

Synthesis and Luminescence Properties of a Lollipop-Shaped Molecule Combined with Rod and Disc-Like Mesogens

E-JOON CHOI,^{1,*} FEI XU,¹ JONG-HO SON,²
AND WANG-CHEOL ZIN²

¹Department of Polymer Science and Engineering, Kumoh National Institute of Technology, Gumi, Gyeongbuk, 730-701, Korea

²Department of Material Science and Engineering, Pohang University of Science and Technology, Pohang, Gyeongbuk, 790-784, Korea

A novel lollipop-shaped molecule containing 1,3,4-oxadiazole moieties was designed and synthesized. The molecular structure of this 1,3,4-oxadiazole derivative was confirmed by FT-IR, ¹H-NMR spectroscopy and elemental analyzer. Its phase behavior and mesomorphic property were investigated by DSC, POM and X-ray diffraction measurements. We found that this compound showed a typical mosaic texture of columnar phase during cooling run. The electron excitation and luminescence properties of this compound were investigated by UV-vis absorption spectroscopy and photo-luminescence spectroscopy both in CHCl₃ solution and in solid state.

Keywords: luminescence properties; 1, 3, 4-oxadiazole; discotic columnar mesophase; lollipop-shaped mesogen; blue light emitting; liquid crystalline OLED

Introduction

Organic light-emitting diodes have been intensively studied due to their potential in next generation full-color displays^{1–5} and solid-state lighting.^{6,7} To date, a considerable number of organic conjugated low molar mass molecules have been synthesized and reported for applications in the field of OLEDs. In order to fabricate full-color OLED displays, we need high performance red,^{8–10} green,^{2,11} and blue^{12,13} materials with high EL efficiencies, good thermal properties and long lifetimes as well as pure color coordinates. However, the most widely studied emissive molecules are predominantly hole-transporting materials which possess low electron affinities,^{14,15} and consequently, the device exhibits relatively low EL efficiency. Its current focus and challenge lie in the optimization of the molecular structure with high electron-transporting property. Typical electron-transporting materials usually contain a π -electron deficient heterocyclic moiety. In addition, the use of heterocycles to tune emission behavior is widely practice since these materials exhibit both interesting electrical and optical properties and have excellent thermal and chemical stability.¹⁶

Among these heterocyclics, oxadiazoles is one of the most widely used moieties for OLED.^{17–19} Various kinds of oxadiazole molecules have been used to obtain high electroluminescence, such as bisoxadiazoles,^{20,21} branched or dendrimeric oxadiazoles,²²

*Corresponding author. E-mail: ejchoi@kumoh.ac.kr

polymers containing oxadiazole units either in the main chain^{23,24} or side chain^{25–27} and so on. Especially, 1,3,4-oxadiazole derivatives have been used as blue emitters as well as electron transport and hole blocking materials due to the electron-withdrawing character of the 1,3,4-oxadiazole rings.^{28,29}

On the other hand, liquid crystalline materials display unique properties which can be exploited in organic light-emitting diodes. Characteristic features of liquid crystals are the anisotropy of electronic properties, a strong coupling to external fields as well as a tendency to form spontaneously homogeneous monodomain films. The self-organization caused likewise the anisotropy of transport properties including the anisotropy of the mobility of charge carriers.³⁰ It is found that liquid crystalline materials can be used in light-emitting diodes to control the state of polarization of the emitted light, the magnitude of the onset field for emission as well as the quantum efficiency. Both low molar mass and polymeric liquid crystals have been introduced with great success in single as well as in multilayer devices. Especially, discotic liquid crystals able to form columns have been found to reveal unusually large mobility for holes and probably also for electrons along the columns.^{31–33}

Our present work was motivated by the above background and succeeded in designing and synthesizing a the lollipop-shaped oxadiazol-phenylene derivative consisting of two different types of mesogens. In addition, the insertion of the flexible alkyl segments on the side chain of the aromatic molecular frame could moderate the molecular flexibility and melting temperature which could promote the solubility of materials in common organic solvents. The thermal properties were investigated by a differential scanning calorimetry (DSC). The mesogenic properties were investigated using crosspolarizing optical microscopy and X-ray diffractometry. The physical properties were investigated by UV-vis absorption and photoluminescence (PL) spectroscopy. Interestingly, found was a blue-light-emitting liquid crystalline molecule which formed a discotic columnar mesophase.

Experimental

Synthesis

The synthesis of the lollipop-shaped compound was carried out by modification of procedure previously reported by us.³⁴

Synthesis of 4-(dodecyloxy)benzohydrazide (1). Ethyl 4-(dodecyloxy)benzoate (4.0 g, 12.0 mmol) and excess hydrazine monohydrate in ethanol was refluxed for 40 h. The resulting solution was poured into water. The precipitate was collected and dried under vacuum. The crude product was recrystallized from ethanol to give pure product **1** in 78.4% yield. IR (KBr Pellet, cm^{-1}): 3319 (NH_2 stretch), 3297, 3243 (NH stretch), 3018 (sp^2 C-H stretch), 2921, 2848 (sp^3 C-H stretch), 1617 (Conj. C=O stretch), 1346, 1124 (C-O stretch); ^1H NMR (CDCl_3 , δ in ppm): 7.69 (d, 2H, Ar-**H**), 7.32 (s, 1H, Ar-CONHNH₂), 6.90 (d, 2H, Ar-**H**), 3.96 (t, 2H, Ar-OCH₂CH₂), 1.76 (m, 2H, Ar-OCH₂CH₂CH₂), 1.33 (m, 2H, Ar-O(CH₂)₁₀CH₂CH₃), 1.24 (m, 16H, Ar-OC₂H₄(CH₂)₈C₂H₅), 0.85 (t, 3H, Ar-O(CH₂)₁₁CH₃).

Synthesis of methyl 4-(2-(4-(dodecyloxy)benzoyl)hydrazinecarbonyl)benzoate (2). At the atmosphere of nitrogen, monomethyl terephthalate (2.0 g, 10.8 mmol) was added into SOCl_2 and then added pyridine into three neck flask. The reaction mixture was refluxed at 80°C for 6 h. The reaction mixture was cooled to 40°C and SOCl_2 was removed at the vacuum state. DCM (30 mL) was added to dissolve the residue absolutely and then

add 4-(dodecyloxy) benzohydrazide (3.5 g, 10.8 mmol) and a little pyridine. The mixture was refluxed at 40°C for 12 h. After cooling at room temperature, the resulting solution was poured into distilled water (500 mL). The precipitate was collected and dried under vacuum. The crude product was recrystallized from ethanol to give pure product **2** in 76.8% yield. IR (KBr Pellet, cm^{-1}): 3222 (NH stretch), 3019 (sp^2 C-H stretch), 2917, 2850 (sp^3 C-H stretch), 1724 (Conj. C=O stretch), 1276, 1105 (C-O stretch); ^1H NMR (CDCl_3 , δ in ppm): 8.09 (d, 2H, Ar-*H*), 7.91 (d, 2H, Ar-*H*), 7.78 (d, 2H, Ar-*H*), 6.87 (d, 2H, Ar-*H*), 4.05 (t, 2H, Ar- OCH_2CH_2), 3.95 (s, 3H, Ar- COOCH_3), 1.74 (m, 2H, Ar- $\text{OCH}_2\text{CH}_2\text{CH}_2$), 1.33 (m, 2H, Ar- $\text{O}(\text{CH}_2)_{10}\text{CH}_2\text{CH}_3$), 1.25 (m, 16H, Ar- $\text{OC}_2\text{H}_4(\text{CH}_2)_8\text{C}_2\text{H}_5$), 0.85 (t, 3H, Ar- $\text{O}(\text{CH}_2)_{11}\text{CH}_3$).

Synthesis of methyl 4-(5-(4-(dodecyloxy)phenyl)-1,3,4-oxadiazol-2-yl)benzoate (3). The purified methyl 4-(2-(4-(dodecyloxy)benzoyl)hydrazine carbonyl)benzoate (2.6 g, 5.3 mmol) was dissolved in phosphorous oxychloride (POCl_3) and refluxed for about 40 h. Excess POCl_3 was removed through distillation under reduced pressure and the residue was slowly added into ice water. The precipitate was collected and dried under vacuum. The crude product was further purified through a column of silica gel using 2% ethyl acetate in chloroform as eluent to afford product **3** in 34.1% yield. IR (KBr Pellet, cm^{-1}): 3070 (sp^2 C-H stretch), 2925, 2846 (sp^3 C-H stretch), 1695 (C=N stretch), 1380, 1120 (C-O stretch); ^1H NMR (CDCl_3 , δ in ppm): 8.18 (s, 4H, Ar-*H*), 8.04 (d, 2H, Ar-*H*), 7.03 (d, 2H, Ar-*H*), 4.05 (t, 2H, Ar- OCH_2CH_2), 3.92 (s, 3H, Ar- COOCH_3), 1.74 (m, 2H, Ar- $\text{OCH}_2\text{CH}_2\text{CH}_2$), 1.33 (m, 2H, Ar- $\text{O}(\text{CH}_2)_{10}\text{CH}_2\text{CH}_3$), 1.24 (m, 16H, Ar- $\text{OC}_2\text{H}_4(\text{CH}_2)_8\text{C}_2\text{H}_5$), 0.86 (t, 3H, Ar- $\text{O}(\text{CH}_2)_{11}\text{CH}_3$).

Synthesis of 4-(5-(4-(dodecyloxy)phenyl)-1,3,4-oxadiazol-2-yl)benzoic acid (4). Methyl 4-(5-(4-(dodecyloxy)phenyl)-1,3,4-oxadiazol-2-yl)benzoate (7.7 g, 23.0 mmol) and sodium hydroxide (4.2 g, 105.0 mmol) were added to the mixture of EtOH/ H_2O (500 mL, v/v = 1:1) under nitrogen. The mixture was stirred at 100°C overnight. After reaction, the solution was acidified with dilute hydrochloric acid to pH = 1 and then the reaction mixture were cooled to room temperature. The resulting solid was collected by filtration and washed with 1000 mL water for three times. The precipitate was collected by filtration and dried under vacuum to afford product **4** in 79.6% yield. IR (KBr Pellet, cm^{-1}): 3295–2443 (COOH stretch), 3068 (sp^2 C-H stretch), 2921, 2844 (sp^3 C-H stretch), 1687 (Conj. C=O stretch), 1606 (C=N stretch), 1292, 1172 (C-O stretch); ^1H NMR ($\text{DMSO}-d_6$, δ in ppm): 8.26 (d, 2H, Ar-*H*), 8.15 (d, 2H, Ar-*H*), 8.09 (d, 2H, Ar-*H*), 7.18 (d, 2H, Ar-*H*), 4.07 (t, 2H, Ar- OCH_2CH_2), 1.73 (m, 2H, Ar- $\text{OCH}_2\text{CH}_2\text{CH}_2$), 1.33 (m, 2H, Ar- $\text{O}(\text{CH}_2)_{10}\text{CH}_2\text{CH}_3$), 1.24 (m, 16H, Ar- $\text{OC}_2\text{H}_4(\text{CH}_2)_8\text{C}_2\text{H}_5$), 0.85 (t, 3H, Ar- $\text{OCH}_2\text{CH}_2(\text{CH}_2)_8\text{CH}_2\text{CH}_3$).

Synthesis of 2-(4-(dodecyloxy)phenyl)-5-(4-(5-(3,4,5-tris(dodecyloxy)phenyl)-1,3,4-oxadiazol-2-yl)phenyl)-1,3,4-oxadiazole (5). At an atmosphere of nitrogen, 4-(5-(4-(dodecyloxy)phenyl)-1,3,4-oxadiazol-2-yl)benzoic acid (2.8 g, 6.2 mmol) was added into SOCl_2 and then added pyridine into a three-neck flask. The reaction mixture was refluxed at 80°C for 6 h. The reaction mixture was cooled to 40°C and SOCl_2 was removed at the vacuum state. DCM (30 mL) was added to dissolve the residue absolutely and then add 3,4,5-tris(dodecyloxy)-benzohydrazide (4.3 g, 6.2 mmol) and a little pyridine. The mixture was refluxed at 40°C for 12 h. After cooling at room temperature, the resulting solution was poured into distilled water (500 mL). The precipitate was collected and dried under vacuum. The crude product which was recrystallized from ethanol (2.5 g, 2.2 mmol) was dissolved in phosphorous oxychloride (POCl_3) and refluxed for about 40 h. Excess POCl_3 was removed through distillation under reduced pressure and the residue was slowly added into ice water. The precipitate was collected and dried under vacuum. The crude product

was further purified through a column of silica gel using 2% ethyl acetate in chloroform as an eluent to afford product **5** in 29.8% yield. IR (KBr Pellet, cm^{-1}): 3077 (sp^2 C-H stretch), 2919, 2854 (sp^3 C-H stretch), 1606 (C=N stretch), 1257, 1118 (C-O stretch); ^1H NMR (CDCl_3 , δ in ppm): 8.28 (s, 4H, Ar-**H**), 7.98 (d, 2H, Ar-**H**), 7.32 (s, 2H, Ar-**H**), 7.00 (d, 2H, Ar-**H**), 4.03 (t, 8H, Ar-OCH₂CH₂), 1.81 (m, 8H, Ar-OCH₂CH₂CH₂CH₃), 1.33 (m, 8H, Ar-OCH₂CH₂(CH₂)₈CH₂CH₃), 1.25 (m, 64H, Ar-OCH₂CH₂(CH₂)₈CH₂CH₃), 0.85 (t, 12H, Ar-OCH₂CH₂(CH₂)₈CH₂CH₃). Anal. Calcd. C: 76.18% H: 10.05% and N: 5.08%, and found C: 76.19% H: 10.30% and N: 5.09%.

Measurements

FT-IR and NMR spectra were obtained by using Jasco 300E FT/IR and Bruker DPX 200 MHz NMR spectrometers, respectively. The chemical shifts were reported in ppm units with tetramethylsilane (TMS) as internal standard. Elemental analysis was performed with a Thermofinnigan EA1108. The transition behaviors were characterized by differential scanning calorimetry (NETZSCH 200 F3). UV-vis absorption spectra were reported on an OPTIZEN 3220UV spectrometer. Photoluminescence was measured by RF-5301PC spectrometer. Optical texture observation was carried out using a polarizing microscope (Carl Zeiss Axioskop 40) with a hot stage (Mettler FP82HT).

Results and Discussion

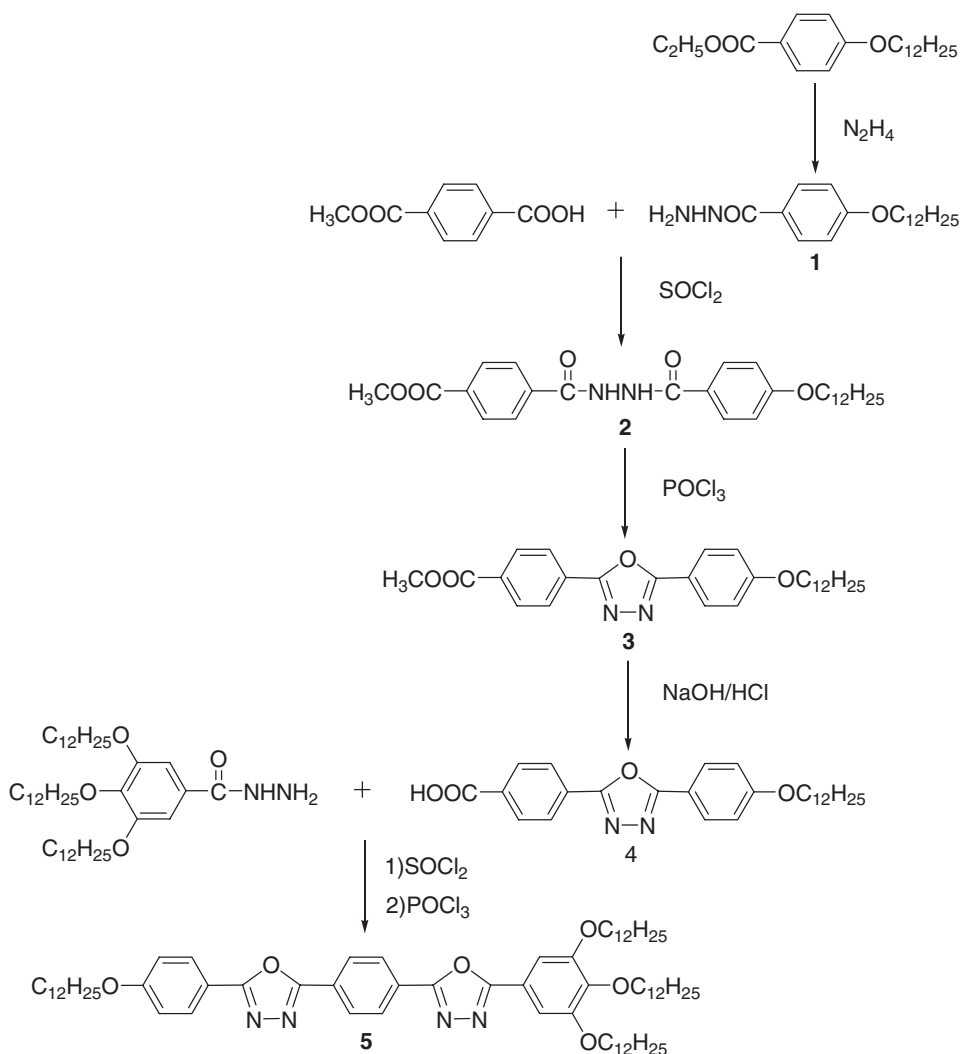
The synthetic route to the lollipop-shaped liquid crystalline molecule is shown in Scheme 1. This compound was prepared by cyclodehydration of the hydrazide precursors using PCl_3 . The structures of all products were identified by using IR and NMR spectrometry as already described in the experimental section. The all resultant data of the spectra were in accordance with expected values. The purities of compounds were confirmed by using an elemental analysis, and the resultant data was tolerable.

The differential scanning calorimetric (DSC) thermograms is presented in Figure 1. The melting temperature (T_m), recrystallization temperature (T_c) and the related enthalpy changes are listed in Table 1. The melting temperature and the enthalpy change for melting were 89.9°C and 148.8 KJ/mol, respectively. During the cooling process, this liquid crystalline molecule exhibited a discotic columnar phase. And the isotropic-to-mesophase transition temperature and the enthalpy change were 72.5°C and 1.5 KJ/mol, respectively. As expected, introduction of trialkoxy groups to the rigid segment lowered the melting temperature and increased the solubility remarkably. This indicates that flexible $-\text{CH}_2-$ subunits can give an entropy benefit to the system and the bulky trialkoxy end group can disturb the packing of molecules.

Table 1. Thermal properties of compound

T_m (°C)	$^a\Delta H_m$ (kJ mol ⁻¹)	bT_c (°C)	ΔH_c (kJ mol ⁻¹)	T_i (°C)	ΔH_i (kJ mol ⁻¹)
89.9	148.8	66.5	27.1	72.5	1.5

$^a\Delta H_m$: total enthalpy changes for multiple melting. bT_c : recrystallization temperature.



Scheme 1. Synthetic route to a lollipop-shaped compound.

Figure 2 showed the crosspolarizing optical micrographs of the liquid crystalline compound obtained during cooling run. A typical mosaic texture of columnar phase was found as shown in Figure 2 (a) and a transition from mesophase to crystal was found at 52.2°C as Figure 2 (b). Figure 4 showed the X-ray diffraction data measured during the first heating and first cooling run. As cooled from the isotropic liquid, a strong peak appeared at the small angle region, showing broad peaks in wide angle region, being matched with the temperature range of mesophase formation ($72.5\text{--}66.5^\circ\text{C}$) defined by DSC.

The UV absorption and fluorescent properties of this liquid crystalline molecule have been studied. The absorption and PL spectra in CHCl_3 solution and in solid state are shown in Figure 3. The data of $\lambda_{\text{abs, max}}$ and $\lambda_{\text{em, max}}$ are presented in Table 2. This compound exhibited a distinctive absorption peak at $342\text{--}346\text{ nm}$. As the UV-vis absorption spectra

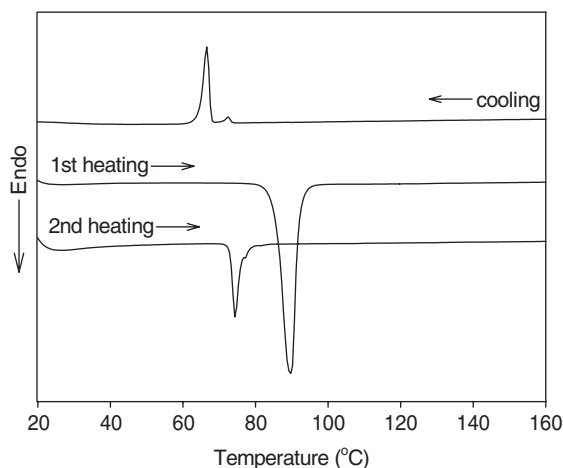


Figure 1. DSC thermograms of compound (heating and cooling rate = 10°C/min).

in CHCl_3 solution and in solid state are compared, a shift to higher wavelength is evident in the case of solid state. The PL spectra of this compound exhibit a well-defined vibronic feature. The table 2 showed that the liquid crystalline compound could emit a blue light both in CHCl_3 solution and in solid state on photoexcitation. The PL maxima of the compound occurred at 451–462 nm.

In order to investigate the OLED performances of this compound, we tried to make the device through thermal evaporation. But it was failed to fabricate OLED device. The reason was our compound's melting temperature is so low that material shows bumping seriously during evaporation, which leads very unstable thin film formation. Therefore, to confirm the OLED performance due to high electron-transporting property of this compound, more studies are needed including structural modification for the fabrication of OLED device.

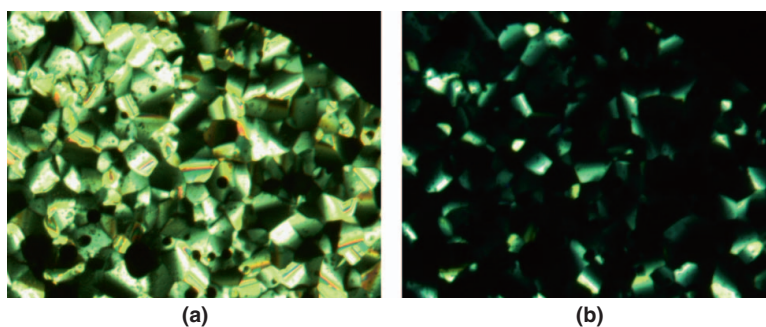


Figure 2. Crosspolarizing optical micrographs of compound on cooling (Magnification 200X): (a) $T = 72.5^\circ\text{C}$; (b) $T = 52.2^\circ\text{C}$.

Table 2. Physical properties of compound

CHCl ₃ Solution		Film on Glass	
$\lambda_{\text{abs, max}}$ (nm)	$\lambda_{\text{em, max}}$ (nm)	$\lambda_{\text{abs, max}}$ (nm)	$\lambda_{\text{em, max}}$ (nm)
342	451	346	462

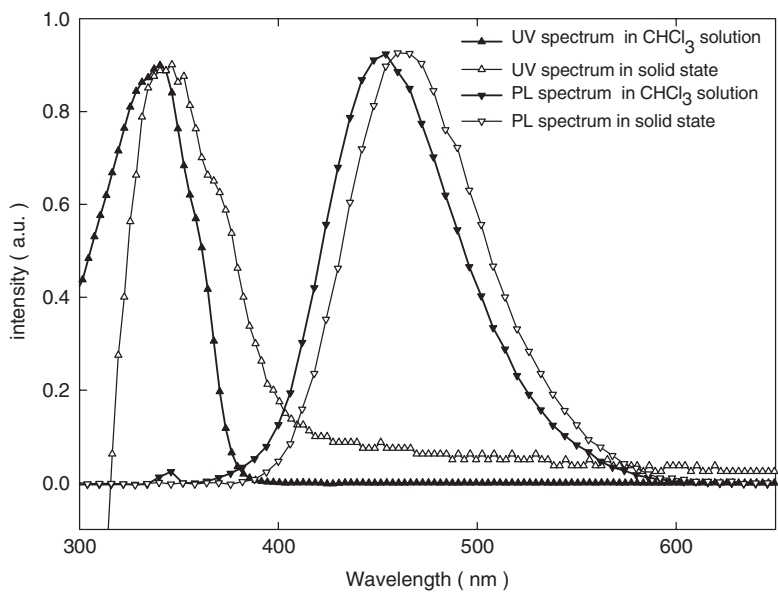


Figure 3. UV-Vis absorption and PL spectra of the liquid crystalline compound at room temperature.

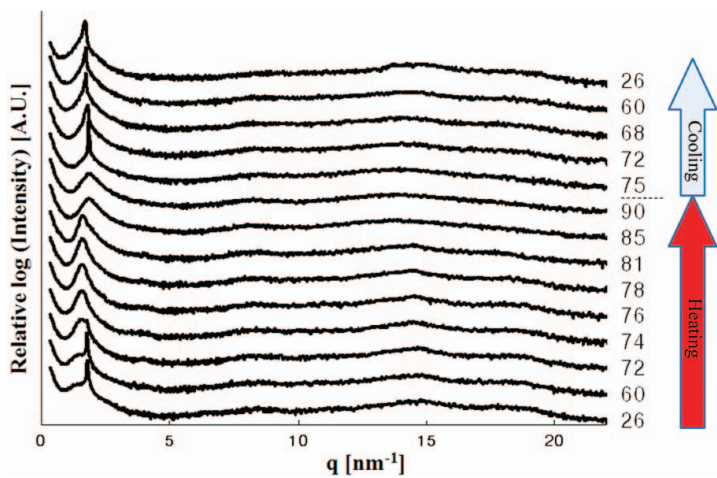


Figure 4. X-ray diffraction patterns of compound at the given temperature from bottom to top: on heating as prepared sample measured from room temperature to 90°C; on cooling the isotropic liquid, measured from 90°C to room temperature.

Conclusions

We have successfully designed and synthesized a lollipop-shaped liquid crystalline compound. Its optical and thermal properties were investigated. The solubility of this 1,3,4-oxadiazole derivative promoted greatly as introducing flexible groups. In general, the UV-vis absorption maxima peaks (342 nm-346 nm) and PL maxima peaks (451 nm-462 nm) were observed at the blue-light-emitting region. Especially, we found that besides possessing electron-transporting capability, a lollipop-shaped molecule based on 1,3,4-oxadiazole combining rod mesogen with disk mesogen could form a discotic columnar mesophase monotropically, which should improve the EL efficiencies.

Acknowledgment

This work was supported by the Korea Science and Engineering Foundation (KOSEF) grant funded by the Korea government (MEST) (No. R01-2008-000-11521-0).

References

- [1] Tang, C. W., Van Slyke, S. A., *Appl. Phys. Lett.*, **51**, 913, (1987).
- [2] Tang, C. W., Van Slyke, S. A., Chen, C. H., *J. Appl. Phys.*, **65**, 3610, (1989).
- [3] Baldo, M. A., Thompson, M. E., Forrest, S. R., *Nature*, **403**, 750, (2000).
- [4] Wu, C. C., Lin, Y. T., Wong, K. T., Chen, R. T., Chien, Y. Y., *Adv. Mater.*, **16**, 61, (2004).
- [5] Adachi, C., Tsutsui, T., Saito, S., *Appl. Phys. Lett.*, **55**, 1489, (1989).
- [6] D'Andrade, B.W., Forrest, S.R., *Adv. Mater.*, **16**, 1585, (2004).
- [7] D'Andrade, B.W., *Nature Photon*, **1**, 33, (2007).
- [8] Picciolo, L. C., Murata, H., Kafafi, Z. H., *Appl. Phys. Lett.*, **78**, 2378, (2001).
- [9] Jung, B. J., Lee, J. I., Chu, H. Y., Do, L. M., Lee, J. M., Shim, H. K., *J. Mater. Chem.*, **15**, 2470, (2005).
- [10] Hwang, E. J., Kim, Y. E., Lee, C. J., Park, J. W., *Thin Solid Films*, **499**, 185, (2006).
- [11] Ding, J., Gao, J., Cheng, Y., Xie, Z., Wang, L., Ma, D., Jing, X., Wang, F., *Adv. Funct. Mater.*, **16**, 575, (2006).
- [12] Ren, X., Li, J., Holmes, R. J., Djurovich, P. I., Forrest, S. R., Thompson, M. E., *Chem. Mater.*, **16**, 4743, (2004).
- [13] Chen, C. H., Wu, F. I., Shu, C. F., Chien, C. H., Tao, Y. T., *J. Mater. Chem*, **14**, 1585, (2004).
- [14] Oyston, S., Wang, C.S., Hughes, G., Batsanov, A.S., Perepichka, I.F., Bryce, M.R., Ahn, J.H., Pearson, C., Petty, M.C., *J. Mater. Chem.*, **15**, 194, (2005).
- [15] Oyston, S., Wang, C.S., Perepichka, I.F., Perepichka, A.S., Bryce, M.R., Ahn, J.H., Pearson, C., Petty, M.C., *J. Mater. Chem.*, **15**, 5164, (2005).
- [16] Roncali, J., *Chem. Rev.*, **92**, 711, (1992).
- [17] Adachi, C., Tsutsui, T., Saito, S., *Appl. Phys. Lett.*, **56**, 799, (1990).
- [18] Ahn, J.H., Wang, C., Pearson, C., Bryce, M.R., Petty, M.C., *Appl. Phys. Lett.*, **85**, 1283, (2004).
- [19] Bettenhausen, J., Strohhriegl, P., *Adv. Mater.*, **8**, 507, (1996).
- [20] Meier, M., Buchwald, E., Karg, S., Pösch, P., Greczmiel, M., Strohhriegl, P., Rieß, W., *Synth. Met.*, **76**, 95, (1996).
- [21] Ahn, J.H., Wang, C., Pearson, C., Bryce, M.R., Petty, M.C., *Appl. Phys. Lett.*, **85**, 1283, (2004).
- [22] Bettenhausen, J., Strohhriegl, P., *Adv. Mater.*, **8**, 507, (1996).
- [23] Yang, Y., Pei, Q., *J. Appl. Phys.*, **77**, 4807, (1995).
- [24] Pei, Q., Yang, Y., *Adv. Mater.*, **7**, 559, (1995).
- [25] Strukelj, M., Papadimitrakopoulos, F., Miller, T.M., Rothberg, L.J., *Science*, **267**, 1969, (1995).
- [26] Li, X.-C., Cacalali, F., Giles, M., Gruner, J., Friend, R.H., Holmes, A.B., Moratti, S.C., Yong, T.M., *Adv. Mater.*, **7**, 898, (1995).
- [27] Cacalali, F., Li, X.-C., Friend, R.H., Moratti, S.C., Holmes, A.B., *Synth. Met.*, **75**, 161, (1995).

- [28] Mitschke, U., Bäuerle, P., *J. Mater. Chem.*, **10**, 1471, (2000).
- [29] Kraft, A., Grimsdale, A. C., Holmes, A. H., *Angew. Chem. Int. Ed.*, **37**, 402, (1998).
- [30] Lüssem, G., Wendorff, J. H., *Polym. Adv. Technol.*, **9**, 443–460, (1998).
- [31] Adam, D., Schuhmacher, P., Simmerer, J., HauBling, L., Siemensmeyer, K., Etzbach, K. H., Ringsdorf, H., Haarer, D., *Nature*, **371**, 141, (1994).
- [32] Adam, D., Closs, F., Frey, T., Funhoff, D., Haarer, D., Ringsdorf, H., Schuhmacher, P., Siemensmeyer, K., *Phys. Rev. Lett.*, **70**, 457, (1993).
- [33] Adam, D., Closs, F., Frey, T., Funhoff, D., Haarer, D., Ringsdorf, H., Schuhmacher, P., Siemensmeyer, K., *Adv. Mater.*, **7**, 276, (1993).
- [34] Choi, E. -J., Xu, F., *Mol. Cryst. Liq. Cryst.*, **527**, 147–156, (2010).

Copyright of Molecular Crystals & Liquid Crystals is the property of Taylor & Francis Ltd and its content may not be copied or emailed to multiple sites or posted to a listserv without the copyright holder's express written permission. However, users may print, download, or email articles for individual use.