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The synthesis, optical properties and x-ray crystal structure of novel 1,3,4-oxadiazole derivatives carrying a thiophene unit

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Novel, 1,3,4-oxadiazole derivatives carrying a thiophene unit were synthezised and their structures confirmed by elemental analysis, FT-IR and ^{1}H NMR. UV–vis absorption and photoluminescence spectroscopy revealed emission peaks located between 427 and 437 nm; the measured absorption λ_{max} and emission λ_{em} reflected the electron-donor character of the 1,3,4-oxadiazole derivatives. The crystal structure of one of the compounds was investigated.

1. Introduction

The optical and electronic properties of 1,3,4-oxadizole [1–3] and thiophene [4,5] derivatives have been paid great attention in the field of electroluminescence. A well known 1,3,4-oxadiazole derivative, 2-(4-biphenyl)-5-(*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) [3,6], has been widely employed as the electron-transporting material in organic electroluminescence device [7]. Later years, many investigations have proven that modifying of side chains or inserting of other heterocycles in 1,3,4-oxadizole system could obtain good electroluminescent molecules as organic electroluminescence materials (OELM) [8–10]. The structural investigation of OELM molecules in solid state is one of the promising research fields because luminescent and electron-transporting behaviors are believed to be dependent not only on the conformation of OELM molecule but also on interactions between the OELM molecule and substrate in molecular level [11–14].

Our present work is motivated by the above background and succeed in designing and synthesizing a new symmetrical series of 1,3,4-oxadiazole derivatives hybridized with thiophene ring. The optical properties of OXD-*X* are investigated by UV–vis absorption and PL spectroscopy, and the crystal structure of the OXD-4 is investigated.

2. Experimental

2.1. Measurement

All compounds were characterized by ^{1}H NMR using Bruker DRX500 MHz spectrometer with $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. The elemental analyses were performed with a Vario El III elemental analyzer. FT-IR spectra were recorded on a Nicolet 360 FT-IR spectrometer by dispersing samples in KBr disks. UV–vis and fluorescence spectra of the 1,3,4-oxadiazole derivatives in $CHCl_3$ solution were measured using Cary 5000 spectrophotometer and Perkin–Elmer LS-50B luminescence spectrometer, respectively.

2.2. Synthesis

The 1,3,4-oxadiazole derivatives named as OXD-*X* ($X = 1–6$) were synthesized according to the similar method to prepare 1,3-bis[2-(4-methylphenyl)-1,3,4-oxadiazol-5-yl]benzene [9], 1,3-bis[2-(4-*N*,*N*-dimethylaminophenyl)-1,3,4-oxadiazol-5-yl]benzene [15] and 1,4-bis[2-(4-*tert*-butylphenyl)-1,3,4-oxadiazol-5-yl]benzene [16]. The synthetic route was shown in Fig. 1.

2.2.1. Thiodiglycolic acid diethyl ester (**1**)

Thiodiglycolic acid (15.0 g, 100 mmol) was dissolved in anhydrous ethanol (100 ml) in a four necked round-bottomed flask. Concentrated sulfuric acid (6 ml) was added slowly under

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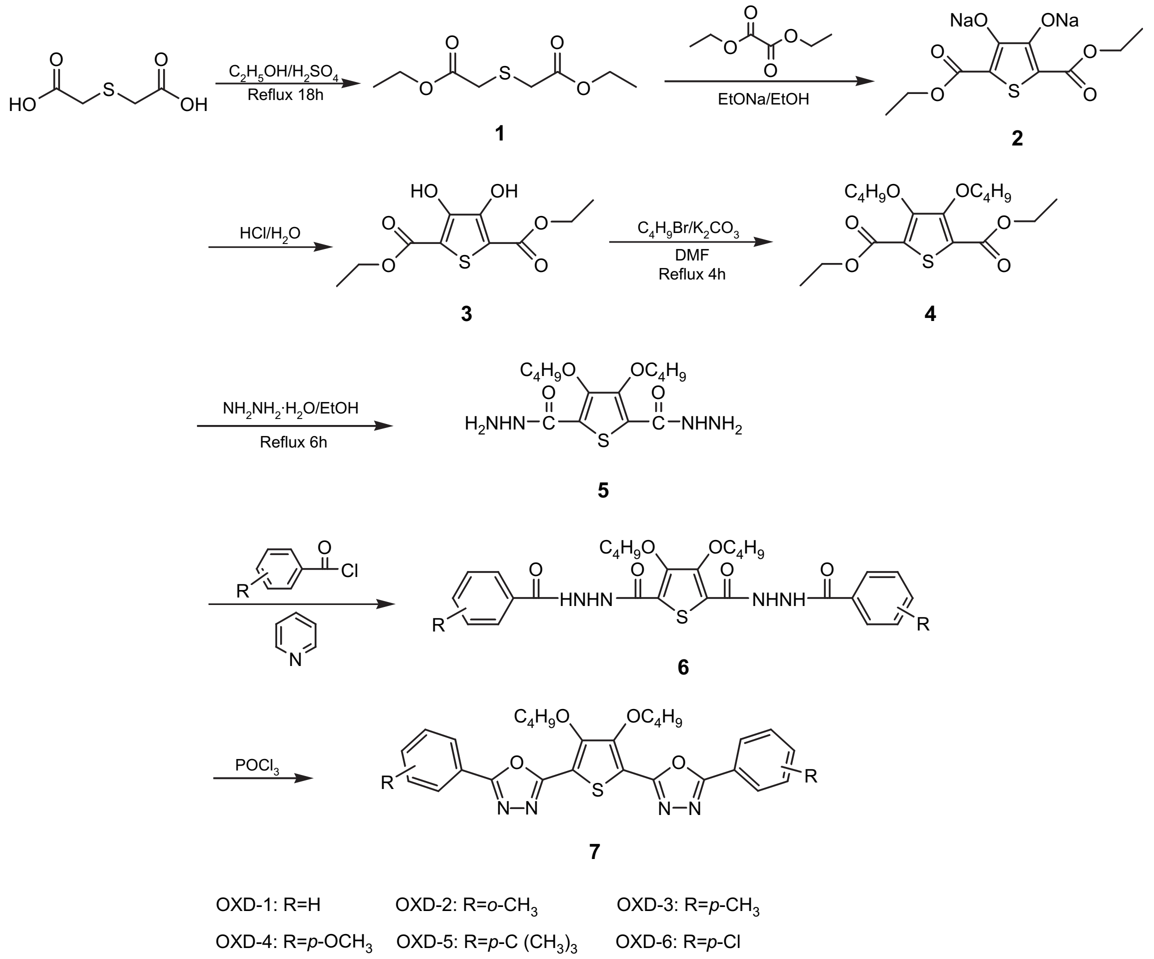

Fig. 1. The synthesis scheme of 1,3,4-oxadiazole derivatives.

continuous stirring. After refluxing for 24 h, the mixture was cooled and poured into water (100 ml). The resulting mixture was then extracted twice with chloroform and the combined organic layer was washed three times with sodium carbonate solution, dried with anhydrous magnesium sulfate, filtrated and concentrated by rotary evaporation to give **1** (18.0 g, 87 mmol) as a yellow liquid in 87.0% yield.

2.2.2. *Diethyl 3,4-dihydroxythiophene-2,5-dicarboxylate (**3**)*

A solution of **1** (18.0 g, 87 mmol) and diethyl oxalate (25 ml, 184 mmol) was added dropwise into a cooled (0–5 °C) solution of sodium ethoxide (27.2 g, 400 mmol) in absolute ethanol (200 ml). The mixture was refluxed for 4 h and yellow precipitate was formed. After cooling and filtered, filter cake was poured into water (300 ml) and acidified with concentrated hydrochloric acid to pH 1–2. The precipitate was filtered, washed with water, dried and recrystallized in ethanol/petroleum ether to give **3** (15.2 g, 58 mmol) as a pale white solid in 66.7% yield, m.p. 133–134 °C.

2.2.3. *Diethyl 3,4-dibutoxythiophene-2,5-dicarboxylate (**4**)*

Into a four necked round-bottomed flask were added **3** (5.2 g, 20 mmol), DMF (30 ml), potassium carbonate (4.0 g, 29 mmol) and 1-bromobutane (5.4 ml, 50 mmol). The mixture was stirred vigorously at 75–80 °C for 4 h. After cooling and filtered, the filtrate was poured into water (100 ml) and extracted twice with chloroform. The combined organic layer was washed twice with sodium chloride solution and dried with anhydrous magnesium sulfate. After the solvent was removed by rotary evaporation, product **4** (6.5 g, 17.5 mmol) was given as a brown liquid in 87.5% yield.

2.2.4. *3,4-Dibutoxythiophene-2,5-dicarbohydrazide (**5**)*

A solution of **4** (6.5 g, 17 mmol), hydrazine hydrate (10 ml, 206 mmol) and ethanol (50 ml) was refluxed for 4 h. Reaction solution was then concentrated by rotary evaporation and residue was poured into water (100 ml). After filtration and recrystallized in ethanol/water to give **5** (3.8 g, 11 mmol) as a pale white solid in 64.7% yield, m.p. 140–141 °C.

2.2.5. *3,4-Dibutoxy-$N^{2'}$,$N^{5'}$-dibenzoylthiophene-2,5-dicarbohydrazide (**6**)*

To a solution of **5** (2.1 g, 6 mmol) in pyridine (20 ml) at 0–5 °C was added benzoyl chloride (2.0 g, 14 mmol) dropwise in 20 min. The reaction solution was heated slowly to 75–80 °C, and stirred at this temperature for 10 h. After cooling, poured into powder ice (100 g). The precipitated product was filtrated and washed with water. The filter cake was dried and recrystallized by chloroform/petroleum ether to give **6** (2.8 g, 5 mmol) as a pale white solid in 83.3%, m.p. 159–160 °C.

2.2.6. *2-(3,4-Dibutoxy-5-(5-phenyl-1,3,4-oxadiazol-2-yl)thiophen-2-yl)-5-phenyl-1,3,4-oxadiazole (OXD-1)*

Into a four necked round-bottomed flask were added **6** (2.8 g, 5 mmol) and fresh phosphorus oxychloride (25 ml), and stirred at 80–85 °C for 12 h. The mixture was cooled and poured into powder ice (150 g). The precipitated product was filtered, dried and recrystallized by chloroform/ethyl acetate to give OXD-1 (2.1 g, 4.1 mmol) as yellow solid in 82.0% yield, m.p. 157–158 °C. FT-IR (KBr, cm^{-1}): 2958, 2871 (CH$_3$, CH$_2$, γ_{CH}), 1619 (–C═N–, $\gamma_{C=N}$), 1570 (–C═C–, $\gamma_{C=C}$), 726 (ArH). ^{1}H NMR (CDCl$_3$, 500 MHz) δ (ppm): 0.97–1.02 (t, 6H, CH$_3$), 1.51–1.63 (m, 4H, CH$_2$), 1.83–1.93 (m, 4H, CH$_2$), 4.32–4.36 (t, 4H, CH$_2$), 7.51–7.58 (t, 6H, ArH), 8.11–8.14 (d, 4H, ArH). Anal. Calcd. C: 65.12%, H: 5.43%, and N: 10.85%, and found C: 65.71%, H: 5.37%, and N: 10.12%.

Other OXD-*X* were synthesized with method same as OXD-1.

2.2.6.1. Compound OXD-2. OXD-2 was obtained as yellow solid in 81.3% yield, m.p. 139–140 °C. FT-IR (KBr, cm^{-1}): 2955, 2870 (CH$_3$, CH$_2$, γ_{CH}), 1625 (–C═N–, $\gamma_{C=N}$), 1585 (–C═C–, $\gamma_{C=C}$), 728 (ArH). ^{1}H NMR (CDCl$_3$, 500 MHz) δ (ppm): 0.96–1.02 (t, 6H, CH$_3$), 1.52–1.56 (m, 4H, CH$_2$), 1.84–1.89 (m, 4H, CH$_2$), 2.77 (s, 6H, CH$_3$), 4.33–4.35 (t, 4H, CH$_2$), 7.34–7.38 (m, 4H, ArH), 7.43–7.46 (t, 2H, ArH), 8.01–8.03 (d, 2H, ArH). Anal. Calcd. C: 66.18%, H: 5.88%, and N: 10.29%, and found C: 66.43%, H: 5.51%, and N: 10.05%.

2.2.6.2. Compound OXD-3. OXD-4 was obtained as yellow solid in 79.1% yield, m.p. 155–157 °C. FT-IR (KBr, cm^{-1}): 2955, 2867 (CH$_3$, CH$_2$, γ_{CH}), 1613 (–C═N–, $\gamma_{C=N}$), 1573 (–C═C–, $\gamma_{C=C}$), 732 (ArH). ^{1}H NMR (CDCl$_3$, 500 MHz) δ (ppm): 0.98–1.01 (t, 6H, CH$_3$), 1.54–1.58 (m, 4H, CH$_2$), 1.85–1.88 (m, 4H, CH$_2$), 2.45 (s, 6H, CH$_3$), 4.31–4.34 (t, 4H, CH$_2$), 7.33–7.35 (d, 4H, ArH), 8.00–8.82 (d, 4H, ArH). Anal. Calcd. C: 66.18%, H: 5.88%, and N: 10.29%, and found C: 66.65%, H: 5.91%, and N: 10.94%.

2.2.6.3. Compound OXD-4. OXD-6 was obtained as yellow solid in 72.5% yield, m.p. 165–166 °C. FT-IR (KBr, cm^{-1}): 2956, 2869 (CH$_3$, CH$_2$, γ_{CH}), 1613 (–C═N–, $\gamma_{C=N}$), 1574 (–C═C–, $\gamma_{C=C}$), 739 (ArH). ^{1}H NMR (CDCl$_3$, 500 MHz) δ (ppm): 0.98–1.01 (t, 6H, CH$_3$), 1.52–1.60 (m, 4H, CH$_2$), 1.84–1.89 (m, 4H, CH$_2$), 3.90 (s, 6H, OCH$_3$), 4.31–4.33 (t, 4H, CH$_2$), 7.03–7.04 (d, 4H, ArH), 8.05–8.07 (d, 4H, ArH). Anal. Calcd. C: 62.50%, H: 5.56%, and N: 9.72%, and found C: 62.91%, H: 5.14%, and N: 9.44%.

2.2.6.4. Compound OXD-5. OXD-7 was obtained as yellow solid in 85.2% yield, m.p. 147–148 °C. FT-IR (KBr, cm^{-1}): 2956, 2869 (CH$_3$, CH$_2$, γ_{CH}), 1612 (–C═N–, $\gamma_{C=N}$), 1567 (–C═C–, $\gamma_{C=C}$), 724 (ArH). ^{1}H NMR (CDCl$_3$, 500 MHz) δ (ppm): 0.99–1.02 (t, 6H, CH$_3$), 1.38 (s, 18H, CH$_3$), 1.53–1.61 (m, 4H, CH$_2$), 1.85–1.91 (m, 4H, CH$_2$), 4.32–4.34 (t, 4H, CH$_2$), 7.55–7.57 (d, 4H, ArH), 8.05–8.06 (d, 4H, ArH). Anal. Calcd. C: 68.79%, H: 7.00%, and N: 8.93%, and found C: 68.11%, H: 7.62%, and N: 8.90%.

2.2.6.5. Compound OXD-6. OXD-8 was obtained as yellow solid in 82.8% yield, m.p. 178–179 °C. FT-IR (KBr, cm^{-1}): 2955, 2861 (CH$_3$, CH$_2$, γ_{CH}), 1604 (–C═N–, $\gamma_{C=N}$), 1579 (–C═C–, $\gamma_{C=C}$), 745 (ArCl), 735 (ArH). ^{1}H NMR (CDCl$_3$, 500 MHz) δ (ppm): 1.00–1.05 (t, 6H, CH$_3$), 1.55–1.63 (m, 4H, CH$_2$), 1.85–1.92 (m, 4H, CH$_2$), 4.34–4.38 (t, 4H, CH$_2$), 7.54–7.57 (d, 4H, ArH), 8.08–8.10 (d, 4H, ArH). Anal. Calcd. C: 57.44%, H: 4.44%, and N: 9.57%, and found C: 57.41%, H: 4.44%, and N: 9.26%.

3. Result and discussion

3.1. Optical properties

The UV–vis and PL spectrum of the OXD-*X* are shown in Figs. 2 and 3, respectively, and the optical characteristics are summarized in Table 1. In Fig. 2, we can see that OXD-*X* displays similar absorptions ranging from 300 to 450 nm and the strong absorption band at about 350 nm (Table 1). The strong absorptions are assigned to the π–π^* electronic transition focusing on the conjugated 1,3,4-oxadiazole and thiophene units. There are also relatively weak absorption bands between 250 and 300 nm in all compounds, which should originate from the substituents of the benzene rings of the molecules. From Table 1, we can see that all λ_{max} of OXD-*X* have a little red shift compared to OXD-1, these results from the electron-donor effect (except OXD-6, R = *p*-Cl) of substituents joined to the conjugated system. The OXD-4 (R = *p*-OCH$_3$) has the maximum red shift 15 nm and the OXD-2 (R = *o*-CH$_3$) has the minimum red shift 2 nm. The absorbance of OXD-4 is stronger than other compounds in the same condition (10^{-5} M in chloroform) due to the strong electron-donor effect of the methoxyl.

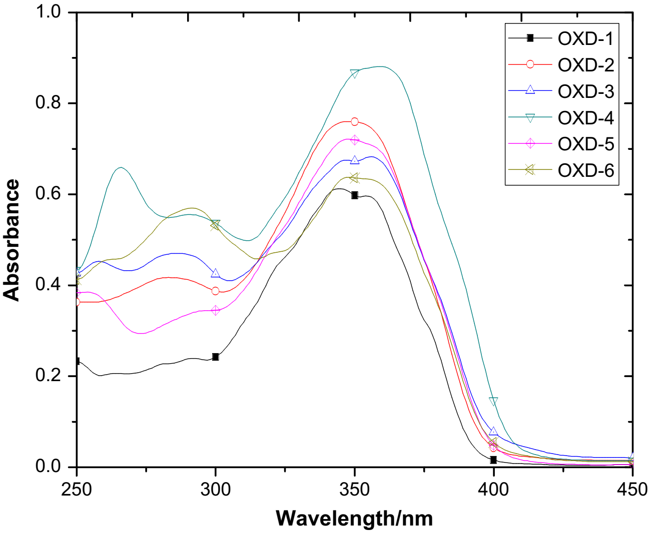

Fig. 2. UV–vis absorption spectra of OXD-*X* in chloroform solution (10^{-5} M).

The emission spectra of the OXD-*X* in chloroform solution are shown in Fig. 3. All the λ_{em} of OXD-*X* have a little red shift compared to OXD-1 and locate between 427 and 437 nm. Similarly, the OXD-4 (R = *p*-OCH$_3$) has the maximum red shift 10 nm and the strongest intensity compared to other compounds in the same condition (10^{-6} M in chloroform). The values of stokes shift of all OXD-*X* are about 80 nm (Table 1).

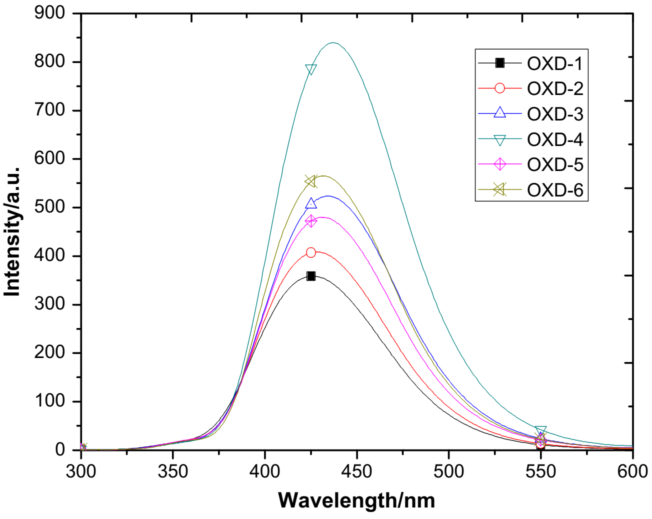

Fig. 3. PL spectrum of OXD-*X* in chloroform solution (10^{-6} M).

Table 1
Optical characteristics (nm)

Compound	UV-λ_{max}	PL-λ_{em}	Stokes shift
OXD-1	344	427	83
OXD-2	346	431	85
OXD-3	356	434	78
OXD-4	359	437	78
OXD-5	347	431	84
OXD-6	348	432	84

3.2. X-ray diffraction spectroscopy of the compound OXD-4 (structure determination and refinement)

Crystal of OXD-4 suitable for X-ray diffraction was obtained by slow evaporation of ethyl acetate and chloroform mixed solution. A very thin colorless crystal of approximate dimensions 0.30 × 0.20 × 0.10 mm was put on a glass fiber. All measurements were collected at $T = 293$ K on a Nonius CAD4/PC (made by ENRAF NONIUS Co. of Holland) single crystal diffractometer using a graphite-monochromatized Mo Kα radiation ($l = 0.71073$ Å) equipped by a CCD two dimensional detector. The structure was solved by direct methods and refined by full-matrix least-squares techniques implemented in the SHEXTL crystallographic software [17,18]. Positions of hydrogen atoms were located by geometrical calculation and refined (x, y, z and U_{iso} fixed to 1.2 times U_{iso} of atom they are bound to). The final refinement converged at $R1 = 0.0738$ and $\omega R2 = 0.1440$ for 1195 reflections [$I > 2\sigma(I)$] with 180 variable parameters and no restraint. Crystal data are reported in Table 2.

The single crystal structure and atomic numbering chosen for OXD-4 are shown in Fig. 4. The C–C distances of the phenyl ring are quasi equal and close to 1.38 Å except C9–C10 and C9–C14, this is because the strong interaction between the 1,3,4-oxadiazole ring and the C9 atom makes the C9 atom close to the 1,3,4-oxadiazole much more. The exocyclic bond C–C distances are longer than endocyclic C–C distances obviously. The bond length C6–C7 (1.406 Å) becomes shorter compared to 3,4-dibutoxy-N^2,$N^{2'}$-bis(-propan-2-ylidene)thiophene-2,5-dicarbohydrazide (C6–C7 1.495 Å) [19], which indicates that conjugation between 1,3,4-oxadiazole and thiophene is enhanced. The dihedral angle between the O2/C7/N1/N2/C8 ring and the C6 ring is 9.30° and 4.80° for the C9 ring, and the dihedral angle between the C6 ring and the C9 ring is 5.90°. Due to centrosymmetry of molecule, the dihedral angles between the O2A/C7A/N1A/N2A/C8A ring and the C6A ring are also 9.30° and 4.80° for the C9A ring, and the dihedral angle between the C6A ring and the C9A ring is 5.90°. All dihedrals are so small that OXD-4 is nearly in the same plane and this coplanar conformation provides a large conjugated system which makes transporting of electrons easy. In order to adjust the molecule flexibility and improve the electron-transporting characteristics, the butoxy and methoxy are introduced into thiophene and benzene rings.

Table 2
Crystal data and structure refinement

Identification code	OXD-4
Empirical formula	$C_{30}H_{32}N_4O_6S$
Formula weight	576.66
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$C2/c$
Unit cell dimensions	$a = 26.5042(2)$ Å, $\alpha = 90°$
	$b = 10.9788(12)$ Å, $\beta = 104.5°$
	$c = 10.2321(11)$ Å, $\gamma = 90°$
Volume	2883.0(5) Å^3
Z	8
Absorption coefficient	0.162 mm^{-1}
$F(000)$	1216
Crystal size	0.30 × 0.20 × 0.10 mm^3
Reflections collected	2580
Independent reflections	1195 [$R(\text{int}) = 0.0611$]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1195/0/180
Goodness-of-fit on F^2	1.007
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0738$, $\omega R2 = 0.1440$
R indices (all data)	$R1 = 0.1521$, $\omega R2 = 0.1781$
Largest diff. peak and hole	0.326 and −0.196 e Å^{-3}

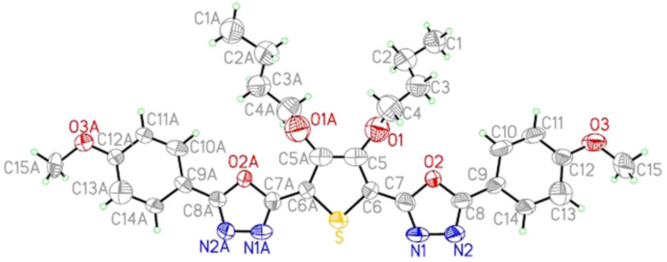

Fig. 4. The crystal structure of OXD-4.

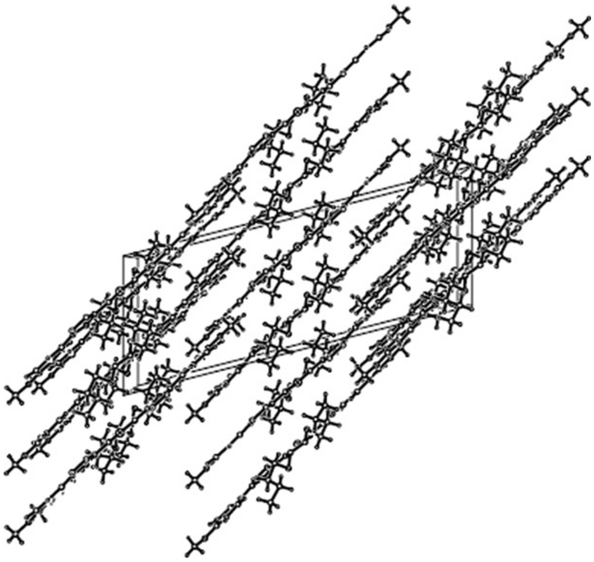

Fig. 5. Crystal molecular packing along the b-axis.

The crystal packing of the OXD-4 is illustrated in Fig. 5 (b-axis). Molecules may be packed by van der Waals force because intra-molecular or intermolecular hydrogen bond is not detected. This regular sandwich of OXD-4 would make transporting of electrons easier between layers.

4. Conclusion

A series of 1,3,4-oxadiazole derivatives carrying thiophene unit, OXD-X, are synthesized, and their optical properties are investigated. The UV–vis absorption maximum peaks (from 344 to 359 nm) and PL emission peaks (from 427 to 437 nm) have a little red shift along with the electron-donor effect of substituents joined to the conjugated system, and the optical properties of OXD-4 are most excellent in the compounds. The molecule structure of the OXD-4 was characterized by X-ray analysis and results show that large conjugated system exists in molecule, and intermolecularly packing is in the form of sandwich. The above-mentioned structure is considered beneficial to improve the electron-transporting ability, and OXD-X is regarded as potential electron-transporting electroluminescent materials.

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