

Synthesis and Optoelectronic Properties of Symmetrical Thiophene Based 2,5-disubstituted 1,3,4-oxadiazoles: Highly Fluorescent Materials for OLED Applications

Shridhar I. Panchamukhi · Ningaraddi Belavagi ·
Mohammed Hussain Rabinal · Imitiyaz Ahmed Khazi

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Abstract Symmetrical 2,5-disubstituted thiophene derivatives containing 1,3,4-oxadiazole moiety bearing different aromatic substitutions were synthesized by employing convenient and simple synthetic protocols using thiophene-2,5-dicarboxylic acid as a starting material. The structures of these target molecules were established by their analytical and spectral data. The photophysical and electrochemical studies were carried out on these compounds and found that they exhibit good fluorescent properties with high quantum yield.

Keywords Symmetrical thiophene derivatives
2,5-disubstituted 1,3,4-oxadiazoles · Photoluminescence
High quantum yield · OLED

Introduction

Conjugated molecules and polymers have been studied extensively, not only to explore their fundamental optical and electrical properties, but also to identify their potential application for various devices, such as organic light emitting diodes (OLED), organic field effect transistors (OFETs) and photovoltaic cells [1–3]. Particularly, thiophene-based oligomers are promising building blocks for these applications due to their unique optical and electrical properties, as well as due to their ease of structural modification [4]. Now a days, compounds with blue

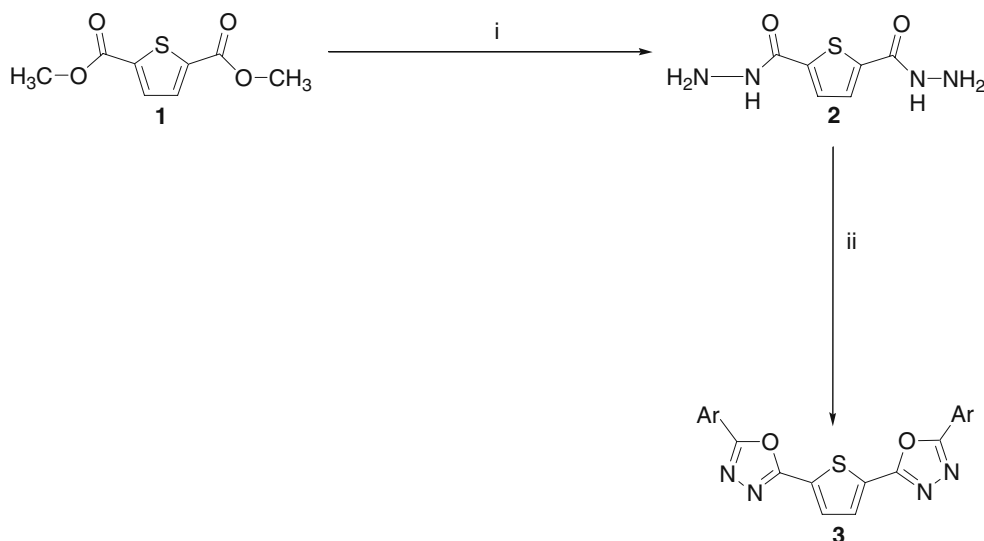
luminescence are highly desirable because of their wide applicability in OLED's to tune the emission colours in the entire region of visible spectrum [5]. The existing organic materials with blue light-emitting capability include styrylarylenes [6], polyphenyls [7], perylenes [8], benzofurans [9], indoles [10], thiophenes, etc. Derivatives of 1,3,4-oxadiazoles are amongst the most widely studied classes of electron-injection/hole-blocking materials due to their electron deficiency, high photoluminescence quantum yield, good thermal, and chemical stabilities. It has been shown that 2-(4-biphenyl)-5-(4-tertbutylphenyl)-[1, 3, 4] oxadiazole (PBD) functions very well as an excellent electron-transport material (ETM) in multilayer OLEDs [11–17]. In the present investigation we have reported the design and synthesis of symmetrical 2,5-disubstituted thiophenic derivatives containing 1,3,4-oxadiazole moiety as blue emitting materials. These oligomers are found to exhibit different emission properties with different substitutions.

Results and Discussion

The present work relates to novel oxadiazole compounds which are useful not only as organic electroluminescent materials and charge transporting materials, but also as fluorescent brightening agents. A relatively simple and efficient synthetic protocol was employed for the synthesis of title compounds. Thiophene-2,5-dicarboxylic acid was converted to the corresponding bis methyl ester and then to the corresponding bis hydrazide by treatment with hydrazine hydrate. ¹H NMR spectra of thiophene-2,5-dicarboxylic acid bishydrazide [18] displayed peaks at 4.54 (s, br, 4H, NH₂, D₂O exchangeable), 7.63 (s, 2H, thiophenic protons), and 9.82 (s, br, 2H, NH, D₂O exchangeable). The compound **2** was further converted to symmetrical 2,5-disubstituted thiophene-1,3,4-oxadiazole deriv-

S. I. Panchamukhi · N. Belavagi · I. A. Khazi (✉)
Department of Chemistry, Karnatak University,
Dharwad 58003, India
e-mail: drimkorgchem@gmail.com

M. H. Rabinal
Department of Physics, Karnatak University,
Dharwad 58003, India



Scheme 1 Synthesis of symmetrical thiophene based 2,5-disubstituted 1,3,4-oxadiazoles. i) Hydrazine Hydrate, reflux, 3 h. ii) R-COOH, POCl₃, reflux 5–10 h. Ar = Thiophen-2-yl (**3a**), Furan-2-yl (**3b**), Naphthalen-2-yl (**3c**), 2-Styryl (**3d**), Antracen-9-yl (**3e**), Naphthalen-1-yl (**3f**).

atives by reacting with various commercially available aromatic carboxylic acids in dry phosphorusoxychloride media (Scheme 1). Formation of 1,3,4-oxadiazole moiety was evident, by the absence of absorption bands at 3350, 3300, 3250 and 1725 cm⁻¹ due to NH₂, NH and -COOH functions respectively in the IR spectra of **3a–f**. ¹H NMR spectra of these compounds exhibited the presence of two thiophene protons at δ 7.6 ppm and aromatic protons of substituted acid revealed the formation of product. ¹³C NMR spectra and GCMS further confirmed the formation of symmetrical thiophene based 2,5-disubstituted 1,3,4-oxadiazoles.

Photoluminescence spectra of compounds **3a–f** were measured in ethanol and Quantum yields [19–21] are presented in (Table 1). The optical band gap value E_g^{opt} were approximated from the onset of the low energy side of the absorption spectra (λ_{onset} , solution) to the baseline [22]. Thus obtained E_g^{opt} values were found to be in good agreement with the theoretically calculated values obtained by using the Gaussian 03 W software programme. Further HOMO-LUMO energy levels of these molecules were calculated from cyclic

voltammetric measurements. HOMO energy levels were calculated using equation $HOMO = -(E_{ox}^{onset} + 4.8)$ (eV). The LUMO levels were estimated from HOMO values and values of optical band gap according to equation: $LUMO = HOMO + E_g^{opt}$ (eV) and were compared with those of coumarin 440 (Table 2). These results revealed the facile reversible redox behavior of the synthesized compounds and hence they can be applied as bipolar transport materials for electroluminescence applications. This in fact would facilitate better sensitization of the dopants such as 2,5-disubstituted-1,3,4-oxadiazole **3a–f** employed for multi-layer OLED.

The fluorescence quantum yields were experimentally determined by comparison with a standard dye Coumarin 440(C120) in ethanol [21]. The quantum yields (QY) of the present samples were estimated by using the below given equation.

$$QY = QY_R \frac{I}{I_R} \frac{OD_R}{OD} \frac{n^2}{n_R^2}$$

Table 1 Summary of physical measurements of π -conjugated molecules **3a–f**

Compound	Reaction ime (h)	Product Yield (%)	Solution $\lambda_{emission}$ (nm)	Full wave Half maxima (nm)	QY
3a	4	72	422.75	82	0.51
3b	5	65	422.19	90	0.47
3c	8	88	438.06	86	0.41
3d	6	80	436–53	92	0.38
3e	7	79	492.67	86	0.16
3f	8	85	420.11	50	0.13
REF	–	–	435.06	65	0.98

QY Quantum yield (QY) in ethanol estimated using Coumarin 440 as standard

Table 2 Energy values of HOMO and LUMO of 3a–f

Compound	E_{ox}^{onset} (eV) ^a	HOMO (eV) ^b	LUMO (eV) ^b	E_g^{opt} (eV)
3a	0.39	-5.19	-2.06	3.13
3b	0.47	-5.27	-2.25	3.02
3c	0.78	-5.58	-2.32	3.26
3d	0.72	-5.52	-2.35	3.17
3e	0.74	-5.54	-2.59	2.95
3f	0.79	-5.59	-2.39	3.22
REF	0.65	-5.45	-2.29	3.16

^a Oxidation potential relative to Ag/AgCl electrode^b HOMO = $-(E_{ox}^{onset} + 4.8)$ (eV), LUMO = (HOMO + E_g^{opt}) (eV)

REF=Coumarin 440

Where QY is quantum yield, I is intensity, OD is optical density and n is refractive index. In the above equation subscript R refers to the standard taken. The concentration of the samples was selected to obtain the optical density of 0.1 at excitation wave length. The quantum yield were measured at an emission wavelength of 435 nm using Coumarin 440 (C120) as standard. Figure 1 illustrates the UV absorption and fluorescence spectra of 3a–f compared to coumarins 440 indicating their potential for OLED applications.

Experimental

General

Melting points were determined by open capillary method and are uncorrected. All the compounds were analyzed satisfactorily for C H N & S. IR spectra (KBr disc) were

recorded on a Nicolet –5700 FT-IR spectrophotometer. ¹H and ¹³C NMR spectra were recorded on a Bruker AM 300-MHz spectrometer (at 300 and 75 MHz, respectively) with SiMe₄ as the internal standard in dimethyl sulfoxide (DMSO-d₆) and CDCl₃. Mass spectra were recorded on GCMS Shimadzu Japan QP-2010S. UV and fluorescence spectra were recorded on a UV-3310-UV-VIS Hitachi spectrophotometer and Hitachi F-7000 Fluorescence spectrometer (300–700 nm). The quantum Yield (QY) measurements were carried out at room temperature in Ethanol solutions, using coumarin 440 as standard reference (QY=0.98).

Synthesis of 2, 5-disubstitued-[1,3,4]-oxadiazole

2,5-Thiophenedicarboxylic acid bishydrazide (**2**), [18] (7.6 g, 50 mmol) and aromatic acids (7.5 g, 50 mmol) were dissolved in 50 ml POCl₃. The mixture was refluxed under stirring for 5–10 h. After cooling to room temperature, the mixture was poured into ice water carefully. The solid that separated was collected by filtration and then crude product was subjected to column chromatography (hexane: ethyl acetate) to get the product, 2,5-disubstitued [1,3,4]oxadiazole, in good yield.

2-(thiophen-2-yl)-5-(5-(5-(thiophen-2-yl)-1,3,4-oxadiazol-2-yl)thiophen-2-yl)-1,3,4-oxadiazole (**3a**)

Yield 72%, m.p 201–203 °C, IR (KBr) cm⁻¹: 3100, 2923, 2853, 1621, 1589, 1020. ¹H NMR (300 MHz, δ, DMSO-d₆): 7.33 (m, 4 H), 7.92 (d, J=3.6 Hz, 2 H), 7.98 (d, J=4.8 Hz, 2 H). ¹³C NMR (75 MHz, δ, DMSO-d₆):125.12, 129.54, 131.63, 133.34, 161.56. MS m/z: 384.9 (m⁺). Anal. Calculated for C₁₆H₈N₄O₂S₃ (%): C, 49.98; H, 2.10; N, 14.57; S, 25.02 Found: C, 50.06; H, 2.14; N, 14.61; S, 25.10.

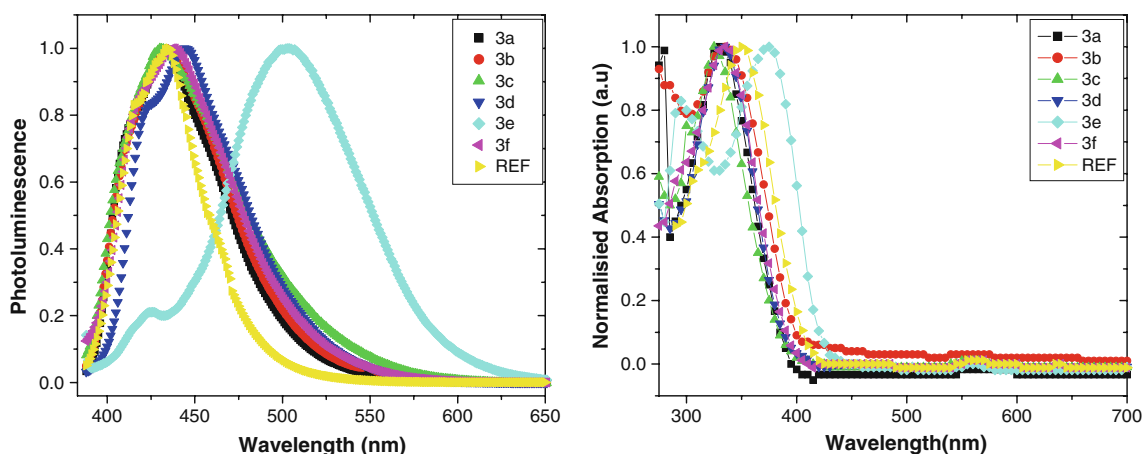


Fig. 1 UV absorption and Photoluminescence spectra of 3a–f in ethanol 2-(thiophen-2-yl)-5-(5-(5-(thiophen-2-yl)-1,3,4-oxadiazol-2-yl)thiophen-2-yl)-1,3,4-oxadiazole (**3a**), 2-(furan-2-yl)-5-(5-(5-(furan-2-yl)-1,3,4-oxadiazol-2-yl)thiophen-2-yl)-1,3,4-oxadiazole (**3b**), 2-(5-(5-(naphthalen-2-yl)-1,3,4-oxadiazol-2-yl)thiophen-2-yl)-5-(naphthalen-

3-yl)-1,3,4-oxadiazole (**3c**), 2-styryl-5-(5-(5-styryl-1,3,4-oxadiazol-2-yl)thiophen-2-yl)-1,3,4-oxadiazole (**3d**), 2-(anthracen-9-yl)-5-(5-(5-(anthracen-9-yl)-1,3,4-oxadiazol-2-yl)thiophen-2-yl)-1,3,4-oxadiazole (**3e**), 2-(naphthalen-1-yl)-5-(5-(5-(naphthalen-1-yl)-1,3,4-oxadiazol-2-yl)thiophen-2-yl)-1,3,4-oxadiazole (**3f**), REF: Coumarin 440

2-(furan-2-yl)-5-(5-(5-(furan-2-yl)-1,3,4-oxadiazol-2-yl)thiophen-2-yl)-1,3,4-oxadiazole (**3b**)

Yield 65%, m.p: 207–209 °C. IR (KBr) cm^{-1} : 3048, 2919, 2850, 1628, 1590, 1021. ^1H NMR (300 MHz, δ , DMSO- d_6), 6.86 (*m*, 4 H), 7.49 (*d*, $J=2.6$ Hz, 2 H), 8.12 (*d*, $J=1$ Hz, 2 H). Anal. Calculated for $\text{C}_{16}\text{H}_8\text{N}_4\text{O}_4\text{S}$ (%): C, 54.54; H, 2.29; N, 15.90; S, 9.10, Found: C, 54.60; H, 2.41; N, 15.98; S, 9.14.

2-(5-(5-(naphthalen-2-yl)-1,3,4-oxadiazol-2-yl)thiophen-2-yl)-5-(naphthalen-3-yl)-1,3,4-oxadiazole (**3c**)

Yield 88%, m.p: 168–170 °C. IR (KBr) cm^{-1} : 3049, 2923, 2854, 1626, 1588, 1016. ^1H NMR (300 MHz, δ , DMSO- d_6) 7.62–8.19 (*m*, 8 H), 8.28 (*d*, $J=9$ Hz, 2 H), 8.41 (*d*, $J=6$ Hz, 2 H), 9.19 (*d*, $J=9$ Hz, 2 H), 9.27 (*d*, $J=9$ Hz, 2 H). MS m/z : 472.3 (m^+). Anal. Calculated for $\text{C}_{28}\text{H}_{16}\text{N}_4\text{O}_2\text{S}$ (%): C, 71.17; H, 3.41; N, 11.86; S, 6.79; Found: C, 71.29; H, 3.50; N, 11.96; S, 6.89.

2-styryl-5-(5-(5-styryl-1,3,4-oxadiazol-2-yl)thiophen-2-yl)-1,3,4-oxadiazole (**3d**)

Yield 80%, m.p: 154–156 °C, IR(KBr) cm^{-1} : 3057, 2924, 2824, 1625, 1518, 1029. ^1H NMR (300 MHz, δ , CDCl_3): 7.10 (*d*, $J=16.3$ Hz, 2 H), 7.46–7.66 (*m*, 14 H), 7.72 (*d*, $J=16$ Hz, 2 H). ^{13}C NMR (75 MHz, δ , CDCl_3) 112.12, 128.43, 130.76, 131.65, 135.36, 140.32, 164.28. Anal. Calculated for $\text{C}_{24}\text{H}_{17}\text{N}_4\text{O}_2\text{S}$ (%): C, 67.91; H, 3.80; N, 13.20; S, 7.55 Found: C, 68.01; H, 3.86; N, 13.29; S, 7.62.

2-(anthracen-9-yl)-5-(5-(5-(anthracen-9-yl)-1,3,4-oxadiazol-2-yl)thiophen-2-yl)-1,3,4-oxadiazole (**3e**)

Yield 79%, m.p: 241–243 °C. IR(KBr) cm^{-1} : 3050, 2961, 2854, 1623, 1565, 1020. ^1H NMR (300 MHz, δ , CDCl_3) 7.60 (*d*, 8.57 Hz, 2 H), 8.14 (*m*, 18 H), ppm. ^{13}C NMR (75 MHz, DMSO- d_6) 125.30, 126.28, 128.43, 129.32, 131.56, 131.96, 140.14: MS m/z : 572.3 (m^+). Anal. Calculated for $\text{C}_{36}\text{H}_{20}\text{N}_4\text{O}_2\text{S}$ (%): C, 75.51; H, 3.52; N, 9.78; S, 5.60 Found C, 75.66; H, 3.59; N, 9.84; S, 5.68.

2-(naphthalen-1-yl)-5-(5-(5-(naphthalen-1-yl)-1,3,4-oxadiazol-2-yl)thiophen-2-yl)-1,3,4-oxadiazole (**3f**)

Yield 85%, m.p 158–160 °C. IR (KBr) cm^{-1} : 3048, 2920, 2854, 1628, 1598, 1016. ^1H NMR (300 MHz, δ , CDCl_3 , ppm) 7.63–7.96 (*m*, 10 H), 8.10 (*d*, $J=7.8$ Hz, 2 H), 8.29 (*d*, $J=6.8$ Hz, 2 H), 9.31 (*d*, $J=8.2$ Hz, 2 H). Anal. Calculated for $\text{C}_{28}\text{H}_{16}\text{N}_4\text{O}_2\text{S}$ (%): C, 71.17; H, 3.4; N, 11.86; S, 6.79 Found: C, 71.27; H, 3.48; N, 11.92; S, 6.83 (Scheme 1).

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References

1. Friend RH, Gymer RW, Holmes AB, Burroughes JH, Marks RN, Taliani C, Bradley DDC, Dos Santos DA, Bredas JL, Longdun M, Salaneck WR (1999) Electroluminescence in conjugated polymers. *Nature* 397:121–127
2. Sirringhaus H (2005) Device physics of solution-processed organic field-effect transistors. *Adv Mater* 17:2411–2425
3. Brabec CJ, Sariciftci NS, Hummelen JC (2001) Plastic solar cells. *Adv Funct Mater* 11:15–26
4. Fichou D (2000) Structural order in conjugated oligothiophenes and its implications on opto-electronic devices. *J Mater Chem* 10:571–588
5. Shen Z, Burrows PE, Bulovic V, Forrest SR, Thompson ME (1997) Three-color, tunable, organic light-emitting devices. *Science* 276:2009–2011
6. Hosokawa C, Higashi H, Nakamura H, Kusumoto T (1995) Highly efficient blue electroluminescence from a distyrylarylene emitting layer with a new dopant. *Appl Phys Lett* 67:3853–3855
7. Zheng S, Shi J (2001) Novel blue-light-emitting polymers containing dinaphthylanthracene moiety. *Chem Mater* 13:4405–4407
8. Jacob J, Sax S, Piok T, List EJW, Grimsdale AC, Mullen K (2004) Ladder-type pentaphenylenes and their polymers: efficient blue-light emitters and electron-accepting materials via a common intermediate. *J Am Chem Soc* 126:6987–6995
9. Anderson S, Taylor PN, Verschoor GLB (2004) Benzofuran trimers for organic electroluminescence. *Chem Eur J* 10:518–527
10. Jin SH, Kim MY, Kim JY, Lee K, Gal YS (2004) High-efficiency poly(*p*-phenylenevinylene)-based copolymers containing an oxadiazole pendant group for light-emitting diodes. *J Am Chem Soc* 126:2474–2480
11. Brunner K, Dijken AV, Borner H, Bastiaansen JJAM, Kiggen NMM, Langeveld BMW (2004) Carbazole compounds as host materials for triplet emitters in organic light-emitting diodes: tuning the HOMO level without influencing the triplet energy in small molecules. *J Am Chem Soc* 126:6035–6042
12. Wang C, Jung GY, Hua Y, Pearson C, Bryce MR, Petty MC, Batsanov AS, Goeta AE, Howard JAK (2001) An efficient pyridine- and oxadiazole-containing hole-blocking material for organic light-emitting diodes: synthesis, crystal structure, and device performance. *Chem Mater* 13:1167–1173
13. Zhan X, Liu Y, Wu X, Wang S, Zhu D (2002) New series of blue-emitting and electron-transporting copolymers based on fluorene. *Macromolecules* 35:2529–2537
14. Lee YZ, Chen X, Chen SA, Wei PK, Fann WS (2001) Soluble electroluminescent poly(phenylene vinylene)s with balanced electron- and hole injections. *J Am Chem Soc* 123:2296–2300
15. Chung SJ, Kwon KY, Lee SW, Jin JL, Lee CH, Lee CE, Park Y (1998) Highly efficient light-emitting diodes based on an organic-soluble poly(*p*-phenylene- vinylene) derivative carrying the electron-transporting PBD moiety. *Adv Mater* 10:1112–1116
16. Kim JH, Park JH, Lee H (2003) Highly efficient novel poly(*p*-phenylene -vinylene) derivative with 1, 3, 4-oxadiazole pendant on a vinylene unit. *Chem Mater* 15:3414–3416
17. Zhu WH, Yao R, Tian H (2002) Synthesis of novel electro-transporting emitting compounds. *Dyes Pigm* 54:147–154
18. Skene WG, Guarin Sergio Andres Perez (2007) Spectral characterization of thiophene acylhydrazides. *J Fluoresc* 17:540–546

19. Balaganesan B, Shen W, Chen CH (2003) Synthesis of t-butylated diphenylanthracene derivatives as bluehost materials for OLED applications. *Tetrahedron Lett* 44:5747–5750
20. Kloepfer JA, Cohen N, Nadeau JL (2004) FRET between CdSe quantum dots in lipid vesicles and water- and lipid-soluble dyes. *J Phys Chem B* 108:17042–17049
21. Bryantseva NG, Sokolova IV, Tsyrenzhapova AB, Selivanov NI, Khilya VP, Garazd YL (2008) Fluorescent characteristics of coumarin photosensitizers. *J Appl Spectrosc* 75:701–705
22. Datta GK, Guha S, Patil S (2010) Synthesis of liquid crystalline benzothiazole based derivatives: a study of their optical and electrical properties. *Org Electron* 1:11–19