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Synthesis, X-ray crystal structure and optical properties of novel 5-(3-aryl-1*H*-pyrazol-5-yl)-2-(6-methoxy-3-methylbenzofuran-2-yl)-1,3,4-oxadiazole

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ABSTRACT

A series of novel 5-(3-aryl-1*H*-pyrazol-5-yl)-2-(6-methoxy-3-methylbenzofuran-2-yl)-1,3,4-oxadiazole derivatives has been synthesized from 6-methoxy-3-methylbenzofuran-2-carboxylic acid and ethyl 3-aryl-1*H*-pyrazole-5-carboxylate. The structures of compounds obtained were determined by IR, ^{1}H NMR and HRMS spectra. Typically, the spatial structure of compound **7e** was determined by using X-ray diffraction analysis. UV–vis absorption and fluorescence spectral characteristics of the compounds in dichloromethane and acetonitrile were investigated. The results showed that the absorption maxima of the compounds vary from 321 to 339 nm depending on the substituents in *N*-1 position of pyrazole moiety and *para* position of benzene moiety. The maximum emission spectra of compounds in two different solvents were mainly dependent on groups in *N*-1 position of pyrazole moiety. The intensity of absorption and fluorescence was also correlated with substituents on the aryl ring bonded to pyrazole moiety. In addition, the absorption and emission spectra of these compounds change with increasing solvent polarity.

1. Introduction

1,3,4-Oxadiazoles are five-membered aromatic heterocycles with great utility in synthetic, medicinal, and material chemistry [1–13]. 1,3,4-Oxadiazole derivatives are highly attractive compounds in the research and development of materials for organic electroluminescent (EL) devices since these compounds possess high electron-accepting properties and exhibit strong fluorescence with high quantum yields [14]. Thus, compounds involving 1,3,4-oxadiazole rings have been used as electron-transporting materials and emitters in organic EL devices [15–17]. Recently, 1,3,4-oxadiazole derivatives have aroused considerable interests in the area of organic light-emitting diodes (OLEDs) [18–21].

Pyrazole and benzofuran unit are important core structures in a number of natural products. Many pyrazole derivatives are known to exhibit a wide range of biological properties such as anti-hyperglycemic, analgesic, anti-inflammatory, anti-pyretic, anti-bacterial, antifungal, anti-hypoglycemic, sedative-hypnotic activity, antitumor and anticoagulant activity [22–24]. Benzofuran derivatives have also been reported to show broad spectrum of biological activities including antimicrobial, anticonvulsant, anti-inflammatory, antitumor, anticancer, anti-HIV-1, etc. [25–28].

The design and synthesis of fluorescent small molecules with desirable bioactivities is of considerable current interest in biology research [29,30]. Thus, in continuation of our efforts in synthesizing various bioactive molecules [31–36] and fluorescent small molecules [37–39], we would like to synthesize novel small molecules with both potential bioactivity and fluorescent property.

Based on a fragmented approach, we proposed that 1,3,4-oxadiazole linking benzofuran and pyrazole might have interesting bioactivities such as anticancer activity. On the other hand, three aromatic rings construct π-conjugation system that has cause for expecting improvement in UV–vis absorption and fluorescence spectral characteristics.

Herein, we would like to report the synthesis and UV–vis absorption and fluorescence spectral characteristics of novel 2-(6-methoxy-3-methylbenzofuran-2-yl)-5-(3-phenyl-1*H*-pyrazol-5-yl)-1,3,4-oxadiazole derivatives.

2. Experimental

2.1. General

Thin-layer chromatography (TLC) was conducted on silica gel 60 F_{254} plates (Merck KGaA). ^{1}H NMR spectra were recorded on a Bruker Avance 400 (400 MHz) spectrometer, using $CDCl_3$ or DMSO-d_6 as solvent and tetramethylsilane (TMS) as internal standard. Melting points were determined on an XD-4 digital micro melting point apparatus. IR spectra were recorded with an IR

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spectrophotometer VERTEX 70 FT-IR (Bruker Optics). HRMS spectra were recorded on a Q-TOF6510 spectrograph (Agilent). UV–vis spectra were recorded on a U-4100 (Hitachi). Fluorescent measurements were recorded on a Perkin-Elmer LS-55 luminescence spectrophotometer.

2.2. General procedure for the synthesis of 3-aryl-N′-(6-methoxy-3-methylbenzofuran-2-carbonyl)-1H-pyrazole-5-carbohydrazide (**6a**–**c**)

The acid chloride **3** (2 mmol) and suitable 3-aryl-1*H*-pyrazole-5-carbohydrazide **5a**–**c** (2 mmol) were taken in dried DMF (20 mL), and then triethylamine (2 mmol) was added. The mixture was stirred at room temperature for 3–4 h, after then the mixture was poured into ice water (50 mL). The precipitate was filtered under reduced pressure, washed with water and dried. The crude product was recrystallized from ethanol to afford desired compound **6a**–**c** in 59–66% yields.

2.3. General procedure for the synthesis of 3-aryl-1-benzyl-N′-(6-methoxy-3-methylbenzofuran-2-carbonyl)-1H-pyrazole-5-carbohydrazide (**6d**–**f**)

The acid chloride **3** (2 mmol) and suitable 3-aryl-1-benzyl-1*H*-pyrazole-5-carbohydrazide **5d**–**f** (2 mmol) were taken in dried dichloromethane (20 mL), then triethylamine (2 mmol) was added. The mixture was stirred at room temperature for 3–4 h, after then the mixture was concentrated under reduce pressure. The residue obtained was recrystallized from methanol to afford desired compound **6d**–**f** in 45–61% yields.

2.4. General procedure for the synthesis of 5-(3-aryl-1H-pyrazol-5-yl)-2-(6-methoxy-3-methylbenzofuran-2-yl)-1,3,4-oxadiazole derivatives (**7a**–**f**)

To a round-bottomed flask *N*′-(6-methoxy-3-methylbenzofuran-2-carbonyl)-3-phenyl-1*H*-pyrazole-5-carbohydrazide **6a**–**f** (1 mmol) and $POCl_3$ (10 mL) were added, and the mixture was stirred at 70–80 °C for 5–8 h. Excess $POCl_3$ was distilled off and the residue was poured into ice water, stirred vigorously and then the mixture was neutralized with diluted sodium hydroxide solution to pH 7. The precipitate was filtered under reduced pressure, washed with water, petroleum ether and dried. The crude solid was purified by column chromatography on silica gel and recrystallized from ethanol to afford desired compound **7a**–**f** in 22–31% yields.

2.5. The spectroscopic data of compounds (**7a**–**f**)

2.5.1. 2-(6-Methoxy-3-methylbenzofuran-2-yl)-5-(3-phenyl-1H-pyrazol-5-yl)-1,3,4-oxadiazole (**7a**)

Orange powder, yield 26%, mp 237–240 °C; IR (KBr, cm^{-1}): 3196 (N–H), 1617 (C=C), 1546 (C=N), 1466 (N-N), 1313 (C–N–N), 1274 (C–O–C). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 2.64 (3H, s, CH_3), 3.86 (3H, s, OCH_3), 7.03 (1H, dd, J = 2.0, J = 8.6 Hz, Ar-H), 7.36 (1H, d, J = 2.0 Hz, Ar-H), 7.41–7.47 (2H, m, Pyrazole-H, Ar-H), 7.52 (2H, t, J = 7.6 Hz, Ar-H), 7.71 (1H, d, J = 8.6 Hz, Ar-H), 7.91 (2H, d, J = 7.4 Hz, Ar-H), 14.16 (1H, s, Pyrazole-NH). HRMS (ESI) calcd for $[M+H]^+$ $C_{21}H_{17}N_4O_3$: 373.1301, found: 373.1300.

2.5.2. 2-(3-(4-Chlorophenyl)-1H-pyrazol-5-yl)-5-(6-methoxy-3-methylbenzofuran-2-yl)-1,3,4-oxadiazole (**7b**)

Orange red powder, yield 27%, mp 270–274 °C; IR (KBr, cm^{-1}): 3190 (N–H), 1611 (C=C), 1491 (C=N), 1440 (N-N), 1313 (C–N–N), 1274 (C–O–C). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 2.64 (3H, s, CH_3), 3.87 (3H, s, OCH_3), 7.03 (1H, d, J = 7.8 Hz, Ar-H), 7.33 (1H, s, Pyrazole-H), 7.47 (1H, s, Ar-H), 7.58 (2H, d, J = 7.0 Hz, Ar-H), 7.70 (1H, d, J = 8.4 Hz, Ar-H), 7.92 (2H, d, J = 6.6 Hz, Ar-H), 14.13 (1H, s, Pyrazole-NH). HRMS (ESI) calcd for $[M+H]^+$ $C_{21}H_{16}N_4O_3Cl$: 407.0911, found: 407.0909.

2.5.3. 2-(6-Methoxy-3-methylbenzofuran-2-yl)-5-(3-(4-methoxyphenyl)-1H-pyrazol-5-yl)-1,3,4-oxadiazole (**7c**)

Orange red powder, yield 30%, mp 284–289 °C; IR (KBr, cm^{-1}): 3232 (N–H), 1618 (C=C), 1509 (C=N), 1456 (N-N), 1314 (C–N–N), 1276 (C–O–C). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 2.64 (3H, s, CH_3), 3.87 (3H, s, OCH_3), 3.92 (3H, d, OCH_3), 7.03 (1H, dd, J = 2.0, J = 8.6 Hz, Ar-H), 7.07 (2H, d, J = 8.7 Hz, Ar-H), 7.35 (1H, d, J = 8.0 Hz, Ar-H), 7.58 (1H, s, Pyrazole-H), 7.71 (1H, d, J = 8.6 Hz, Ar-H), 7.83 (2H, d, J = 8.0 Hz, Ar-H), 13.98 (1H, s, Pyrazole-NH). HRMS (ESI) calcd for $[M+H]^+$ $C_{22}H_{19}N_4O_4$: 403.1406, found: 403.1400.

2.5.4. 2-(1-Benzyl-3-phenyl-1H-pyrazol-5-yl)-5-(6-methoxy-3-methylbenzofuran-2-yl)-1,3,4-oxadiazole (**7d**)

Pale yellow powder, yield 22%, mp 200–201 °C; IR (KBr, cm^{-1}): 1615 (C=C), 1493 (C=N), 1469 (N-N), 1349 (C–N–N), 1278 (C–O–C). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.66 (3H, s, CH_3), 3.90 (3H, s, OCH_3), 6.02 (2H, s, CH_2), 6.98 (1H, dd, J = 2.1, J 8.7 Hz, Ar-H), 7.08 (1H, d, J = 2.1 Hz, Ar-H), 7.24 (1H, s, Pyrazole-H), 7.28–7.31 (3H, t, J = 7.2 Hz, Ar-H), 7.36 (1H, t, J = 7.3 Hz, Ar-H), 7.43–7.47 (4H, m, Ar-H), 7.51 (1H, d, J = 8.7 Hz, Ar-H), 7.91 (2H, d, J = 7.3 Hz, Ar-H). HRMS (ESI) calcd for $[M+H]^+$ $C_{28}H_{23}N_4O_3$: 463.1770, found: 463.1773.

2.5.5. 2-(1-Benzyl-3-(4-chlorophenyl)-1H-pyrazol-5-yl)-5-(6-methoxy-3-methylbenzofuran-2-yl)-1,3,4-oxadiazole (**7e**)

Pale yellow powder, yield 29%, mp 217–221 °C; IR (KBr, cm^{-1}): 1616 (C=C), 1494 (C=N), 1470 (N-N), 1350 (C–N–N), 1278 (C–O–C). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.66 (3H, s, CH_3), 3.90 (3H, s, OCH_3), 6.01 (2H, s, CH_2), 6.98 (1H, d, J = 8.6 Hz, Ar-H), 7.08 (1H, s, Ar-H), 7.26–7.30 (4H, m, Pyrazole-H, Ar-H), 7.43 (4H, m, Ar-H), 7.52 (1H, d, J = 8.6 Hz, Ar-H), 7.83 (2H, d, J = 8.0 Hz, Ar-H). HRMS (ESI) calcd for $[M+H]^+$ $C_{28}H_{22}N_4O_3Cl$: 497.1380, found: 497.1383.

2.5.6. 2-(1-(4-(Tert-butyl)benzyl)-3-(4-chlorophenyl)-1H-pyrazol-5-yl)-5-(6-methoxy-3-methyl benzofuran-2-yl)-1,3,4-oxadiazole (**7f**)

Pale yellow powder, yield 31%, mp 205–206 °C; IR (KBr, cm^{-1}): 1612 (C=C), 1494 (C=N), 1470 (N-N), 1324 (C–N–N), 1275 (C–O–C). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.26 (9H, s, *tert*-butyl), 2.67 (3H, s, CH_3), 3.90 (3H, s, OCH_3), 5.98 (2H, s, CH_2), 6.98 (1H, dd, J = 2.1, J = 8.7 Hz, Ar-H), 7.08 (1H, d, J = 2.1 Hz, Ar-H), 7.24 (1H, s, Pyrazole-H), 7.32 (2H, d, J = 8.3 Hz, Ar-H), 7.40 (4H, m, J = 8.0 Hz, Ar-H), 7.52 (1H, d, J = 8.7 Hz, Ar-H), 7.8 (2H, d, J = 8.3 Hz, Ar-H). HRMS (ESI) calcd for $[M+H]^+$ $C_{32}H_{30}N_4O_3Cl$: 553.2006, found: 553.1996.

2.6. X-ray crystallography

Suitable single crystals of **7e** for X-ray structural analysis were obtained by slow evaporation of a solution of the solid in dichloromethane at room temperature for 10 days. The crystals with approximate dimensions of 0.10 mm × 0.10 mm × 0.08 mm for **7e** were mounted on a Bruker Smart Apex II CCD equipped

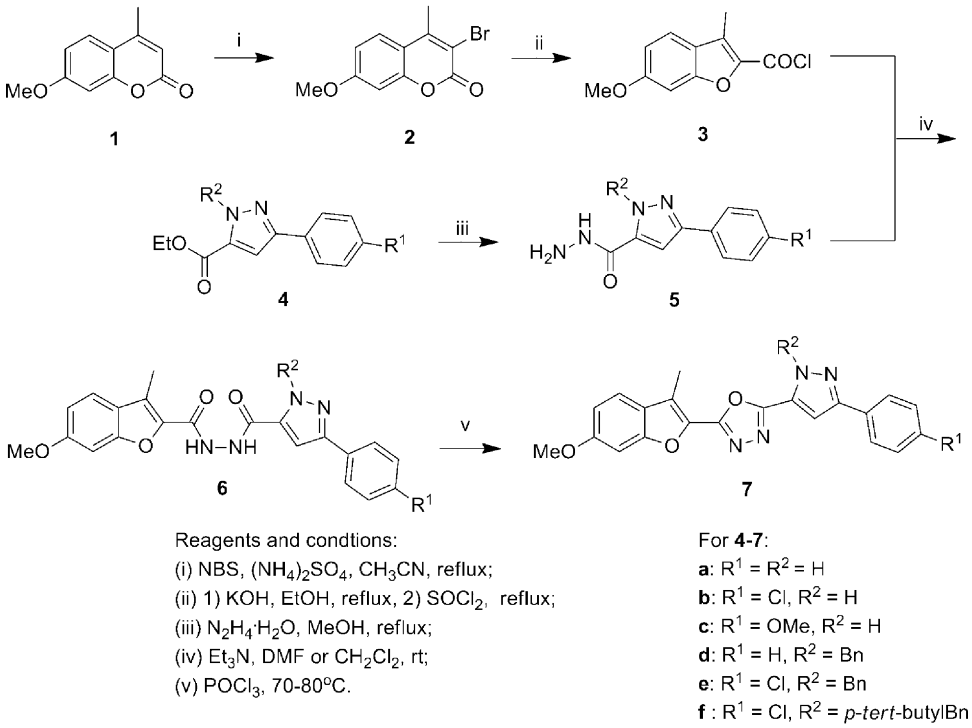

Fig. 1. Synthetic route for the new 1,3,4-oxadiazoles.

with a graphite monochromated MoKα radiation (λ = 0.71073 Å) by using φ and ω scan modes and the data were collected at 298(2) K. The structure of the crystal was solved by direct methods and refined by full-matrix least-squares techniques implemented in the SHELXTL-97 crystallographic software. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms bound to carbon were located by geometrical calculations, with their position and thermal parameters being fixed during the structure refinement. The final refinement converged at $R1 = 0.0437$, $wR2 = 0.1178$ for **7e**.

3. Results and discussion

3.1. Synthesis

Most of protocols reported in the literature for the synthesis of 1,3,4-oxadiazoles mainly involve the cyclization of diacylhydrazides with a variety of reagents such as thionyl chloride, phosphorus oxychloride, or PPA, usually under harsh reaction conditions [40–42], the oxidation of acylhydrozones [43–45], and the condensation of carboxylic acids with acyl hydrazides [46,47]. In the present study, we adopted the strategy in which diacylhydrazide cyclized in the presence of phosphorus oxychloride to afford desired compounds as shown in Fig. 1.

Starting 7-methoxy-4-methyl-2*H*-chromen-2-one **1** can be easily synthesized by the reaction of commercially available 3-methoxyphenol and ethyl acetoacetate according to the literature [48]. Then compound **2** was obtained by the bromination of compound **1** with NBS in the presence of ammonium sulfate in acetonitrile, a modified literature method [49], in 69% yield. Acid chloride **3** was synthesized by the reaction of compound **2** with 10% ethanolic potassium hydroxide at reflux for 2 h and followed the reaction with thionyl dichloride in 82–87% yields.

3-Aryl-1*H*-pyrazole-5-carbohydrazide derivatives **5** were synthesized by the reaction of ethyl 3-aryl-1*H*-pyrazole-5-carboxylate derivatives **4** and hydrate hydrazine according to our previous report [50]. Subsequently, diacylhydrazides **6** were synthesized by the reaction of acid chloride **3** and 3-aryl-1*H*-pyrazole-5-carbohydrazide derivatives **5** in 45%-66% yields. It is noted that the solvents used in the reaction for 3-aryl-1*H*-pyrazole-5-carbohydrazide **6a**–**c** and 3-aryl-benzyl-1*H*-pyrazole-5-carbohydrazide derivatives **6d**–**f** were different. That is, for **6a**–**c**, DMF must be employed to ensure substrates soluble, in the case of **6d**–**f**, however, dichloromethane was used for feasible reaction and workup. Finally, proposed compounds **7a**–**f** were synthesized by the cyclization of diacylhydrazides **6** in the presence of phosphorus oxychloride in 22–31% yields.

3.2. Structure characterization

The proposed structures of compounds **7a**–**f** were proved by IR, ^{1}H NMR and HRMS spectra. For example compound **7a**, obtained as orange solid, gave a [M+H]-ion peak at *m*/*z* 373.1300 in the HRESIMS, in accord with the molecular formula $C_{21}H_{16}N_4O_3$. The IR spectra of compound **7a** showed the characteristic absorption bands at 3196 (N–H), 1617 (C=C), 1546 (C=N), 1466 (N-N), and 1274 (C–O–C) cm^{-1}. The ^{1}H NMR spectra (DMSO-d_6) of compound **7a** revealed three singlet peaks at δ 2.64 (3H, CH_3), 3.86 (3H, OCH_3) and 14.16 (1H, Pyrazole-NH) ppm which were readily assigned to the proton of methyl, methoxyl and NH of pyrazole moiety, respectively. It is noted that another proton of pyrazole moiety should reveal singlet peak inserts region of 7.41–7.47 ppm. Moreover, the double doublet peaks in 7.03 ppm with coupling constant 2.0 and 8.6 Hz assigned to the proton in 5-position of benzofuran ring. The doublet peaks revealed in 7.36 ppm with coupling constant 2.0 Hz were assigned to the proton in 7-position of benzofuran ring. The proton in 4-position of benzofuran ring revealed in 7.71 ppm as doublet peaks with coupling constant 8.6 Hz. The protons of benzene bonded to 3-position of pyrazole moiety showed doublet peaks in 7.91 ppm with coupling constant 7.4 Hz and multiplet peaks in region of 7.41–7.47 and 7.50–7.54 ppm.

Table 1
Summary of crystallographic data and structure refinement details for **7e**.

	7e
Empirical formula	$C_{28}H_{21}ClN_4O_3$
Formula weight	496.94
Temperature	298(2)
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	*P*2(1)/*n*
Unit cell dimensions	$a = 11.4821(10)$ Å, $\alpha = 90.00°$ $b = 15.7957(14)$ Å, $\beta = 96.570(2)°$ $c = 12.9560(11)$ Å, $\gamma = 90.00°$
Volume	2334.4(4) A^3
Z	4
Calculated density	1.414 Mg/m^3
Absorption coefficient	0.204 mm^{-1}
F(000)	1032
Crystal size	0.10 mm × 0.10 mm × 0.08 mm
θ range for data collection	2.04–23.26°
Limiting indices	$-10 \le h \le 12$, $-17 \le k \le 16$, $-14 \le l \le 14$
Reflections collected/unique	9787/3344 [*R*(int) = 0.0336]
Completeness to θ	99.6%
Absorption correction	None
Max. and min. transmission	0.9839 and 0.9799
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3344/0/326
Goodness-of-fit on F^2	1.023
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0437$, $wR_2 = 0.1178$
R indices (all data)	$R_1 = 0.0670$, $wR_2 = 0.1367$
Largest diff. peak and hole	0.716 and −0.213 e $Å^{-3}$
CCDC No.	830,628

3.3. X-ray crystallography analysis

The spatial structure of compound **7e** was determined by using X-ray diffraction analysis. A summary of crystallographic data collection parameters and refinement parameters for **7e** are compiled in Table 1.

Fig. 2 shows that **7e** contains a 1,3,4-oxadiazole bound to benzofuran and pyrazole rings. The molecular structure is dominated by the arrangement of the rings of the 1,3,4-oxadiazole, benzofuran, pyrazole, benzyl and the phenyl. The molecular conformation is stabilized by intramolecular C10–H10A···N3 weak hydrogen bond (C10···N3 3.097(4) Å and C10–H10A···N3 118°). The rings of 1,3,4-oxadiazole, benzofuran and pyrazole are almost coplanar with dihedral angle 3.32(13)° and 1.10(16)° respectively, indicating that they are conjugated. However, the benzene ring C1–C6 is deviated from the conjugated plane (pyrazole ring) with dihedral angle of 14.21(15)°. The distance of C9–C17 1.442(4) Å is almost same as that of C18–C19 1.443(4) Å, and that of C4–C7 is 1.475(4) Å.

The crystal packing of **7e** is stabilized by the C–H···π intermolecular hydrogen bonds and the π···π stacking interactions (Table 2 and Fig. 3). Interestingly, two C21–H21B···Cg2

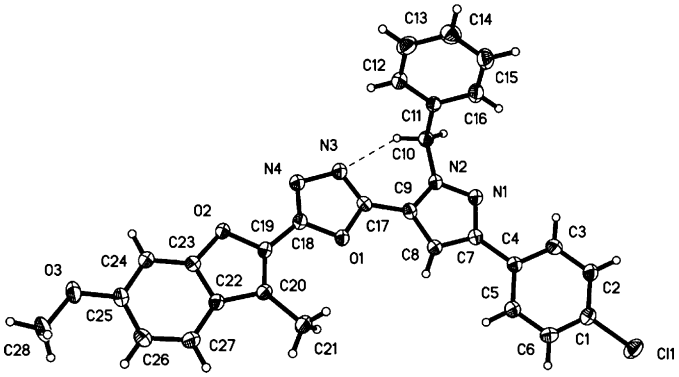

Fig. 2. The molecular structure of compound **7e**.

Table 2
Hydrogen-bond geometry for **7e**.

X–H···A/π[a]	X–H	H···A/π	X···A/π	X–H···A/π	Symmetry codes
C10–H10$_A$···N3	0.97	2.52	3.097(4)	118	
C6–H6···*Cg*1	0.93	2.98	3.394(4)	109	3/2 − *x*, 1/2 + *y*, 1/2 − *z*
C21–H21$_B$···*Cg*2	0.96	2.91	3.783(4)	151	2 − *x*, −*y*, 1 − *z*

[a] Cg1 and *Cg*2 are the centriods of 1,3,4-oxadiazole ring and the furan ring, respectively.

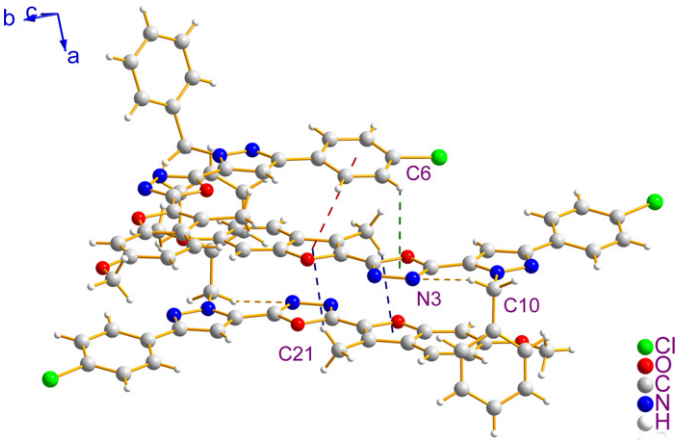

Fig. 3. Molecular packing in **7e**, showing details of the hydrogen bonds connectivity and the π···π interactions.

intermolecular hydrogen bonds generate centrosymmetric $R_2^2(8)$ dimmers, which are linked to each other through C6–H9···*Cg*1 intermolecular hydrogen bonds and the π···π stacking interactions between 4-chlorophenyl and furan rings (Cg2···Cg4 3.8092(17) Å with symmetry operation: 3/2 − *x*, −1/2 + *y*, 1/2 − *z*; Cg2 and Cg4 are the centroids of furan and benzene ring, respectively), forming a networks structure.

3.4. Absorption spectral

UV–vis absorption spectra of compounds **7a**–**f** were observed in dichloromethane and acetonitrile solution with the concentration of 1×10^{-5} M, respectively, as shown in Figs. 4 and S1 and Table 3. The results showed that the absorption maxima of the compounds

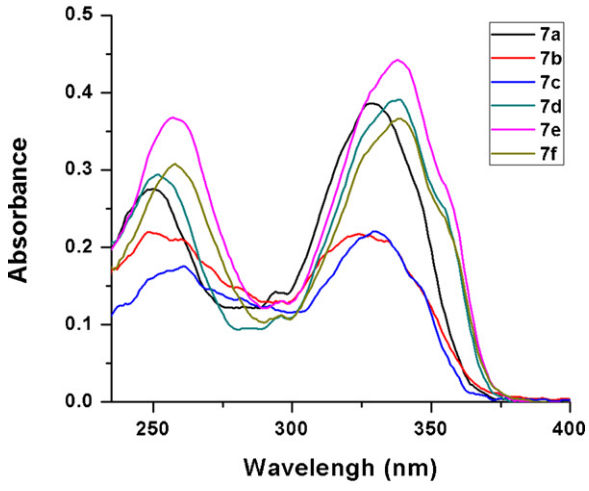

Fig. 4. UV–vis absorption spectra of compounds **7a**–**f** taken in dichloromethane ($c = 1 \times 10^{-5}$ M).

Table 3
The optical characteristics of compounds **7a–f**.

Compound	λ_{max} (nm)				ε_{max} ($L\,mol^{-1}\,cm^{-1}$)			
(**7a–f**)	CH_2Cl_2		CH_3CN		CH_2Cl_2		CH_3CN	
7a	329	250	325	251	38,600	27,500	41,300	24,500
7b	324	249	321	257	21,700	21,900	22,200	21,000
7c	330	261	326	257	22,000	17,500	24,500	18,400
7d	339	252	333	252	39,100	29,400	42,300	29,600
7e	338	257	332	256	44,200	36,800	49,100	39,200
7f	339	258	333	256	36,600	30,800	40,700	31,400

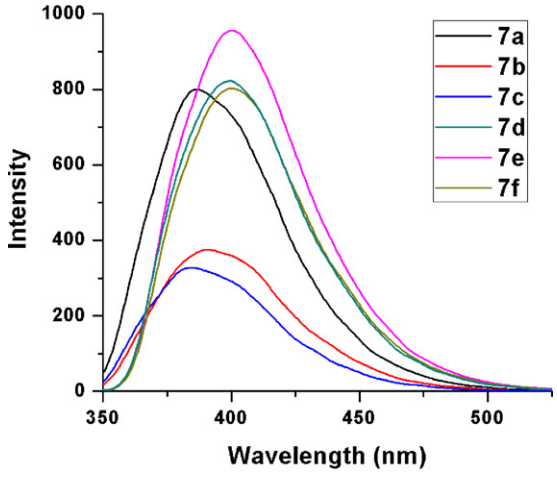

Fig. 5. Emission spectra of **7a–f** in dichloromethane ($c = 5 \times 10^{-7}$ M).

vary from 321 to 339 nm that are attributed to π–π* transition depending on the substituents in *N*-1 position of pyrazole moiety and *para* position of benzene moiety. It can be found that compounds **7d–f** with phenyl in *N*-1 position of pyrazole moiety have red shift than that without benzyl group 7**a–c**. Moreover, the compound **7b** with chlorine group in *para*-position of phenyl group bonded to pyrazole has a blue shift compared with **7a** without substituent and **7c** with methoxy, an electron-donating group. These phenomena can be explained by the enhancement of electron delocalization in conjugation system. In addition, the effects of polarity of solvent on the absorption maxima were also obvious. That is, the maximum absorption wavelength of **7a–f** in dichloromethane is larger than that in acetonitrile resulting in red shift about 5 nm.

3.5. Fluorescence

Fluorescence spectral characteristics of the compounds **7a–f** in dichloromethane and acetonitrile solution with the concentration of 5×10^{-7} M were investigated. From Figs. 5 and S2 and Table 4 it can be found that the maximum emission spectra of compounds in two different solvents are also mainly dependent on the groups in *N*-1 position of pyrazole moiety. Thus, compounds **7d–f** with phenyl group in *N*-1 position of pyrazole have red shift than that without benzyl group **7a–c**. In acetonitrile, for example, compounds **7d–f** red shifted about 17–22 nm. In addition, compound **7b** with chlorine group in *para*-position of phenyl moiety bonded to pyrazole has less red shift compared with **7a** without substituent and **7c** with methoxy, an electron-donating group. The intensity of fluorescence was also correlated with substituents on two aryl rings. Generally, intensity of fluorescence **7d–f** was stronger then **7a–c** in two different solvents, respectively.

Table 4
Data of fluorescence spectra of compounds **7a–f** at 5×10^{-7} M.

Compound	λ_{ex} (nm)		λ_{em} (nm)		Stoke's shift (nm)	
(**7a–f**)	CH_2Cl_2	CH_3CN	CH_2Cl_2	CH_3CN	CH_2Cl_2	CH_3CN
7a	330	330	385	388	55	58
7b	330	330	390	389	60	59
7c	330	330	384	385	54	55
7d	340	340	399	408	59	68
7e	340	340	399	406	59	66
7f	340	340	400	406	60	66

4. Conclusion

A series of novel benzofuran and pyrazole linked 1,3,4-oxadiazole derivatives has been synthesized from 6-methoxy-3-methylbenzofuran-2-carboxylic acid and ethyl 3-aryl-1*H*-pyrazole-5-carboxylate. The structures of compounds were determined by IR, ^{1}H NMR and HRMS spectra, typically, the spatial structure of compound **7e** was determined by using X-ray diffraction analysis. Absorption and fluorescence spectral characteristics of the compounds in dichloromethane and acetonitrile were investigated and results showed that the absorption spectra and fluorescence characteristics were mainly dependent on the groups in *N*-1 position of pyrazole moiety.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.saa.2011.10.021.

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