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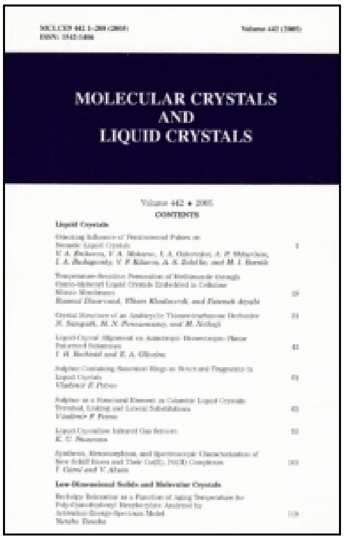

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Synthesis and Luminescence Properties of Dumbbell-Shaped Molecules Combined with Rod and Disc-Like Mesogens

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A novel series of dumbbell-shaped molecules containing 1,3,4-oxadiazole moieties (OXD_n: n = 1, 2, and 3) was designed and synthesized. The molecular structures of these 1,3,4-oxadiazole derivatives were confirmed by FT-IR, ^{1}H-NMR spectroscopy and elemental analyzer. The electron excitation and luminescence properties of these compounds were investigated by UV-vis absorption spectroscopy and photoluminescence spectroscopy both in $CHCl_3$ solution and in solid state. The absorption peaks were found at 336 nm-351 nm, and the photoluminescent peaks at 410 nm-450 nm. The thermal properties were investigated by DSC method. Their melting temperatures were in the range of 81-95°C depending on the structure. Especially, OXD_1 could show a discotic columnar mesophase at 75°C monotropically.

Keywords 1,3,4-oxadiazole; blue light emitting; discotic columnar mesophase; dumbbell-shaped mesogen; organic light-emitting diode

Introduction

Since the Cambridge group discovered that poly (p-phenylene vinylene) (PPV) can be used as a light-emitting layer for LEDs in 1990 [1], organic (OLEDs) and polymeric light-emitting diodes (PLEDs) have drawn great attention. Over last two decades, a considerable number of new low molecular mass compounds have been synthesized and analyzed for applications in the field of OLEDs. However, the most widely studied emissive molecules are predominantly hole-transporting materials which possess low electron affinities [2,3], and consequently, the device exhibits relatively low efficiency. In order to fabricate more efficient and high performance device, new materials with high electron-transporting capability are demanded. 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 [4].

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Among these heterocyclics, oxadiazoles is one of the most widely used moieties for OLED [5–7]. Various kinds of oxadiazole molecules have been used to obtain high electroluminescence, such as bisoxadiazoles [8,9], branched or dendrimeric oxadiazoles [10], polymers containing oxadiazole units either in the main chain [11,12] or side chain [13–15] 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 [16,17]. However, the applicability of the OLED materials based on 1,3,4-oxadiazole is limited because these materials have poor solubility in common organic solvents [18–22]. The solubility of these materials could be improved by introducing the flexible groups, but some attempts to improve solubility occasionally induced the conjugation to be interrupted [23–25].

On the other hand, examples of mesomorphic 1,3,4-oxadiazole [26] were relatively limited, and most of them were generally rod-like molecules exhibiting nematic/smectic mesophases, such as 2,5-bis(4-octadecyloxybenzylidene-4-aminophenyl)-1,3,4-oxadiazole [27]. A star-shaped discotic molecule containing 1,3,5-triethynylbezene and oxadiazole-based rigid arms was reported [28] to exhibit a discotic nematic phase, while 1,3,4-oxadiazole derivatives [28,29] formed scarcely discotic columnar mesophases.

Our present work was motivated by the above background and succeeded in designing and synthesizing a novel series of oxadiazol-phenylene derivatives 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. Their thermal properties were investigated by a differential scanning calorimetry (DSC). The physical textures were observed under crosspolarizing optical microscope. The optical properties were investigated by UV-vis absorption and photoluminescence (PL) spectroscopy. The variation of luminescence properties was investigated as increasing the length of the central rod mesogen. Interestingly, of the three dumbbell-shaped molecules, 1,4-bis(5-(3,4,5-tris(dodecyloxy)phenyl)-1,3,4-oxadiazol-2-yl)benzene exhibited a discotic columnar mesophase was found.

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Experimental

Synthesis

Synthesis of ethyl 3,4,5-tris(dodecyloxy)benzoate (1). Anhydrous Na_2CO_3 (2.54 g, 24.0 mmol) and ethyl 3,4,5-trihydroxy benzoate (1.19 g, 6.00 mmol) were added to the mixture of DMF (40 mL) and 1-bromododecane (4.31 mL, 18.0 mmol) under nitrogen [30]. The mixture was stirred at 80°C for 6 h. The reaction mixture was cooled to room temperature. The resulting solution was poured into water. The precipitate was collected and dried under vacuum. The crude product was chromatographed on a silica gel column with chloroform as the eluent to afford product **1** in 78.6% yield. IR (KBr Pellet, cm^{-1}): 3060 (sp^2 C-H stretch), 2915, 2854 (sp^3 C-H stretch), 1718 (Conj. C=O stretch), 1581, 1471 (Aromatic C=C stretch), 1330, 1108 (C-O stretch); ^1H NMR ($CDCl_3$, δ in ppm): 7.22 (s, 2H, Ar-$\boldsymbol{H}$), 4.31 (m, 2H, Ar-$COOC\boldsymbol{H}_2CH_3$), 3.98 (t, 6H, Ar-$OC\boldsymbol{H}_2CH_2$), 1.71 (m, 6H, Ar-$OCH_2C\boldsymbol{H}_2CH_2$), 1.33 (m, 6H, Ar-$O(CH_2)_{10}C\boldsymbol{H}_2CH_3$), 1.30 (t, 3H, Ar-$COOCH_2C\boldsymbol{H}_3$), 1.29 (m, 48H, Ar-$OC_2H_4(C\boldsymbol{H}_2)_8C_2H_5$), 0.85 (t, 9H, Ar-$O(CH_2)_{11}C\boldsymbol{H}_3$).

Synthesis of 3,4,5-tris(dodecyloxy)benzoylhydrazide (2). Compound 1 (1.00 g, 1.42 mmol) and excess hydrazine monohydrate in ethanol was refluxed for 40 h [31]. The resulting solution was poured into water. The precipitate was collected and dried under vacuum. The crude product was recrystallized from a mixture of ethanol and water (2:1 v/v) to give pure product **2** in 95.3% 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); ^{1}H NMR (CDCl$_3$, δ in ppm): 6.89 (s, 2H, Ar-$\boldsymbol{H}$), 3.98 (t, 6H, Ar-OC$\boldsymbol{H}_2$CH$_2$), 1.80 (m, 6H, Ar-OCH$_2$C$\boldsymbol{H}_2$CH$_2$), 1.33 (m, 6H, Ar-O(CH$_2$)$_{10}$C$\boldsymbol{H}_2$CH$_3$), 1.29 (m, 48H, Ar-OC$_2$H$_4$(C$\boldsymbol{H}_2$)$_8$C$_2$H$_5$), 0.85 (t, 9H, Ar-O(CH$_2$)$_{11}$C$\boldsymbol{H}_3$).

Synthesis of N'^{1},N'^{4}-bis(3,4,5-tris(dodecyloxy)benzoyl) terephthaloylhydrazide (3–1). At the atmosphere of nitrogen, terephthalic acid (1.00 g, 5.80 mmol) was added into SOCl$_2$ and then a catalystic amount of pyridine was added. This mixture was refluxed at 80°C for 6 h. After reaction, excess SOCl$_2$ was removed at 40°C under vacuum. To dissolve the obtained terephthaloyl chloride, DCM (30 mL) was added. Compound 2 (8.00 g, 11.6 mmol) and a little pyridine were then added into the solution. The mixture was refluxed at 40°C for 12 h and then cooled to 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 **3–1** in 86.5% yeild. IR (KBr Pellet, cm^{-1}): 3172 (NH stretch), 3018 (sp^2 C-H stretch), 2917, 2852 (sp^3 C-H stretch), 1579 (Conj. C=O stretch), 1330, 1120 (C-O stretch); ^{1}H NMR (CDCl$_3$, δ in ppm): 8.00 (d, 4H, Ar-$\boldsymbol{H}$), 7.01 (s, 4H, Ar-$\boldsymbol{H}$), 3.95 (t, 12H, Ar-OC$\boldsymbol{H}_2$CH$_2$), 1.71 (m, 12H, Ar-OCH$_2$C$\boldsymbol{H}_2$CH$_2$), 1.33 (m, 12H, Ar-O(CH$_2$)$_{10}$ C$\boldsymbol{H}_2$CH$_3$), 1.22 (m, 96H, Ar-OC$_2$H$_4$(C$\boldsymbol{H}_2$)$_8$C$_2$H$_5$), 0.85 (t, 18H, Ar-O(CH$_2$)$_{11}$C$\boldsymbol{H}_3$).

Synthesis of 1,4-bis(5-(3,4,5-tris(dodecyloxy)phenyl)-1,3,4-oxadiazol-2-yl)benzene (OXD$_1$). The purified compound **3–1** was dissolved in phosphorous oxychloride (POCl$_3$) and refluxed for about 40 h [33]. After reaction, excess POCl$_3$ was removed through distillation and then the residue was slowly added into ice water. After the removal of solvent under reduced pressure, the crude product was further purified through a column of silica gel using 2% ethyl acetate in chloroform as the eluent to afford white product **OXD$_1$** in 40.2% yeild. 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);^{1}H NMR (CDCl$_3$, δ in ppm): 8.29 (d, 4H, Ar-$\boldsymbol{H}$), 7.31 (s, 4H, Ar-$\boldsymbol{H}$), 4.05 (t, 12H, Ar-OC$\boldsymbol{H}_2$CH$_2$), 1.71 (m, 12H, Ar-OCH$_2$C$\boldsymbol{H}_2$CH$_2$), 1.33 (m, 12H, Ar-O(CH$_2$)$_{10}$C$\boldsymbol{H}_2$CH$_3$), 1.22 (m, 96H, Ar-OC$_2$H$_4$(C$\boldsymbol{H}_2$)$_8$C$_2$H$_5$), 0.85 (t, 18H, Ar-O(CH$_2$)$_{11}$C$\boldsymbol{H}_3$). Anal. Calcd. C: 76.68% H: 10.82% and N: 3.81%, and found C: 76.38% H: 11.25% and N: 3.67%.

Other compound 3-n and OXD$_n$ molecules were synthesized with methods same as compound 3–1 and OXD$_1$.

Synthesis of N'^{4},$N'^{4''}$-bis(3,4,5-tris(dodecyloxy)benzoyl)biphenyl-4,4′-dicarbohydrazide (3–2). Compound **3–2** was obtained as a gray powder in 83.0% yield. IR (KBr Pellet, cm^{-1}): 3180 (NH stretch), 3016 (sp^2 C-H stretch), 2917, 2852 (sp^3 C-H stretch), 1585 (Conj. C=O stretch), 1336, 1120 (C-O stretch); ^{1}H NMR (CDCl$_3$, δ in ppm): 8.26 (d, 4H, Ar-$\boldsymbol{H}$), 7.80 (d, 4H, Ar-$\boldsymbol{H}$), 7.32 (s, 4H, Ar-$\boldsymbol{H}$), 4.05 (t, 12H, Ar-OC$\boldsymbol{H}_2$CH$_2$), 1.73 (m, 12H, Ar-OCH$_2$C$\boldsymbol{H}_2$CH$_2$), 1.33 (m, 12H, Ar-O(CH$_2$)$_{10}$C$\boldsymbol{H}_2$CH$_3$), 1.22 (m, 96H, Ar-OC$_2$H$_4$(C$\boldsymbol{H}_2$)$_8$C$_2$H$_5$), 0.85 (t, 18H, Ar-O(CH$_2$)$_{11}$C$\boldsymbol{H}_3$).

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Synthesis of 4,4′-bis(5-(3,4,5-tris(Dodecyloxy)phenyl)-1,3,4-oxadiazol-2-yl)biphenyl (OXD_2). Compound $\mathbf{OXD_2}$ was obtained as a white powder in 33.1% yield. IR (KBr Pellet, cm^{-1}): 3093 (sp^2 C-H stretch), 2917, 2852 (sp^3 C-H stretch), 1589 (C=N stretch), 1324, 1118 (C-O stretch); ^1H NMR ($CDCl_3$, δ in ppm): 8.25 (d, 4H, Ar-***H***), 7.80 (d, 4H, Ar-***H***), 7.32 (s, 4H, Ar-***H***), 4.05 (t, 12H, Ar-$OC\boldsymbol{H}_2CH_2$), 1.71 (m, 12H, Ar-$OCH_2C\boldsymbol{H}_2CH_2$), 1.33 (m, 12H, Ar-$O(CH_2)_{10}C\boldsymbol{H}_2CH_3$), 1.22 (m, 96H, Ar-$OC_2H_4(C\boldsymbol{H}_2)_8C_2H_5$), 0.85 (t, 18H, Ar-$O(CH_2)_{11}C\boldsymbol{H}_3$). Anal. Calcd. C: 77.57% H: 10.55% and N: 3.62%, and found C: 76.67% H: 10.88% and N: 3.57%.

Synthesis of $N'^4,N'^{4''}$-bis(3,4,5-tris(dodecyloxy)benzoyl)p-terphenyl-4,4″-dicarbohydrazide (3–3). Compound **3–3** was obtained as a gray power in 80.0% yield. IR (KBr Pellet, cm^{-1}): 3178 (NH stretch), 3033 (sp^2 C-H stretch), 2917, 2848 (sp^3 C-H stretch), 1581 (Conj. C=O stretch), 1336, 1122 (C-O stretch); ^1H NMR ($CDCl_3$, δ in ppm): 7.93 (d, 4H, Ar-***H***), 7.70 (d, 4H, Ar-***H***), 7.65 (s, 4H, Ar-***H***), 7.07 (s, 4H, Ar-***H***), 3.95 (t, 12H, Ar-$OC\boldsymbol{H}_2CH_2$), 1.71 (m, 12H, Ar-$OCH_2C\boldsymbol{H}_2CH_2$), 1.33 (m, 12H, Ar-$O(CH_2)_{10}C\boldsymbol{H}_2CH_3$), 1.22 (m, 96H, Ar-$OC_2H_4(C\boldsymbol{H}_2)_8C_2H_5$), 0.85 (t, 18H, Ar-$O(CH_2)_{11}C\boldsymbol{H}_3$).

Synthesis of 4,4″-bis(5-(3,4,5-tris(dodecyloxy)phenyl)-1,3,4-oxadiazol-2-yl)p-terphenyl (OXD_3). Compound $\mathbf{OXD_3}$ was obtained as a yellow powder in 29.6% yield. IR (KBr Pellet, cm^{-1}): 3033 (sp^2 C-H stretch), 2917, 2848 (sp^3 C-H stretch), 1606 (C=N stretch), 1324, 1120 (C-O stretch); ^1H NMR ($CDCl_3$, δ in ppm): 8.20 (d, 4H, Ar-***H***), 7.83 (d, 4H, Ar-***H***), 7.77 (s, 4H, Ar-***H***), 7.32 (s, 4H, Ar-***H***), 4.00 (t, 12H, Ar-$OC\boldsymbol{H}_2CH_2$), 1.71 (m, 12H, Ar-$OCH_2C\boldsymbol{H}_2CH_2$), 1.33 (m, 12H, Ar-$O(CH_2)_{10}C\boldsymbol{H}_2CH_3$), 1.22 (m, 96H, Ar-$OC_2H_4(C\boldsymbol{H}_2)_8C_2H_5$), 0.85 (t, 18H, Ar-$O(CH_2)_{11}C\boldsymbol{H}_3$). Anal. Calcd. C: 78.37% H: 10.30% and N: 3.45%, and found C: 78.38% H: 10.55% and N: 3.46%.

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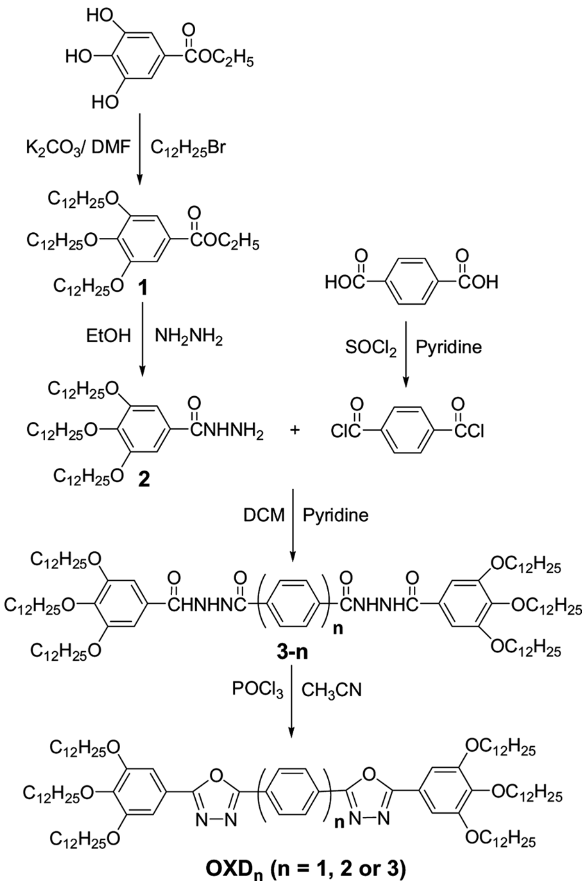
Measurements

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 1,3,4-oxadiazole derivatives (OXD_n: $n = 1$, 2, and 3) is shown in Scheme 1. Compounds OXD_n were prepared by cyclodehydration with PCl_3 of the hydrazide precursors (**3-n**) which were obtained by reaction of terephtaloyl dichloride and trialkoxy-benzhydrazide (**2**). The structures of all products were identified by using IR and NMR spectrometry. 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.



Scheme 1. Synthetic route to dumbbell-shaped compounds.

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The differential scanning calorimetric (DSC) thermograms of compounds are presented in Figure 1. All compounds show melting temperature (T_m), solid to solid transition temperature ($T_{k\text{-}k}$) and recrystallization temperature (T_c). The related enthalpy changes are listed in Table 1. The T_m are in the range of 81–95°C depending on the structure. Interestingly, the T_ms of compounds differ insignificantly with the structure, while the heat of melting for compound with $n = 1$ was greatly higher than other compounds with $n = 2$ or 3. This means that the crystal structure of compound with $n = 1$ can be very different from the others. As expected, introduction of trialkoxy groups to the rigid segment lowered the melting temperature and increased the solubility remarkably. For example, the melting temperature of compound with $n = 3$ decreased 348°C compared to bis(5-phenyl-1,3,4-oxadiazole-2-diyl) 4′,4″-o-terphenyl [33]. This indicates that flexible $-CH_2-$ subunits can give an entropy benefit to the system and the bulky trialkoxy end group can disturb the packing of molecules. Remarkably, compound with $n = 1$ shows an isotropic-to-mesophase transition temperature at 76°C monotropically. Hence, to choose the suitable combination of two different mesogenic units such as rod and disk is important for designing the liquid crystalline OLED materials.

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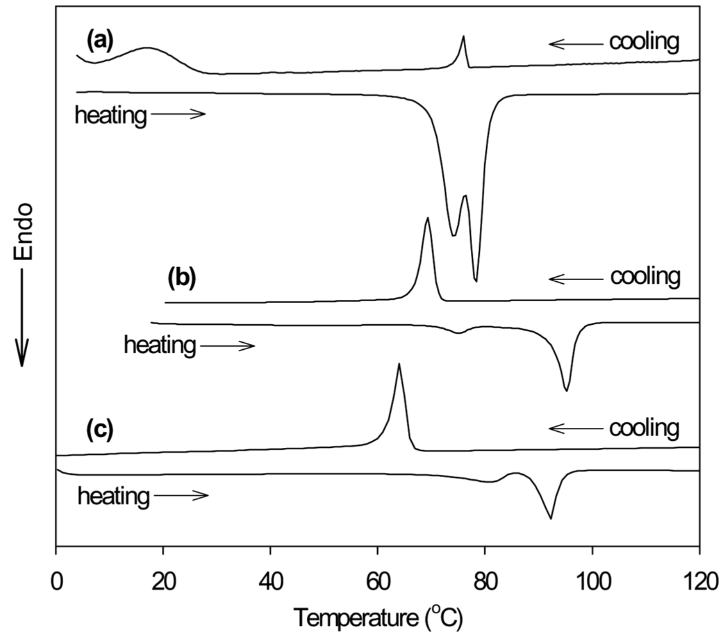
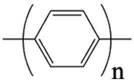


Figure 1. DSC thermograms of OXD_n (heating and cooling rate = 10°C/min): (a) n = 1; (b) n = 2; (c) n = 3.

Figure 2 shows crosspolarizing optical micrographs of compounds obtained during cooling run. Compound with n = 1 (OXD_1) showed a typical mosaic texture of columnar phase as shown in Figure 1a. The OXD_1 showed a transition from mesophase to crystal at 37°C (Figure 1b), and as further cooled to room temperature a crystal texture was found (Figure 1c). However, this compound did not show any recrystallization exotherm on its DSC cooling curve (see Figure 1a). Although the remaining two compounds OXD_2 and OXD_3 showed a distinctive recrystallization exotherm on their DSC cooling curves, these compounds could not show a well developed crystal texture as shown in Figures 2d and 2e.

The UV absorption and fluorescent properties of OXD_n have been studied. The absorption spectra of compounds in $CHCl_3$ solution and in solid state are shown in Figure 3. The data of $\lambda_{abs,\ max}$ are presented in Table 2. All compounds exhibited a

Table 1. Thermal properties of compounds

Sample code		$^aT_{k\text{-}k}$ (°C)	T_m (°C)	$^b\Delta H_m$ (kJ mol^{-1})	^cT_c (°C)	ΔH_c (kJ mol^{-1})	T_i (°C)	ΔH_i (kJ mol^{-1})
OXD_1	1	73	81	191	17	10.4	76	2.9
OXD_2	2	74	95	59.8	69	79.4	–	–
OXD_3	3	81	93	28.3	64	35.1	–	–

[a] $T_{k\text{-}k}$: solid-to-solid transition temperature.
[b] ΔH_m: total enthalpy changes for multiple melting.
[c] T_c: recrystallization temperature.

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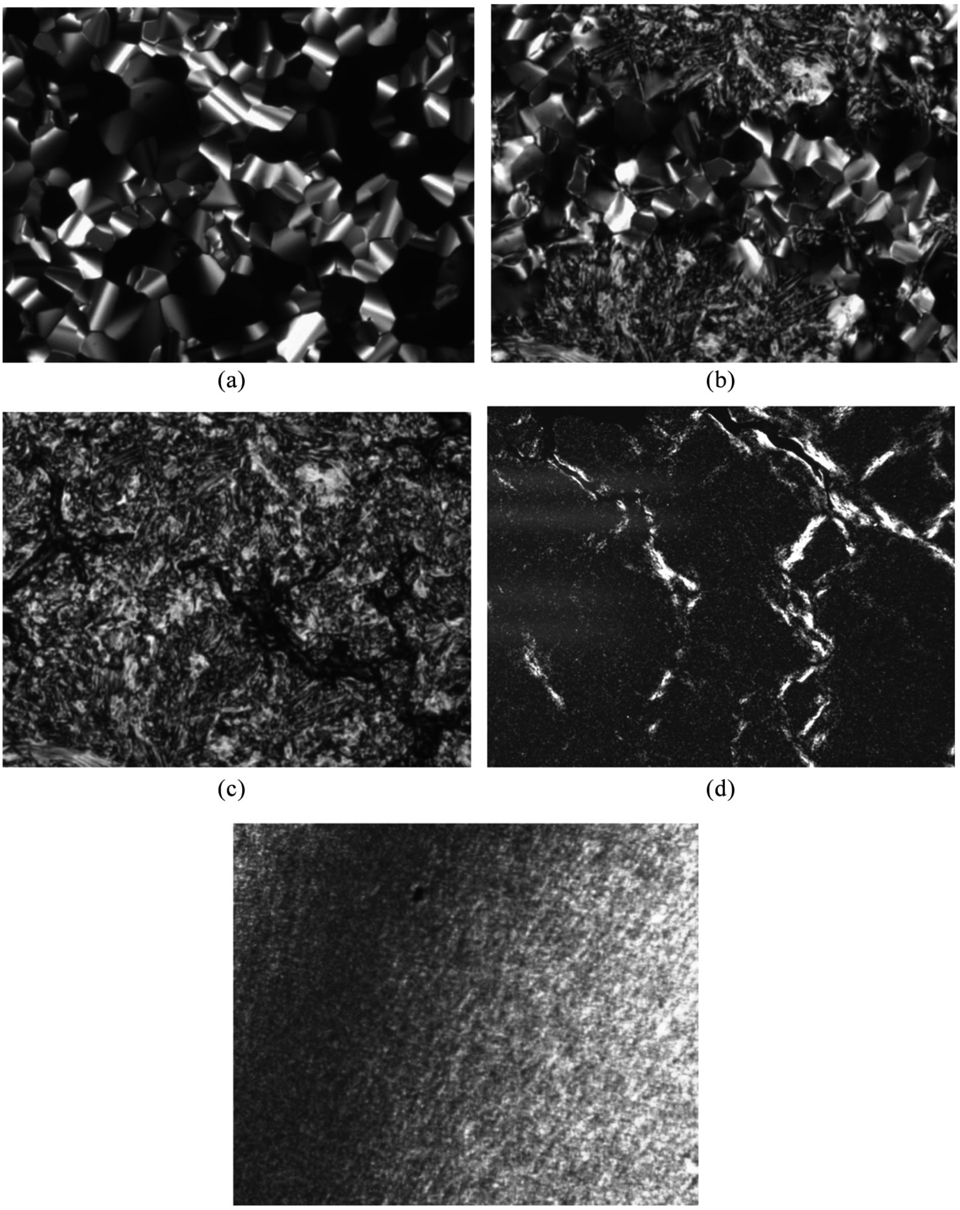
(a) (b) (c) (d) (e)

Figure 2. Crosspolarizing optical micrographs of OXD_n on cooling (Magnification 200X): $n = 1$: (a) $T = 75°C$; (b) $T = 37°C$; (c) $T = 25°C$; (d) $n = 2$: $T = 25°C$; and (e) $n = 3$: $T = 25°C$.

distinctive absorption peak at 336–351 nm. Although the compounds have a different length of the central rod ($n = 1$–3), those absorption spectra measured in the solution were very similar in their shapes. As the UV-vis absorption spectra of OXD_1, OXD_2 and OXD_3 in $CHCl_3$ solution and in solid state are compared, a shift to higher wavelength is evident in the case of solid state. Note that the most broad peak shape of OXD_1 in solid state should be related with its unique crystalline structure.

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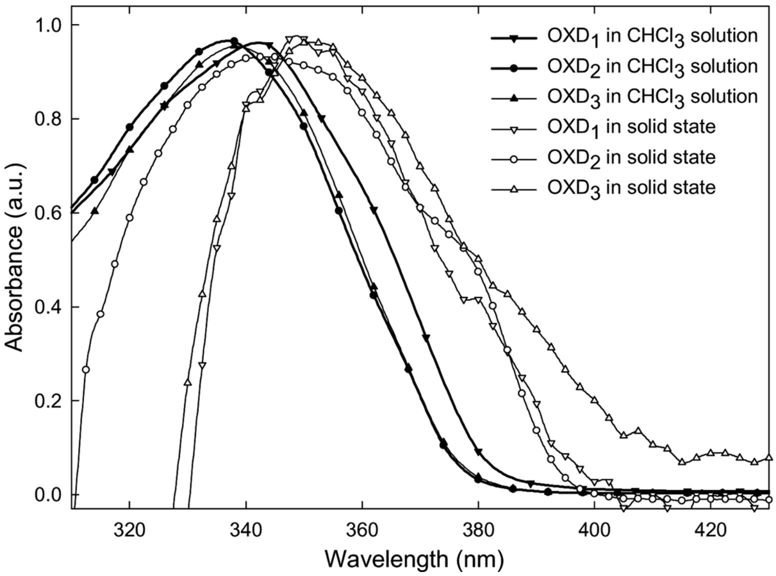

Figure 3. UV-Vis absorption spectra of compounds obtained at room temperature.

The PL spectra of compounds in $CHCl_3$ solution and in solid state are shown in Figure 4, which exhibit a well-defined vibronic feature. The data of $\lambda_{em,\ max}$ in $CHCl_3$ solution and in solid state are presented in Table 2. The emission peaks appeared at 412–449 nm. The OXD_3 in $CHCl_3$ solution has a more complex spectrum than others both in spectra shape and λ_{max}, which exhibits two λ_{max}s at 389 and 412 nm and a shoulder at 439 nm. The compound OXD_2 in film state has a λ_{max} at 420 nm and a shoulder at higher 451 nm. From the PL results, we found that in $CHCl_3$ solution compound OXD_1 and OXD_2 could radiate blue emission, while in solid state compound OXD_1 and OXD_3 could radiate blue emission. In the solution state, increasing the length of the central rod mesogen ($OXD_1 \rightarrow OXD_3$) showed a blue shift by 37 nm. In solid state, compared with OXD_1, OXD_3 showed a red shift, while compared with OXD_1, OXD_2 showed a blue shift. Note that OXD_1 showed two broad peaks in solid state due to its unique crystalline structure.

Table 2. Physical properties of compounds[a]

		$CHCl_3$ Solution		Film on glass	
Sample code	n	$\lambda_{abs,\ max}$ (nm)	$\lambda_{em,\ max}$ (nm)	$\lambda_{abs,\ max}$ (nm)	$\lambda_{em,\ max}$ (nm)
OXD_1	1	341	449	349	425, 442
OXD_2	2	336	442	344	420 (451)
OXD_3	3	340	412, 439 (389)	351	447

[a] Data in paranthesis is for shoulder peaks.

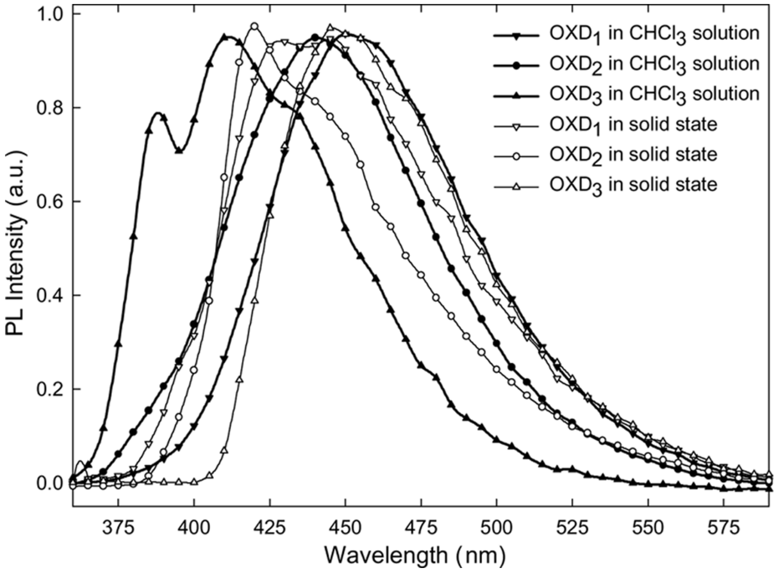

Figure 4. Photoluminescence emission spectra of compounds obtained at room temperature.

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Conclusions

We have successfully designed and synthesized a new series of 1,3,4-oxadiazole derivatives. Their optical and thermal properties were investigated. The solubility of 1,3,4-oxadiazole derivatives promoted greatly as introducing flexible groups. In general, the UV-vis absorption maximum peaks (336 nm–351 nm) and PL emission peaks (410 nm–450 nm) showed a blue shift along with increasing the length of central rod mesogen. Compounds with $n = 1$ and 2 could radiate blue emission in $CHCl_3$ solution, whereas compounds with $n = 1$ and 3 could radiate blue emission in solid state. Especially, we found that besides possessing electron-transporting capability, a dumbbell-shaped molecule based on 1,3,4-oxadiazole combining rod mesogen with disk mesogen (OXD_1) could form a discotic columnar mesophase monotropically.

Acknowledgments

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