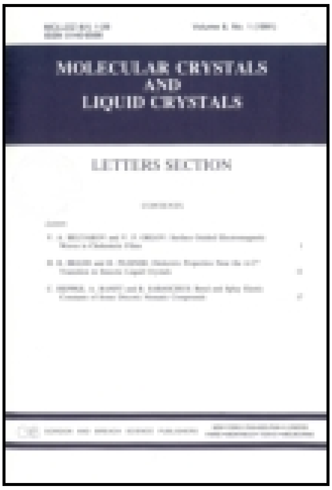
This article was downloaded by: [University Of Gujrat]
On: 11 December 2014, At: 13:41
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Luminescence Gap in Regioregular Poly(3-hexylthiophene) Film

Masatoshi Saito[a], Ryo Mizokawa[a], Yuichiro Yanagi[b], Yasushiro Nishioka[a] & Kazuro Murayama[a]
[a] CHS, Nihon University, Setagaya, Tokyo, Japan
[b] CST, Nihon University, Funabashi, Chiba, Japan

Published online: 17 Nov 2014.

To cite this article: Masatoshi Saito, Ryo Mizokawa, Yuichiro Yanagi, Yasushiro Nishioka & Kazuro Murayama (2014) Luminescence Gap in Regioregular Poly(3-hexylthiophene) Film, Molecular Crystals and Liquid Crystals, 597:1, 146-152, DOI: 10.1080/15421406.2014.932659

To link to this article: http://dx.doi.org/10.1080/15421406.2014.932659

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the “Content”) contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

Mol. Cryst. Liq. Cryst., Vol. 597: pp. 146–152, 2014
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2014.932659

Luminescence Gap in Regioregular Poly(3-hexylthiophene) Film

MASATOSHI SAITO,[1] RYO MIZOKAWA,[1]
YUICHIRO YANAGI,[2] YASUSHIRO NISHIOKA,[1]
AND KAZURO MURAYAMA[1,*]

[1]CHS, Nihon University, Setagaya, Tokyo, Japan
[2]CST, Nihon University, Funabashi, Chiba, Japan

The luminescence gap in the regioregular poly(3-hexylthiophene) film is shown to be 1.93 eV at 16 K from the excitation energy dependence of the luminescence spectrum. The self-trapped exciton, of which the luminescence is due to the recombination, is suggested to consist of a self-trapped hole and an electron bound around the hole. The power law decay described by $t^{-1.14}$ is observed, which is explained from the diffusion in the fractal structure of the electron bound around the self-trapped hole.

Keywords Poly(3-hexylthiophene) film; luminescence; self-trapped exciton; structural disorder; power law decay; diffusion in fractal

1. Introduction

In regioregular poly(3-hexylthiophene) (rrP3HT) film, the luminescence spectrum with vibronic structures of the spacing of 0.18 eV is observed in the photon energy range 1.2 to 1.9 eV [1, 2]. Electron-hole pairs optically-excited turn to self-trapped excitons or charged pairs, and the luminescence is explained to be due to the recombination of the self-trapped excitons [2]. The spacing of 0.18 eV shows that the exciton couples with the C=C symmetric stretching mode [1], which suggests that the exciton is self-trapped at the C=C bond. The life time of the exciton luminescence is 235 ps [2]. The power law luminescence decay observed together with the exponential decay of the exciton luminescence is explained as due to the tunneling process between the self-trapped exciton and the charged pair [2].

The rrP3HT film has amorphous-like structures, in which crystalline rrP3HT domains with nanometer scale with different band gaps for the random distribution of the size and the crystal axis are embedded in amorphous matrix [3]. The dispersive charge transport observed originates in the amorphous-like structure [4], which results in low charge-carrier mobilities [3, 5]. The amorphous-like structure makes the band edge obscure. In the case of amorphous semiconductors the exponential band tail consisting of localized states appears near the band edge [6].

In the case of hydrogenated amorphous silicon (a-Si:H), electron-hole pairs excited deeply in the bands relax in the extended states by emitting phonons, then relax in the localized band tail states by hopping between localized band tail states, finally reach a

---

[*] Address correspondence to Kazuro Murayama, CHS, Nihon University, Setagaya, Tokyo 156-8550, Japan; Tel.: 81-3-5317-9362, Fax:+81-3-5317-9432; E-mail: murayama@phys.chs.nihon-u.ac.jp

definite localized band tail state at which the density is too low to make the hopping relaxation, and recombine radiatively to emit the luminescence with a constant peak energy [7]. On the other hand, the electron-hole pairs created at the localized band tail states lower than the definite band tail state by the low energy excitation recombine radiatively without the hopping relaxation. Therefore, the peak energy of the luminescence induced with the low energy excitation decreases with decreasing excitation energy. The excitation energy at which the luminescence peak energy changes from constant to decreasing, names the luminescence gap [7].

Here, the luminescence gap in the rrP3HT film with amorphous-like structure is investigated.

2. Experimental

Solutions of rrP3HT were made in dichlorobenzene and heated to 60°C for 1 hour in order to make the film. A rrP3HT film with the thickness of $d{\sim}1\ \mu$m was prepared by spin-coating a SiO_2 substrate with rough surface by the hot solution and was subsequently heated to 150°C for 20 minites.

The film was kept at a temperature (T_m) from 4.2 to 250 K in an ultra-low temperature refrigerator and was excited with a monochromatic light from 500 to 700 nm obtained by passing light from the Xe lamp through the monochrometer or a pulse YAG laser with the pulse energy of 2.33 eV and the duration of 5 ns. The luminescence from the film was passed through a double monochromator and was detected with a InP/InGaAs (HAMAMATSU R5509-71) photomultiplier.

3. Results and Discussions

The band gap of the P3HT film is reported to be about 1.89 eV from the optical absorption spectrum [8]. We have tried to estimate the band gap from the excitation energy evolution of the luminescence spectrum by using the excitation energy near the band gap. The observed excitation energy evolution of the luminescence spectrum at excitation energies from 1.78 to 2.0 eV at 16 K in the rrP3HT film is shown in Fig. 1. In the excitation energy range higher than 1.93 eV, the luminescence spectrum does not change. However, in the excitation energy range lower than 1.93 eV the luminescence spectrum shifts on the low energy side with decreasing excitation energy. In Fig. 2, the excitation energy dependences of the (0,0), (0,1), (0,2) and (0,3) luminescence peaks at 16 K are shown. The luminescence peak energy increases with increasing excitation energy up to the excitation energy of 1.93 eV, and at the higher excitation energies the peak energy is constant. The luminescence gap is concluded to be 1.93 eV at 16 K.

The excitation energy dependences of the peak energies E_{Ln} of the (0,n) luminescence at 16 K where n = 1, 2, 3, shown in Fig. 2, are described with the equation,

$$E_{Ln} = 0.5\,(E_x - 1.93) + E_{0n},\ \text{at}\,E_X < 1.93\,\text{eV}, \tag{1}$$
$$E_{Ln} = E_{0\,n},\ \text{at}\,E_X > 1.93\,\text{eV},$$

where E_X is the excitation energy and $E_{01} = 1.67$, $E_{02} = 1.50$ and $E_{03} = 1.33$ eV.

The luminescence in the rrP3HT film is shown to be due to the radiative recombination of the exciton self-trapped at C=C bond [2]. Here, let us assume that the hole of the exciton is self-trapped there and the electron is bound around the self-trapped hole by the Coulomb

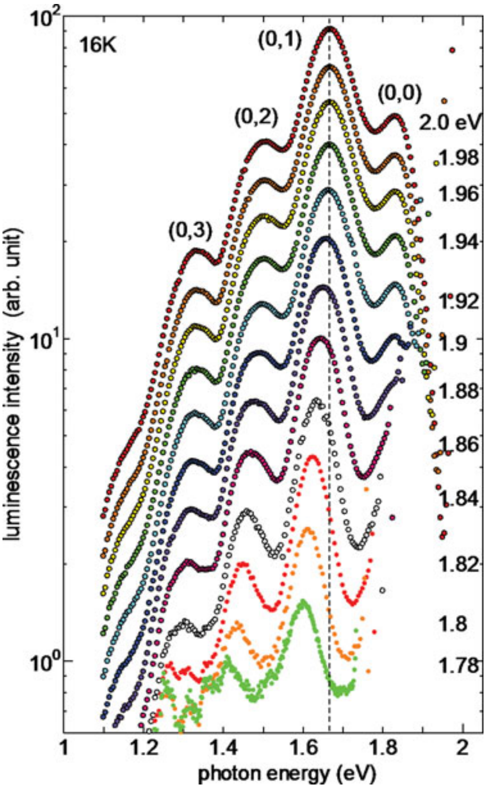


Figure 1. The excitation energy evolution of the luminescence spectrum at 16 K in the rrP3HT film. The luminescence spectra excited with the photon energies from 2.0 to 1.78 eV are shown.

interaction. It is considered that the energy level in the band gap of the self-trapped hole is not affected by the fluctuation of the size and axis of the rrP3HT domains because the extent of the self-trapped hole is restricted in the C=C which is much smaller than the domain size.

The band edges of the rrP3HT film with the amorphous-like structure, the self-trapped hole state, and the excitation and radiative recombination process are shown in Fig. 3. The exciton band gap of the rrP3HT domain at a site **r** is given by the equation,

$$E_g(\mathbf{r}) = \{E_{LO} - \Delta E(\mathbf{r})\} - \{E_{HO} + \Delta E(\mathbf{r})\} - E_B, \qquad (2)$$

where E_{L0} and E_{H0} are the average energies of LUMO and HOMO in the rrP3HT film. $\Delta E(\mathbf{r})$ is the shift of the band edge from the average energies. E_B is the exciton binding energy which is neglected in Fig. 3. The average band gap E_{AG} of the exciton is given by

$$E_{AG} = E_{L0} - E_{H0} - E_B. \qquad (3)$$

The luminescence energy due to the recombination of the self-trapped exciton is given by the equation,

$$E_L(\mathbf{r}) = \{E_{LO} - \Delta E(\mathbf{r})\} - \{(E_{HO} + U)\} - E_B, \qquad (4)$$

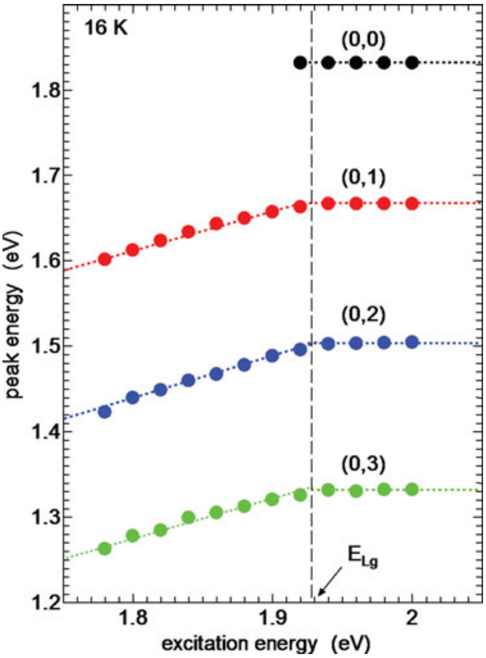


Figure 2. The excitation energy dependence of the (0,0), (0,1), (0,2) and (0,3) luminescence peak energies. E_{Lg} is the luminescence gap.

where U is the trapping energy of the self-trapped hole. The relation between the luminescence energy and the exciton band gap is derived using eqs. (2), (3) and (4), as follows,

$$E_L(\mathbf{r}) = \frac{1}{2}\{E_g(\mathbf{r}) - E_{AG}\} + E_{AG} - U. \tag{5}$$

In the excitation energy range lower than E_{AG}, the rrP3HT domain with the exciton band gap equal to the excitation energy is selectively excited. Then, the luminescence peak energy E_L is related to the excitation energy with the equation

$$E_L = \frac{1}{2}(E_X - E_{AG}) + E_{AG} - U, \text{ at } E_X < E_{AG}, \tag{6}$$

where E_X is the excitation energy. The E_L in eq. (6) with the slope of 0.5 to E_X agrees with that in eq. (1) obtained by the experiment. Furthermore, by comparing eq. (1) with eq. (6), $U = 0.08$ eV is obtained if the luminescence gap is equal to the average band gap.

The excitation energy dependences of the (0,1) luminescence peak energy observed at different temperatures from 16 to 300 K are shown in Fig. 4. At temperatures lower than 150 K, the luminescence peak energy excited with photon energies lower than 1.93 eV is seen to increase with increasing excitation energy, where the increasing rate of the peak energy to the excitation energy is 0.5 as in the case of 16 K. However, in the temperature higher than 200 K, the increasing rate is smaller. At 300 K, the luminescence peak energy is almost constant. This is explained by considering that the excitons created in the localized band tail states by the excitation energies lower than the luminescence gap of 1.93 eV are thermally excited to the average band edge and recombine radiatively, because the average

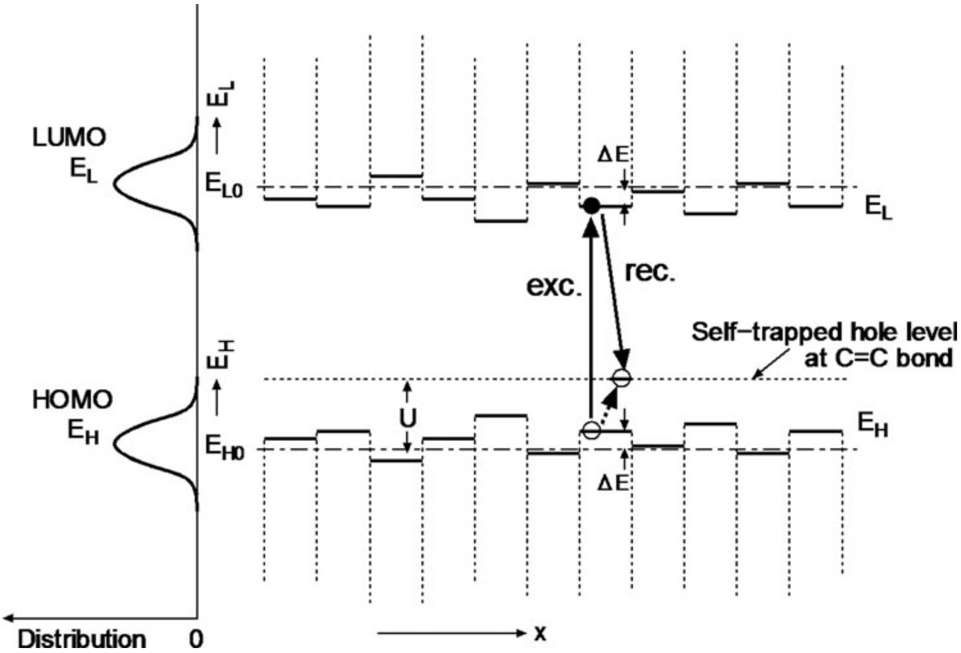


Figure 3. The distribution of the LUMO and HOMO levels of the nanometer-scale rrP3HT domains, the self-trapped hole and the excitation and recombination processes of an electron-hole pair. The nanometer-scale rrP3HT domains have different band gaps for the distribution of the size and axis of the domains. E_{L0} and E_{H0} show the average energies of the LUMO level E_L and the HOMO level E_H, respectively. ΔE is the energy shift of E_L and E_H due to the difference of the size and the axis. The dotted line shows the energy level of the hole self-trapped at a C=C bond and U is the trapping energy of the self-trapped hole.

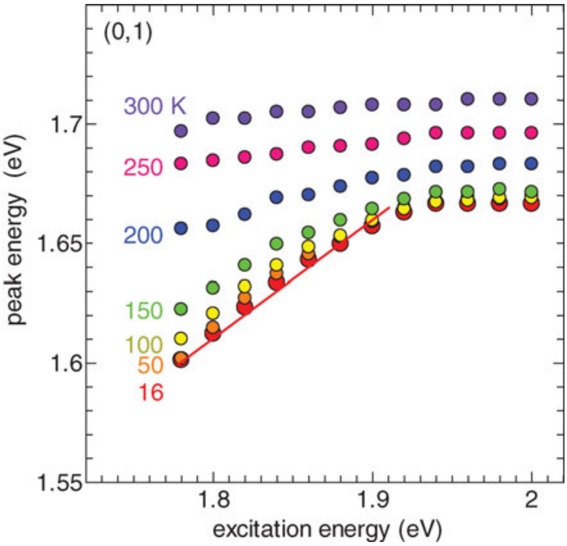


Figure 4. The excitation energy dependences of the (0,1) luminescence peak energy at different temperatures from 16 to 300 K in the rrP3HT film. A solid straight line with the slope of 0.5 is shown.

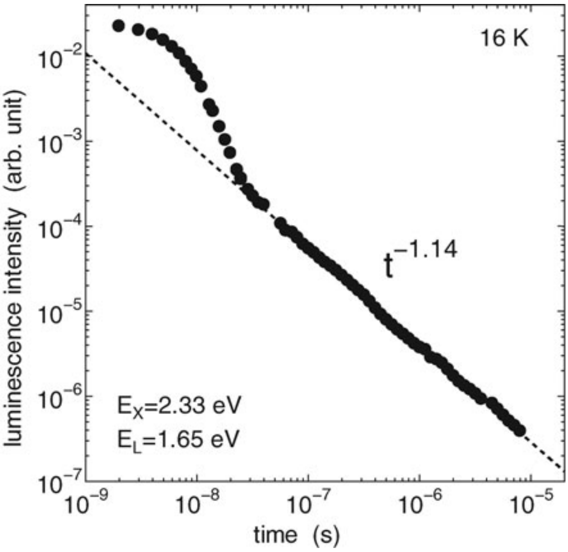


Figure 5. The decay of the 1.65 eV luminescence at 16 K in the rrP3HT film. The luminescence has been excited with the pulse light of 2.33 eV. A dotted straight line shows the power law decay of $t^{-1.14}$.

depth of the localized band tail states is estimated to be $E_S = 8$meV which is almost the same as the thermal energy of the exciton at 150 K.

The luminescence decay of the rrP3HT film at 16 K is observed with the pulse YAG laser with the photon energy of 2.33 eV and the pulse duration of ~5 ns as shown in Fig. 5. The luminescence decay consists of the exponential decay of the life time of ~6 ns and the power law decay described with $t^{-1.14}$ observed in the time range 3×10^{-8} to 1×10^{-5} s. The life time obtained does not agree with 235 ps in [2]. The reason is because the luminescence decay in this experiment is observed with the pulse laser with the duration of ~5 ns in this experiment. The exponent in the power law decay is -1.14, contrary to -1.54 in [2]. We consider that -1.14 is better because the power law decay is observed in the time range wider than that in [2]. The power law decay with the same exponent is observed in a-Si:H [9, 10], which is supported with the Monte Carlo simulation of the luminescence decay controlled by the electron random walk in the fractal structure [11].

We consider the self-trapped exciton model that the hole is self-trapped at a C=C bond and the electron is bound around the hole by the coulomb interaction. If the electron moves to another site by tunneling, then the charged pair is formed as suggested in [2]. Here, let us consider that electrons in self-trapped excitons diffuse by tunneling in the fluctuating band edge to form charged pairs. It is possible that the sites in which electrons can move by the tunneling form the fractal structure for the random band edge fluctuation. Then, the distribution of electrons around the self-trapped hole is described by a stretched Gaussian [12],

$$< P(\mathrm{r,t}) > \sim \left\{\frac{1}{< \mathrm{r}^2(\mathrm{t}) >}\right\}^{\mathrm{d}_{f/2}} \exp\left\{-\left(\frac{\mathrm{r}^2}{< \mathrm{r}^2(\mathrm{t}) >}\right)^{\mathrm{u}}\right\}, \tag{7}$$

where $u = d_w/(d_w - 1)$. r is the distance to the electron from the self-trapped hole, $< r^2(t) >$ the mean square displacement and d_w the fractal dimension of random walk. The <P(0,t)> is the probability that the electron-hole pairs remains as excitons. The luminescence intensity $I_L(t)$ is proportional to <P(0,t)>. Therefore, the luminescence decay controlled by the tunneling process of electrons is given by,

$$I_L(t) \sim < P(0,t) > \sim (1/ < r^2(t) >)^{d_f/2}. \tag{8}$$

At long delayed time, $< r^2(t) > \sim t$ [10]. Therefore, the luminescence decay is given by,

$$I_L(t) \sim t^{-d_f/2}. \tag{9}$$

The exponent of the power law decay of −1.14 observed shows that the fractal dimension of the sites on which electrons can move by the tunneling is $d_f \sim 2.3$.

4. Conclusions

The band gap in the rrP3HT film estimated from the excitation energy dependence of the luminescence peak energy, the so called luminescence gap, is shown to be 1.93 eV at 16 K. Furthermore, the self-trapped exciton, of which the luminescence is due to the recombination, is suggested to consist of the self-trapped hole and the electron bound around the hole. The electron bound around the self-trapped hole diffuses apart from the hole to form the charged pair.

References

[1] Clark, J., Silva, C., Friend, R. H., & Spano, F. C. (2007). *Phys. Rev. Lett. 98*, 206406.

[2] Paquin, F., Latini, G., Sakowicz, M., Karsenti, P., Wang, L., Beljonne, D., Stingelin, N., & Silva, C., (2011). *Phys. Rev. Lett. 106*, 197401.

[3] Sirringhaus, H., Brown, P. J., Friend, R. H., Nielsen, M. M., Bechgaad, K., Langeveld-Voss, B. M. W., Spiering, A. J. H., Janssen, R. A. J., Meijer, E. W., Herwig, P., & de Leeuw, D. M. (1999). *Nature.*, *401*, 685.

[4] Choulis, S. A., Kim, Y., Nelson, J., Bradley, D. D. C., Giles, M., Shkunov, M. & McCulloch, I. (2004). *Applied Phys. Lett.*, *85*, 3890.

[5] Vukmirovic, N. & Wang, L. - Wang, (2010). *Applied Phys. Lett. 97*(2010), 043305.

[6] Tauc, J., (1974). "*Amorphous and Liquid Semiconductors*" edited by J. Tauc, Plenum Press2539: London and New York(1974), p.159.

[7] Murayama, K., Sagawa, R., Monji, K., Tsushima, K., & Deki, H., (2012). *J. Non-Cryst. Solids.*, *358*, 2027.

[8] Banerji, N., Cowan, S., Vauthey, E. & Heeger, A.J., *J. Phys. Chem.C.*, *115*(2011), 9726.

[9] Murayama, K., & Ninomiya, T., (1985). *J. Non-Cryst. Solids.*, 77/78(1985), 699.

[10] Tsushima, K., Nakata, H., Monji, K., Deki, H. & Murayama, K., (2012). *J. Non-Cryst. Solids.*, *358*(2012), 2090.

[11] Ando, Y., Sasaki, S., Shingai, M. & Murayama, K., (2002). *Physica Status Solidi (b).*, *230*(2002), 15.

[12] Havlin, S. & Bunde, A., (1996). "*Fractals and Disordered Systems*" edited by A. Bunde and S. Havelin, Springer, p.115.