on the difference in the number of gain-narrowed emission peaks.

EXPERIMENTAL SECTION

BP2T (99.5%) was purchased from Sigma-Aldrich Co. LLC, while BPFT and BP2F were newly synthesized in our laboratory.¹⁹ All three materials were purified by sublimation. Single crystals were grown by physical vapor transport under argon gas (99.998%) flow. The thin plate-like crystals were electrostatically attached on a heavily doped silicon substrate with a 200 nm thick SiO₂ layer. Absorption spectra were measured on quartz substrates with a UV/vis spectrophotometer (JASCO Corporation, V-650DS). PL spectra were measured using a fluorescence spectrophotometer (Hitachi High-Tech Science Corporation, F-7000) with the excitation wavelength at 380 nm. A nitrogen nanosecond-pulsed laser at 337.1 nm (Stanford Research Systems, Inc., NL100) was

Received: October 27, 2016

Revised: January 12, 2017

Published: January 24, 2017

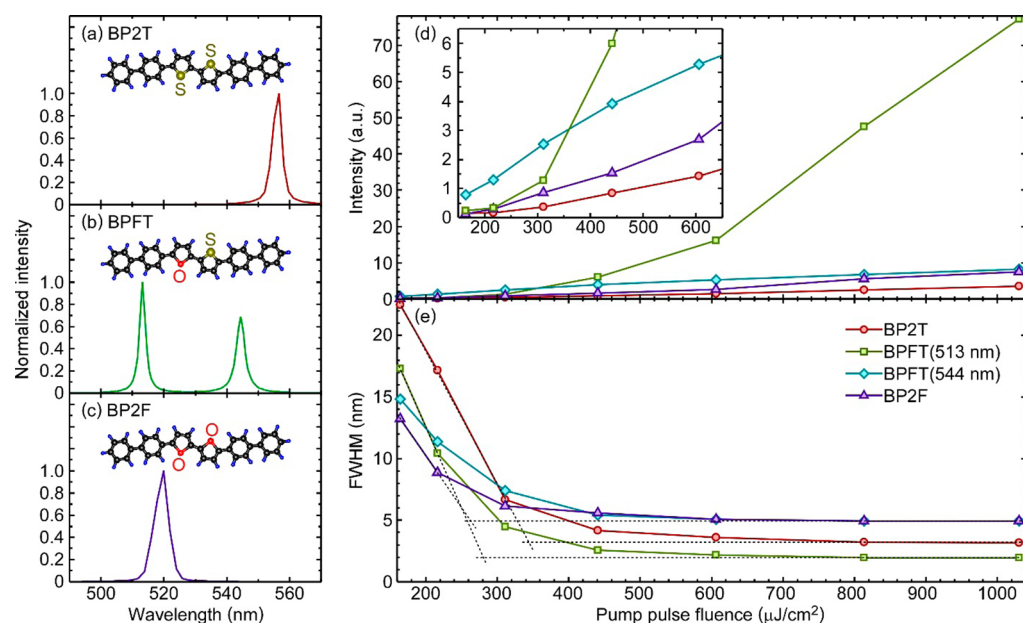


Figure 1. (a–c) Gain-narrowed emission spectra for single crystals of 2,5-bis(4-biphenyl)bithiophene (BP2T), 2-(4-biphenyl)-5-[5-(4-biphenyl)-2-thienyl]furan (BPFT), and 2,5-bis(4-biphenyl)bifuran (BP2F), respectively. Insets show their molecular structures. (d, e) Peak intensity (inset: expansion) and full width at half-maximum (fwhm), respectively, versus the pump pulse fluence for BP2T, BPFT at 513 nm, BPFT at 544 nm, and BP2F.

employed as a pump source with a focused radius of about 0.5 mm for ASE measurements. The excitation pulse laser was irradiated along the *c*-axis of crystals.^{19,23} The total pulse energy was controlled by a neutral density filter. The emissions were detected parallel to the *ab*-plane of crystals by an optical fiber spectrometer (Hamamatsu Photonics K.K., PMA-12 Photonic Multichannel Analyzer C10027). Transient absorption spectra were measured with an excitation pulse laser of 400 nm in wavelength, whose pulse width was 100 fs and pulse fluence was $760 \mu\text{J}/\text{cm}^2$. A white-light probe beam was applied with a delay of 0.5 ps after pumping, and a multichannel photodiode detector was used for spectrum detection.²¹

RESULTS AND DISCUSSION

Single gain-narrowed peaks were observed at 557 and 520 nm for BP2T and BP2F, respectively, in ASE spectra shown in Figure 1a and c. In contrast, BPFT showed two gain-narrowed peaks at 513 and 544 nm (Figure 1b). The numbers of gain-narrowed peaks did not change by polarizing the pump source to various polarization angles, as shown in Figure S1. It should be noted that the intensity of the peak at 513 nm for BPFT more markedly increased than the others as the fluence of the pump pulse increased (Figure 1d). Because the three crystals are similar in size (area, 0.4 mm^2 ; thickness, $1 \mu\text{m}$), these results are consistent with the highest PL efficiency of BPFT among the three.^{19,20}

A similar conclusion can be deduced from the full width at half-maximum (fwhm). The fwhm's of the gain-narrowed peaks of BP2T, BPFT, and BP2F single crystals were 4.0, 1.93 (at 513 nm), and 4.91 nm, respectively (see Figure 1e).

One may imagine that a possible reason for the dual gain-narrowed emission peaks would be the fact that the π -electron system for BPFT consists of two parts of conjugated moieties of BP2T and BP2F. However, this can be excluded, because the PL spectrum of BPFT is not a superposition of those of BP2T and BP2F (Figure 2). Instead, the structures in the PL spectra

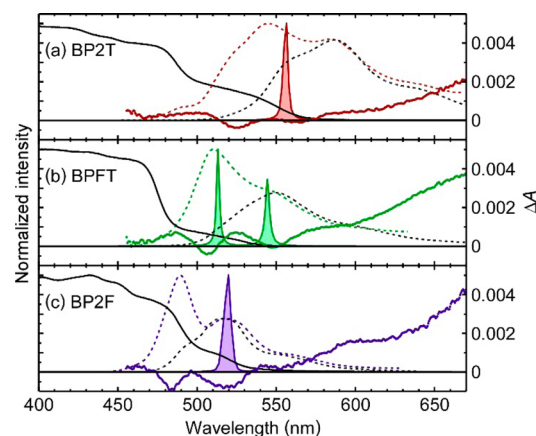


Figure 2. Absorption and PL spectra for single crystals and thin films of BP2T, BPFT, and BP2F, respectively: black solid lines, ground-state absorption spectra for single crystals; dashed colored lines, PL spectra for thin films; dashed black lines, PL spectra for single crystals; filled colored lines, gain-narrowed spectra; thick colored lines, transient absorption spectra. The PL spectra for the single crystals are normalized to those of the thin films at their maximum-intensity wavelength.

are attributable to vibronic transitions. We assigned the positions of vibronic emission of these three materials from PL spectra of their thin films. According to ref 22, BP2T has vibronic emissions of $0 \rightarrow 0$, $0 \rightarrow 1$, and $0 \rightarrow 2$ at 485, 524, and 564 nm, respectively. Correspondingly, the vibronic emissions of $0 \rightarrow 0$, $0 \rightarrow 1$, and $0 \rightarrow 2$ for BPFT are at 489, 510, and 551 nm, respectively, and the vibronic emissions of $0 \rightarrow 0$, $0 \rightarrow 1$, and $0 \rightarrow 2$ for BP2F are at 462, 489, and 519 nm, respectively. Therefore, ASE peaks at 513 and 544 nm in BPFT were ascribed to the $0 \rightarrow 1$ and $0 \rightarrow 2$ transitions, respectively, and the ASE peaks of both BP2T and BPFT were ascribed to the $0 \rightarrow 2$ transitions.

The most likely reason for the difference in the number of gain-narrowed emission peaks is then the fact that the self-absorption in BPFT is much weaker than those in the other materials. Because the transition dipole moments are almost perpendicular to the *ab* plane of the crystals,^{19,23} and the refractive indices of organic single crystals are so high that the fluorescence can be confined between the two parallel crystal faces, emitted light propagates via a waveguide effect.^{24,25} Therefore, the emitted light is strongly absorbed by the organic material itself in the case of the crystalline form. Figure 2 clearly shows that the suppression of the PL peaks at 521, 510, and 489 nm for BP2T, BPFT, and BP2F single crystals, respectively, is due to the strong absorption at these wavelengths, as compared with those for the thin films. The absorbance of BPFT at the 0 → 1 emission peak (510 nm), which only showed gain-narrowed emission among the 0 → 1 emission peaks of the three materials, is the weakest among the three materials. Therefore, the emergent gain-narrowed peaks are concluded to be closely related to the intensity of self-absorption. Also, the absence of gain narrowing for the other PL peaks is attributable to overlaps with absorption bands of excited states.

The above conclusion is supported by the ASE intensities plotted against the pump pulse fluence, as shown in Figure 1d. The PL spectrum of a BPFT thin film (Figure 2) shows that the transition probability of 0 → 1 is markedly larger than that of 0 → 2. However, the relative intensities of the two vibronic emissions in a single crystal are not constant due to the self-absorption. The 0 → 1 emission is strongly suppressed by the self-absorption when the pump pulse fluence is low, but it becomes predominant because of its largest transition probability when the self-absorption is partially bleached under high pump pulse fluence.

It is expected that the other two materials would also show dual gain-narrowed peaks, if the self-absorptions could be bleached enough. To support this interpretation, we measured transient absorption spectra of single crystals of the three materials. All three transient absorption spectra showed two clear dips, as shown in Figure 2. From the fact that the wavelengths of ASE peaks correspond well with the wavelength of the dips, it is suggested that the dips can be ascribed to the stimulated emissions from excited states, which can potentially emit ASE. This idea is supported by temporal evolution of the transient absorption spectra shown in Figure 3. Because dips in all of the materials showed a similar behavior, only the plot observed for a BPFT single crystal is shown. On the one hand, the transient absorptions at 505 and 680 nm increased just after excitation with a relatively weak laser pulse (Figure 3a). On the other hand, the dip at 505 nm showed a rise time of 0.09 ± 0.02 ps. The results indicate the initial excited state, which has a broad transient absorption band, is different from the excited state, which shows stimulated emission, and stimulated emission was observed after relaxation to the latter state. When the crystal was excited with a relatively strong laser pulse (Figure 3b), the transient absorptions and the dip rose similarly to the weak excitation, but the dip and the transient absorption at 680 nm decreased rapidly in 3 ps. The rapid decreases are attributed to a decrease of excited states by ASE. Therefore, it is concluded that the excited states showing the dips emit ASE.

Further investigations were carried out to elucidate the natures of two gain-narrowed emissions of BPFT. In general, coherent emission can be attributed to either ASE or SF. When a sufficient amount of transition dipole moments is excited,

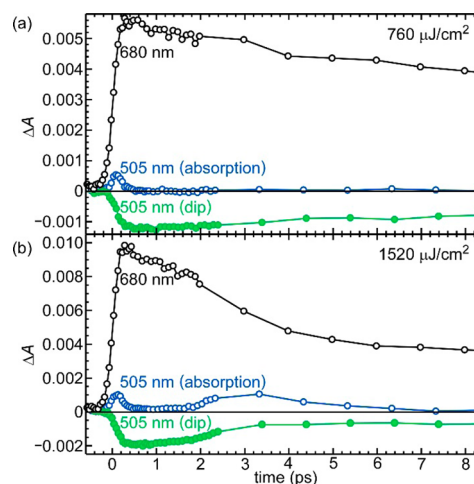


Figure 3. Temporal evolution of the transient absorption spectra of a BPFT single crystal. (a) Excited by a $760 \mu\text{J}/\text{cm}^2$ laser pulse. (b) Excited by a $1520 \mu\text{J}/\text{cm}^2$ laser pulse. Open blue and black circles indicate transient absorbance at 505 and 680 nm. Closed green circles indicate the intensity of the dip at 505 nm.

their coherent coupling results in cooperative spontaneous emission, which is known as SF. Since the excited molecules participate in building up the macroscopic dipole moment in a crystal, the process is governed by the total number of excited states, being irrespective of the density of excited states. On the other hand, when the density of excited molecules reaches a threshold prior to reaching the SF regime, ASE can occur.

To assign the gain-narrowed emissions of a BPFT single crystal to the above two processes, we measured the threshold pump pulse energy of gain narrowing by exciting with a strip-shaped laser at various beam widths ranging from 97 to $517 \mu\text{m}$ by changing the position of a condensing cylindrical lens. The incident angle of the excitation laser was 15° . By changing the width, the pump pulse fluence, which corresponds to the density of excited molecules, can be changed without changing the pump pulse power, which corresponds to the total number of excited molecules.

Figure 4 clearly shows a different laser beam width dependence of the threshold pump pulse energy of gain narrowing of peaks at 513 and 544 nm. The threshold pump pulse energy of the former peak is proportional to the laser beam width. This means the threshold pump pulse fluence is constant irrespective of the laser beam width. Therefore, the gain-narrowed emission is attributed to ASE. On the other

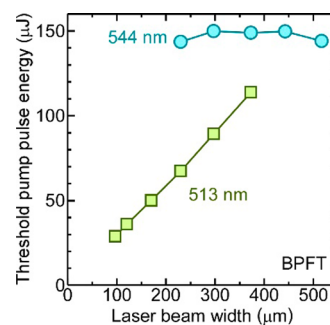


Figure 4. Changes in the threshold of pump pulse energy for peaks at 513 nm (yellow-green squares) and 544 nm (cyan circles) of BPFT as a function of excitation laser beam width.

hand, the threshold pump pulse energy of the latter peak is constant irrespective of the laser beam width, and is attributed to SF. The SF process in an organic semiconductor at room temperature was also reported by Frolov et al. for a polymer semiconductor.²⁶ Coexistence of ASE and SF is previously reported for 5,5''-bis(4-biphenyl)-2,2':5',2''-terthiophene.¹⁰

It is noted that the occurrence of ASE requires superior optical confinement in the gain media, while SF occurs even when there is radiation leakage.^{10,26} In the case of single crystals of BPFT, their thickness is so thin that the spread of optical field outside the crystal causes an optical loss. Because the shorter the wavelength, the narrower the spread of the optical field is, the emission at shorter wavelength (513 nm) is more efficiently confined in the crystal cavity than the emission at 544 nm. The same experiments and analyses for BP2T and BP2F showed their gain-narrowed emissions originate in ASE.

CONCLUSIONS

In conclusion, we proposed reasonable interpretations on the dual gain-narrowed emissions in terms of the $0 \rightarrow n$ vibronic transitions from comparisons of both absorption and emission of the three organic semiconductors. In addition, on the basis of transient and ground-state absorption spectra, we showed that the gain-narrowing behaviors of each vibronic emission are greatly affected by self-absorption. Both ASE and SF processes occurred with strong competition via the vibronic transitions of $0 \rightarrow 1$ and $0 \rightarrow 2$, respectively, in BPFT. The above conclusions suggest that preferable gain media for organic semiconductor lasers have only one vibronic transition route with the highest transition probability so that the emission can ideally be confined in a window existing between the absorption bands of both ground and excited states.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b10827.

Polarization angle dependences of gain-narrowed photoluminescent spectra of BP2T, BPFT, and BP2F (PDF)

AUTHOR INFORMATION

Corresponding Authors

*E-mail: shimotani@m.tohoku.ac.jp.

*E-mail: tanigaki@m.tohoku.ac.jp.

ORCID

Hidekazu Shimotani: 0000-0003-3238-9420

Naoki Asao: 0000-0001-9315-3142

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by JSPS KAKENHI Grant Number JP24684023, JP25610084, and JP16K13826, JGC-S Scholarship Foundation, and CASIO Science Promotion Foundation. H. Shang is grateful for the CSC scholarship from the Chinese government as well as the Tohoku University president scholarship for research and education.

REFERENCES

- (1) Bisri, S. Z.; Piliago, C.; Gao, J.; Loi, M. A. Outlook and emerging semiconducting materials for ambipolar transistors. *Adv. Mater.* **2014**, *26*, 1176–1199.
- (2) Pisignano, D.; Anni, M.; Gigli, G.; Cingolani, R.; Zavelani-Rossi, M.; Lanzani, G.; Barbarella, G.; Favaretto, L. Amplified spontaneous emission and efficient tunable laser emission from a substituted thiophene-based oligomer. *Appl. Phys. Lett.* **2002**, *81*, 3534–3536.
- (3) Samuel, I. D. W.; Namdas, E. B.; Turnbull, G. A. How to recognize lasing. *Nat. Photonics* **2009**, *3*, 546–549.
- (4) Fang, H.; Ding, R.; Lu, S.; Yang, J.; Zhang, X.; Yang, R.; Feng, J.; Chen, Q.; Song, J.; Sun, H. Distributed feedback lasers based on thiophene/phenylene co-oligomer single crystals. *Adv. Funct. Mater.* **2012**, *22*, 33–38.
- (5) Hide, F.; Díaz-García, M. A.; Schwartz, B. J.; Andersson, M. R.; Pei, Q.; Heeger, A. J. Semiconducting Polymers: A new class of solid-state laser materials. *Science* **1996**, *273*, 1833–1836.
- (6) Tessler, N. G.; Denton, J.; Friend, R. H. Lasing from conjugated polymer microcavities. *Nature* **1996**, *382*, 695–697.
- (7) Li, X.; Gao, N.; Xu, Y.; Li, F.; Ma, Y. Self-cavity laser oscillations with very low threshold from a symmetric organic crystal waveguide. *Appl. Phys. Lett.* **2012**, *101*, 063301.
- (8) Ichikawa, M.; Hibino, R.; Inoue, M.; Haritani, T.; Hotta, S.; Araki, K.; Koyama, T.; Taniguchi, T. Laser oscillation in monolithic molecular single crystals. *Adv. Mater.* **2005**, *17*, 2073–2077.
- (9) Mizuno, H.; Haku, U.; Marutani, Y.; Ishizumu, A.; Yanagi, H.; Sasaki, F.; Hotta, S. Single crystals of 5,5'-Bis(4'-methoxybiphenyl-4-yl)-2,2'-bithiophene for organic laser media. *Adv. Mater.* **2012**, *24*, 5744.
- (10) Hiramoto, T.; Matsuoka, N.; Yanagi, H.; Sasaki, F.; Hotta, S. Gain-narrowed emissions of thiophene/phenylene co-oligomer single crystals. *Phys. Status Solidi C* **2009**, *6*, 338–341.
- (11) Bisri, S. Z.; Takenobu, T.; Yomogida, Y.; Shimotani, H.; Yamao, T.; Hotta, S.; Iwasa, Y. High mobility and luminescent efficiency in organic single-crystal light-emitting transistors. *Adv. Funct. Mater.* **2009**, *19*, 1728–1735.
- (12) Gwinner, M. C.; Khodabakhsh, S.; Song, M. H.; Schweizer, H.; Giessen, H.; Siringhaus, H. Integration of a rib waveguide distributed feedback structure into a light-emitting polymer field-effect transistor. *Adv. Funct. Mater.* **2009**, *19*, 1360–1370.
- (13) Fichou, D.; Delysse, S.; Nunzi, J. First evidence of stimulated emission from a monolithic organic single crystal: α -octithiophene. *Adv. Mater.* **1997**, *9*, 1178–1181.
- (14) Horowitz, G.; Kouki, F.; Kassmi, A. E.; Valat, P.; Wintgens, V.; Garnier, F. Structure-dependent fluorescence in sexithiophene single crystals. *Adv. Mater.* **1999**, *11*, 234–238.
- (15) Nagawa, M.; Hibino, R.; Hotta, S.; Yanagi, H.; Ichikawa, M.; Koyama, T.; Taniguchi, Y. Emission gain narrowing from single crystals of a thiophene/phenylene co-oligomer. *Appl. Phys. Lett.* **2002**, *80*, 544–546.
- (16) Losio, P. A.; Hunziker, C.; Gunter, P. Amplified spontaneous emission in para-sexiphenyl bulk single crystals. *Appl. Phys. Lett.* **2007**, *90*, 241103.
- (17) Polo, M.; Camposeo, A.; Tavazzi, S.; Raimondo, L.; Spearman, P.; Papagni, A.; Cingolani, R.; Pisignano, D. Amplified spontaneous emission in quaterthiophene single crystals. *Appl. Phys. Lett.* **2008**, *92*, 083311.
- (18) Kabe, R.; Nakanotani, H.; Sakanoue, T.; Yahiro, M.; Adachi, C. Effect of molecular morphology on amplified spontaneous emission of bis-styrylbenzene derivatives. *Adv. Mater.* **2009**, *21*, 4034–4038.
- (19) Oniwa, K.; Kanagasekaran, T.; Jin, T.; Akhtaruzaman, Md.; Yamamoto, Y.; Tamura, H.; Shimotani, H.; Asao, N.; Ikeda, S.; Tanigaki, K. Single crystal biphenyl end-capped furan-incorporated oligomers: influence of unusual packing structure on carrier mobility and luminescence. *J. Mater. Chem. C* **2013**, *1*, 4163–4170.
- (20) Tamura, H.; Hamada, I.; Shang, H.; Oniwa, K.; Akhtaruzaman, Md.; Jin, T.; Asao, N.; Yamamoto, Y.; Kanagasekaran, T.; Shimotani, H.; et al. Theoretical analysis on the optoelectronic properties of single crystals of thiophene-furan-phenylene co-oligomers: efficient photo-

luminescence due to molecular bending. *J. Phys. Chem. C* **2013**, *117*, 8072–8078.

(21) Kosumi, D.; Abe, K.; Karasawa, H.; Fujiwara, M.; Cogdell, R. J.; Hashimoto, H.; Yoshizawa, M. Ultrafast relaxation kinetics of the dark S1 state in all-trans β -carotene explored by one- and two photon pump-probe spectroscopy. *Chem. Phys.* **2010**, *373*, 33–37.

(22) Bando, K.; Nakamura, T.; Fujiwara, S.; Masumoto, Y.; Sasaki, F.; Kobayashi, S.; Shimoi, Y.; Hotta, S. Optical selection rule for the lower Davydov excitons in co-oligomer single crystals. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2008**, *77*, 045205.

(23) Hotta, S.; Goto, M.; Azumi, R.; Inoue, M.; Ichikawa, M.; Taniguchi, Y. Crystal structures of thiophene/phenylene co-oligomers with different molecular shapes. *Chem. Mater.* **2004**, *16*, 237–241.

(24) Katoh, R.; Suzuki, K.; Furube, A.; Kotani, M.; Tokumaru, K. Fluorescence quantum yield of aromatic hydrocarbon crystals. *J. Phys. Chem. C* **2009**, *113*, 2961–2965.

(25) Shang, H.; Wang, H.; Gao, N.; Shen, F.; Li, X.; Ma, Y. Large organic single crystal sheets grown from the gas–liquid and gas–liquid–solid interface. *CrystEngComm* **2012**, *14*, 869–874.

(26) Frolov, S. V.; Vadenny, Z. V.; Yoshino, K. Cooperative and stimulated emission in poly(*p*-phenylene-vinylene) thin films and solutions. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1998**, *57*, 9141–9147.