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ORIGINAL PAPER

Synthesis, X-Ray Crystal Structures and Optical Properties of Novel Substituted Pyrazoly 1,3,4-Oxadiazole Derivatives

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Abstract Novel pyrazoly 1,3,4-oxadiazole derivatives were synthesized and characterized by ^{1}H NMR, IR, HRMS and X-ray diffraction analysis. UV–vis absorption and fluorescence properties of these compounds in different solutions showed that the maximum absorption wavelength was not significantly changed in different solvents; however, maximal emission wavelength was red-shifted with the increase of solvent polarity. Absorption λ_{max} and emission λ_{max} was less correlated with substituent groups on aryl rings.

Keywords 1,3,4-Oxadiazole · Synthesis · X-ray · UV–vis absorption · Fluorescence

Introduction

As an important class of five-membered heterocyclic compounds, 1,3,4-oxadiazoles have been widely studied as materials in electroluminescent (EL) devices due to their electron deficiency, high thermal and oxidative stability, especially high quantum yields [1–3]. In recent years, many 1,3,4-oxadiazole derivatives have been described as electron transporting and hole blocking materials in organic light-emitting diodes (OLEDs) [4–7] and polymer light-emitting diodes (PLEDs) [8, 9]. In addition, electron-transporting 1,3,4-oxadiazole moiety has been connected to many chelating ligands to obtain luminescent complexes with more new functions [10–18].

The heterocyclic moiety can improve electron injection and transport properties of the molecules. Thus, many heterocyclic compounds based 1,3,4-oxadiazole have been investigated, such as 1,3,4-oxadiazole–pyridine hybrids [19], 1,3,4-oxadiazole–pyrimidine hybrids [19] and 1,3,4-oxadiazole-spirobifluorene [20]. Furthermore, 1,3,4-oxadiazole derivatives have been a focus of attention in medical chemistry for a long time because of their wide range of biological activities including antiinflammatory [21], anticancer [22, 23] and antibacterial [24, 25] activities.

We are interested in design, synthesis, structural characterization and fluorescence property of novel compounds with potential bioactivity in order to investigate the localization of small molecule in cells. In our previous work we reported a series of novel 2,5-disubstituted 1,3,4-oxadiazole derivatives and investigated their optical properties [26]. Herein, we report synthesis, X-ray crystal structures and optical properties of novel 1,3,4-oxadiazole derivatives combined with pyrazole, an electron-rich heterocycle, in order to investigate their potential application in localization of small molecule in cells.

Experimental

General

Thin-layer chromatography (TLC) was conducted on silica gel 60 F_{254} plates (Merck KGaA). ^{1}H NMR spectra were

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recorded on a Bruker Avance 400 (400 MHz) spectrometer, using $CDCl_3$ 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 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). Fluorescence measurements were recorded on a Perkin–Elmer LS-55 luminescence spectrophotometer.

General Procedure for Preparation of 2-(1-aryl-3-(4-chlorophenyl)-1*H*-pyrazol-5-yl)-5-(chloromethyl)-1,3,4-oxadiazole (**4**)

To a solution of 1-arylmethyl-3-aryl-1*H*-pyrazole-5-carbohydrazide (**1**) (3.5 mmol) in dichloromethane (50 ml) was added 15 drops of Et_3N. Subsequently, the solution of 2-chloroacetyl chloride (**2**) (4.2 mmol) dissolved in dichloromethane (5 ml) was added dropwise in 20 min at room temperature. The reaction mixture was stirred for 3 h at room temperature, after which the solvent was removed under reduced pressure. Water (30 ml) was added to the residue to remove soluble impurity and the precipitate was filtrated, washed with water (10 ml×3) and dried to give **3** without further purification.

The mixture of **3** (3.5 mmol) and $POCl_3$ (15 ml) was refluxed for 5 h. After cooling, it was poured into powder ice (100 g). The precipitate was filtrated, washed with water and dried. Product **4** was obtained by column chromatography on silica gel using PE/EtOAc (1:1) as an eluent.

General Procedure for Preparation of 2-(1-aryl-3-(4-chlorophenyl)-1*H*-pyrazol-5-yl)-5-(aryloxymethyl)-1,3,4-oxadiazole (**5a-j**)

A mixture of **4** (1 mmol), substituted phenol (1 mmol), anhydrous potassium carbonate (3 mmol) and dry acetonitrile (25 ml) was refluxed for 0.5–2.5 h, after which the solution was condensed under reduced pressure. The residue was extracted with dichloromethane (30 ml). The organic phase was washed with 5% NaOH solution (10 ml), water (10 ml×3) and dried over $MgSO_4$. After filtered, the filtrate was concentrated under reduced pressure to afford title compound **5** in 86–99% (Fig. 1).

The Spectroscopic Data of Compounds **5**

*2-(1-(4-(tert-Butyl)benzyl)-3-(4-chlorophenyl)-1 H-pyrazol-5-yl)-5-((p-tolyloxy)methyl)-1,3,4-oxadiazole (***5a***)* White solid, yield 99%; mp 159–161 °C; IR (KBr, cm^{-1}) ν: 3114, 3036, 2954, 2866, 1614, 1578, 1511, 1459, 1225; ^1H NMR ($CDCl_3$): δ 1.26 (s, 9 H, $C(CH_3)_3$), 2.30 (s, 3 H, CH_3), 5.29 (s, 2 H, OCH_2), 5.89 (s, 2 H, NCH_2), 6.93 (d, 2 H, *J*=8.4 Hz, Ar-H), 7.12 (d, 2 H, *J*=8.4 Hz, Ar-H), 7.16 (s, 1 H, Pyrazole-H), 7.28 (d, 2 H, *J*=8.4 Hz, Ar-H), 7.32 (d, 2 H, *J*=8.4 Hz, Ar-H), 7.39 (d, 2 H, *J*=8.4 Hz, Ar-H), 7.78 (d, 2 H, *J*=8.4 Hz, Ar-H); HRMS calcd for $[M+H]^+$ $C_{30}H_{30}ClN_4O_2$: 513.2057, found 513.2052.

*2-(1-(4-(tert-Butyl)benzyl)-3-(4-chlorophenyl)-1 H-pyrazol-5-yl)-5-((2-methoxyphenoxy)methyl)-1,3,4-oxadiazole (***5b***)* White solid, yield 93%; mp 121–122 °C; IR (KBr, cm^{-1}) ν: 3146, 3062, 2961, 2868, 1614, 1594, 1509, 1473, 1257; ^1H NMR ($CDCl_3$): δ 1.26 (s, 9 H, $C(CH_3)_3$), 3.85 (s, 3 H, OCH_3), 5.36 (s, 2 H, OCH_2), 5.89 (s, 2 H, NCH_2), 6.87–6.95 (m, 2 H, Ar-H), 7.02–7.10 (m, 2 H, Ar-H), 7.16 (s, 1 H, Pyrazole-H), 7.28 (d, 2 H, *J*=8.4 Hz, Ar-H), 7.32 (d, 2 H, *J*=8.4 Hz, Ar-H), 7.39 (d, 2 H, *J*=8.4 Hz, Ar-H), 7.78 (d, 2 H, *J*=8.4 Hz, Ar-H); HRMS calcd for $[M+H]^+$ $C_{30}H_{30}ClN_4O_3$: 529.2006, found 529.1978.

*2-(1-(4-(tert-Butyl)benzyl)-3-(4-chlorophenyl)-1 H-pyrazol-5-yl)-5-((4-chlorophenoxy)methyl)-1,3,4-oxadiazole (***5c***)* White solid, yield 95%; mp 179–181 °C; IR (KBr, cm^{-1}) ν: 3113, 3038, 2955, 2867, 1616, 1596, 1489, 1227; ^1H NMR ($CDCl_3$): δ 1.26 (s, 9 H, $C(CH_3)_3$), 5.29 (s, 2 H, OCH_2), 5.89 (s, 2 H, NCH_2), 6.97 (d, 2 H, *J*=9.2 Hz, Ar-H), 7.15 (s, 1 H, Pyrazole-H), 7.27–7.34 (m, 6 H, Ar-H), 7.39 (d, 2 H, *J*=8.4 Hz, Ar-H), 7.79 (d, 2 H, *J*=8.4 Hz, Ar-H); HRMS calcd for $[M+H]^+$ $C_{29}H_{27}Cl_2N_4O_2$: 533.1511, found 533.1507.

*2-(1-(4-(tert-Butyl)benzyl)-3-(4-chlorophenyl)-1 H-pyrazol-5-yl)-5-((2,4-dichlorophenoxy)methyl)-1,3,4-oxadiazole (***5d***)* White solid, yield 98%; mp 131–132 °C; IR (KBr, cm^{-1}) ν: 3144, 3071, 2961, 2869, 1614, 1581, 1478, 1218; ^1H NMR ($CDCl_3$): δ 1.26 (s, 9 H, $C(CH_3)_3$), 5.36 (s, 2 H, OCH_2), 5.89 (s, 2 H, NCH_2), 7.07 (d, 1 H, *J*=9.2 Hz, Ar-H), 7.17 (s, 1 H, Pyrazole-H), 7.22 (dd, 1 H, *J*=2.4, 9.2 Hz, Ar-H), 7.29 (d, 2 H, *J*=8.8 Hz, Ar-H), 7.32 (d, 2 H, *J*=8.8 Hz, Ar-H), 7.39 (d, 2 H, *J*=8.4 Hz, Ar-H), 7.41 (d, 1 H, *J*=2.4 Hz, Ar-H), 7.79 (d, 2 H, *J*=8.4 Hz, Ar-H); HRMS calcd for $[M+H]^+$ $C_{29}H_{26}Cl_3N_4O_2$: 567.1121, found 567.1104.

*2-(1-(4-(tert-Butyl)benzyl)-3-(4-chlorophenyl)-1 H-pyrazol-5-yl)-5-((4-nitrophenoxy)methyl)-1,3,4-oxadiazole (***5e***)* Yellow solid, yield 97%; mp 165–167 °C; IR (KBr, cm^{-1}) ν: 3113, 3083, 2959, 2866, 1614, 1591, 1517, 1496, 1346, 1255; ^1H NMR ($CDCl_3$): δ 1.26 (s, 9 H, $C(CH_3)_3$), 5.42 (s, 2 H, OCH_2), 5.91 (s, 2 H, NCH_2), 7.14 (d, 2 H, *J*=9.2 Hz, Ar-H), 7.16 (s, 1 H, Pyrazole-H), 7.29 (d, 2 H, *J*=8.6 Hz, Ar-H), 7.33 (d, 2 H, *J*=8.6 Hz, Ar-H), 7.39 (d, 2 H, *J*=8.4 Hz, Ar-H), 7.78 (d, 2 H, *J*=8.4 Hz, Ar-H), 8.25 (d, 2 H, *J*=9.2 Hz, Ar-H); HRMS calcd for $[M+H]^+$ $C_{29}H_{27}ClN_5O_4$: 544.1752, found 544.1730.

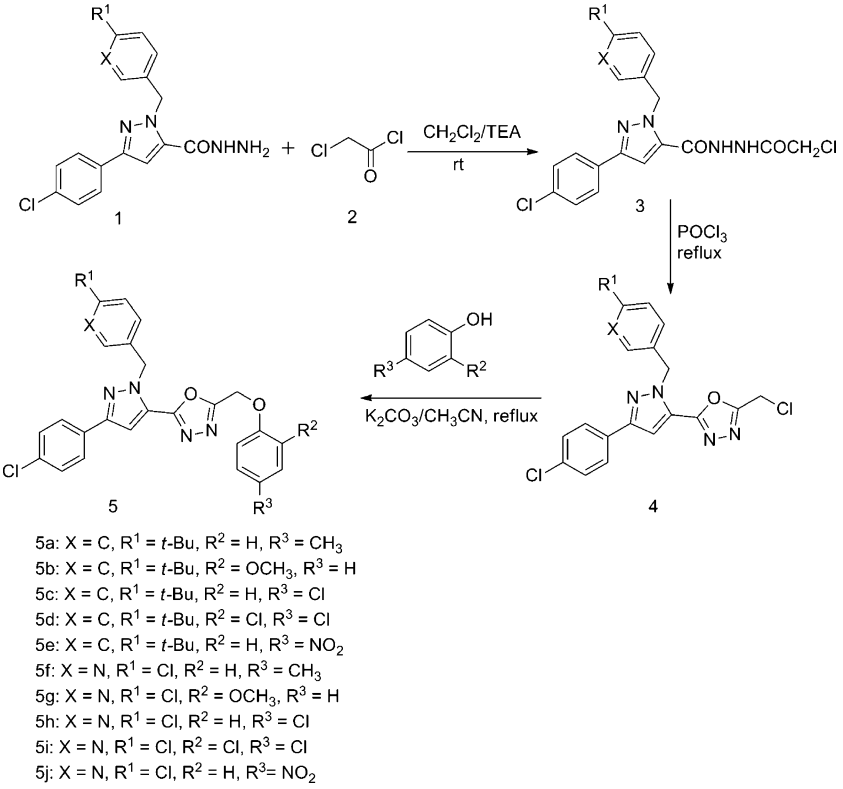

Fig. 1 The synthetic route of unsymmetrical 1,3,4-oxadiazole derivatives

*2-(3-(4-Chlorophenyl)-1-((6-chloropyridin-3-yl)methyl)-1 H-pyrazol-5-yl)-5-((p-tolyloxy)methyl)-1,3,4-oxadiazole (***5f***)* White solid, yield 87%; mp 168–171 °C; IR (KBr, cm^{-1}) ν: 3153, 3055, 2945, 2859, 1619, 1583, 1510, 1473, 1240; ^{1}H NMR ($CDCl_3$): δ 2.30 (s, 3 H, CH_3), 5.30 (s, 2 H, OCH_2), 5.93 (s, 2 H, NCH_2), 6.92 (d, 2 H, *J*=8.4 Hz, Ar-H), 7.12 (d, 2 H, *J*=8.4 Hz, Ar-H), 7.17 (s, 1 H, Pyrazole-H), 7.24 (d, 1 H, *J*=6.6 Hz, Pyridine-H), 7.40 (d, 2 H, *J*= 8.5 Hz, Ar-H), 7.73 (dd, 1 H, *J*=2.2, 6.6 Hz, Pyridine-H), 7.76 (d, 2 H, *J*=8.5 Hz, Ar-H), 8.50 (d, 1 H, *J*=2.2 Hz, Pyridine-H); HRMS calcd for $[M+H]^+$ $C_{25}H_{20}Cl_2N_5O_2$: 492.0994, found 492.0985.

*2-(3-(4-Chlorophenyl)-1-((6-chloropyridin-3-yl)methyl)-1 H-pyrazol-5-yl)-5-((2-methoxyphenoxy)methyl)-1,3,4-oxadiazole (***5 g***)* White solid, yield 90%; mp 149–151 °C; IR (KBr, cm^{-1}) ν: 3113, 3072, 2956, 2863, 1615, 1586, 1507, 1460, 1259, 1214; ^{1}H NMR ($CDCl_3$): δ 3.87 (s, 3 H, OCH_3), 5.38 (s, 2 H, OCH_2), 5.93 (s, 2 H, NCH_2), 6.89–6.98 (m, 2 H, Ar-H), 7.03-7.10 (m, 2 H, Ar-H), 7.18 (s, 1 H, Pyrazole-H), 7.25 (d, 1 H, *J*=7.2 Hz, Pyridine-H), 7.41 (d, 2 H, *J*=8.5 Hz, Ar-H), 7.74 (dd, 1 H, *J*=2.4, 7.2 Hz, Pyridine-H), 7.76 (d, 2 H, *J*=8.5 Hz, Ar-H), 8.51 (d, 1 H, *J*=2.4 Hz, Pyridine-H); HRMS calcd for $[M+H]^+$ $C_{25}H_{20}Cl_2N_5O_3$: 508.0943, found 508.0935.

*2-((4-Chlorophenoxy)methyl)-5-(3-(4-chlorophenyl)-1-((6-chloropyridin-3-yl)methyl)-1 H-pyrazol-5-yl)-1,3,4-oxadiazole (***5 h***)* White solid, yield 86%; mp 179–181 °C; IR (KBr, cm^{-1}) ν: 3142, 3077, 2951, 2871, 1616, 1584, 1489, 1470, 1238; ^{1}H NMR ($CDCl_3$): δ 5.31 (s, 2 H, OCH_2), 5.94 (s, 2 H, NCH_2), 6.97 (d, 2 H, *J*=8.8 Hz, Ar-H), 7.17 (s, 1 H, Pyrazole-H), 7.26 (d, 1 H, *J*=8.0 Hz, Pyridine-H), 7.29 (d, 2 H, *J*=8.8 Hz, Ar-H), 7.40 (d, 2 H, *J*=8.4 Hz, Ar-H), 7.74 (dd, 1 H, *J*=2.6, 8.0 Hz, Pyridine-H), 7.76 (d, 2 H, *J*=8.4 Hz, Ar-H), 8.51 (d, 1 H, *J*=2.6 Hz, Pyridine-H); HRMS calcd for $[M+H]^+$ $C_{24}H_{17}Cl_3N_5O_2$: 512.0448, found 512.0436.

*2-(3-(4-Chlorophenyl)-1-((6-chloropyridin-3-yl)methyl)-1 H-pyrazol-5-yl)-5-((2,4-dichlorophenoxy)methyl)-1,3,4-oxadiazole (***5i***)* White solid, yield 93%; mp 211–213 °C; IR (KBr, cm^{-1}) ν: 3125, 3053, 2955, 1615, 1585, 1477, 1244; ^{1}H NMR ($CDCl_3$): δ 5.37 (s, 2 H, OCH_2), 5.93 (s, 2 H, NCH_2), 7.07 (d, 1 H, *J*=8.8 Hz, Ar-H), 7.18 (s, 1 H, Pyrazole-H), 7.22 (d, 1 H, *J*=1.7 Hz, Ar-H), 7.26 (dd, 1 H, *J*=1.7, 8.8 Hz, Ar-H), 7.40 (d, 1 H, *J*=6.4 Hz, Pyridine-H), 7.41 (d, 2 H, *J*=8.5 Hz, Ar-H), 7.74 (dd, 1 H, *J*=2.2, 6.4 Hz, Pyridine-H), 7.77 (d, 2 H, *J*=8.5 Hz, Ar-H), 8.51 (d, 1 H, *J*=2.2 Hz, Pyridine-H); HRMS calcd for $[M+H]^+$ $C_{24}H_{16}Cl_4N_5O_2$: 548.0029, found 548.0019.

*2-(3-(4-Chlorophenyl)-1-((6-chloropyridin-3-yl)methyl)-1 H-pyrazol-5-yl)-5-((4-nitrophenoxy)methyl)-1,3,4-oxadiazole (***5j***)* Yellow solid, yield 91%; mp 200–202 °C; IR (KBr, cm^{-1}) ν: 3112, 3084, 2954, 1615, 1590, 1517, 1491, 1340, 1253; ^{1}H NMR ($CDCl_3$): δ 5.43 (s, 2 H, OCH_2), 5.94

(s, 2 H, NCH_2), 7.13 (d, 2 H, *J*=9.2 Hz, Ar-H), 7.18 (s, 1 H, Pyrazole-H), 7.27 (d, 1 H, *J*=7.0 Hz, Pyridine-H), 7.41 (d, 2 H, *J*=8.5 Hz, Ar-H), 7.75 (dd, 1 H, *J*=2.2, 7.0 Hz, Pyridine-H), 7.77 (d, 2 H, *J*=8.5 Hz, Ar-H), 8.26 (d, 2 H, *J*= 9.2 Hz, Ar-H), 8.51 (d, 1 H, *J*=2.2 Hz, Pyridine-H); HRMS calcd for $[M+H]^+$ $C_{24}H_{17}Cl_2N_6O_4$: 523.0688, found 523.0664.

X-Ray Crystallography

Suitable single crystals of **5c** and **5e** for X-ray structural analysis were obtained by evaporation of ethyl acetate solution. The diffraction data for both structures were collected with a Bruker SMART CCD diffractometer using a graphite monochromated Mo Kα radiation (λ=0.71073 Å) at 273(2) K. The structures were solved by direct methods with SHELXS-97 program and refinements on F^2 were performed with SHELXL-97 program by full-matrix least-squares techniques with anisotropic thermal parameters for the non-hydrogen atoms. All H atoms were initially located in a difference Fourier map. The methyl H atoms were then constrained to an ideal geometry, with C–H=0.96 Å and U_{iso}(H) $1.5U_{eq}$(C). All other H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C–H=0.93 Å and U_{iso}(H)=$1.2U_{eq}$(C).

Results and Discussion

Synthesis and Characterization

The synthesis of 2-(1-aryl-3-(4-chlorophenyl)-1*H*-pyrazol-5-yl)-5-(aryloxymethyl)-1,3,4-oxadiazole (**5a-j**) was out-

Table 1 Summary of crystallographic data and structure refinement details for 5c and 5e

	5c	5e
Empirical formula	$C_{29}H_{26}Cl_2N_4O_2$	$C_{29}H_{26}ClN_5O_4$
Formula weight	533.44	544.00
Temperature	273(2)	298(2)
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Triclinic
space group	*P*–1	*P*–1
Unit cell dimensions	*a*=9.2259(13) Å,	*a*=8.931(5) Å,
	α=94.166(3)	α=96.435(12)
	b=11.2525(16) Å,	*b*=11.302(7) Å,
	β=96.227(2)°	β=97.049(11)°
	c=13.817(2) Å,	*c*=14.140(8) Å,
	γ=110.292(3)°	γ=108.102(11)°
Volume	1328.1(3) A^3	1329.2(14) A^3
Z	2	2
Calculated density	1.334 Mg/m^3	1.359 Mg/m^3
Absorption coefficient	0.278 mm^{-1}	0.189 mm^{-1}
F(000)	556	568
Crystal size	0.10×0.10×0.10 mm	0.15×0.10×0.05 mm
θ range for data collection	1.49 to 27.59°	1.47 to 23.73°
Limiting indices	−10≤h≤11, −13≤k≤14, −17≤l≤17	−10≤h≤10, −10≤k≤12, −15≤l≤15
Reflections collected/unique	7878/5760 [*R*(int)=0.0365]	5835/3934 [*R*(int)=0.0216]
Completeness to θ	93.7%	97.4%
Absorption correction	none	Multi–scan
Max. and min. transmission	0.9727 and 0.9727	0.9906 and 0.9722
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5760/0/338	3934/1/356
Goodness-of-fit on F^2	0.931	1.030
Final *R* indices [$I>2\sigma(I)$]	R_1=0.0723, wR_2=0.1969	R_1=0.0744, wR_2=0.2196
R indices (all data)	R_1=0.1890, wR_2=0.2600	R_1=0.1189, wR_2=0.2666
Largest diff. peak and hole	0.612 and −0.271 e $Å^{-3}$	0.429 and −0.365 e $Å^{-3}$
CCDC No.	787253	787254

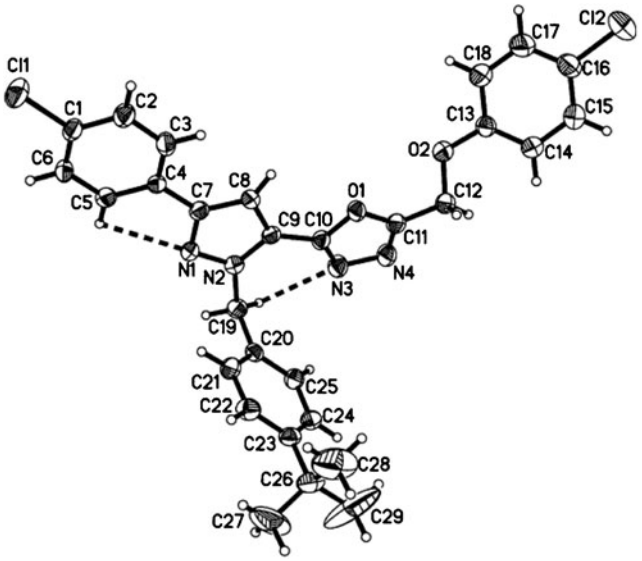

Fig. 2 The molecular structure of compound **5c**, with displacement ellipsoids drawn at the 30% probability level

lined in Fig. 1. The starting 1-arylmethyl-3-aryl-1*H*-pyrazole-5-carbohydrazide derivatives (**1**) can be easily prepared according to the procedure reported in our previous paper [27]. The reaction of **1** and 2-chloroacetyl chloride (**2**) in the presence of triethylamine in dichloromethane at room temperature afforded intermediate (**3**) that can be used to next reaction step without further purification. Then **3** reacted with phosphoryl trichloride to give 2-(1-aryl-3-(4-chlorophenyl)-1*H*-pyrazol-5-yl)-5-(chloromethyl)-1,3,4-oxadiazole (**4**) that can be purified by column chromatography on silica gel using PE/EtOAc (1:1) as an eluent. The reaction of **4** and substituted phenol in the presence of anhydrous potassium carbonate in dry acetonitrile at reflux temperature afforded compound (**5**) in 86–99%.

The proposed structures were confirmed by IR, ^{1}H NMR spectra, HRMS, and X-ray single crystal diffraction.

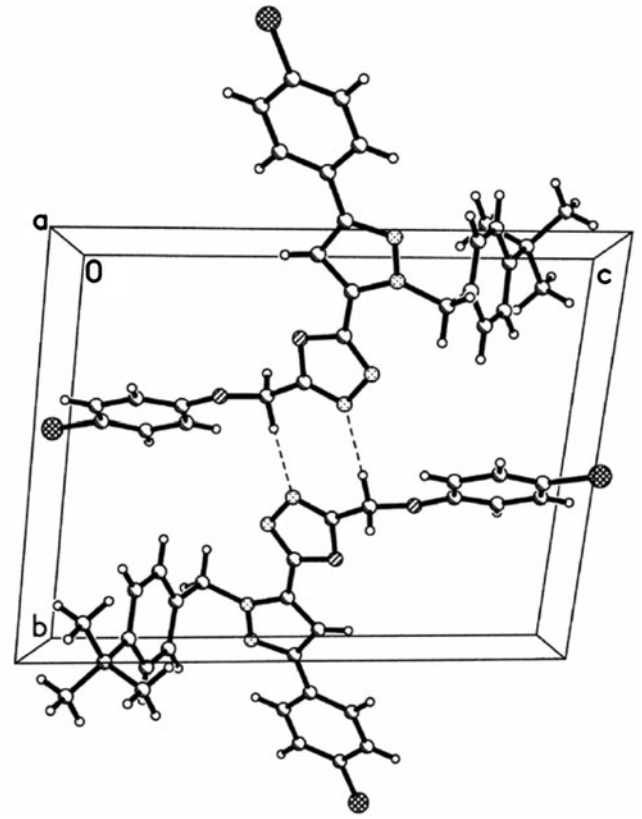

Fig. 3 The structure of centrosymmetric dimmer of **5c**, showing C–H···N intermolecular hydrogen bonds as dashed lines

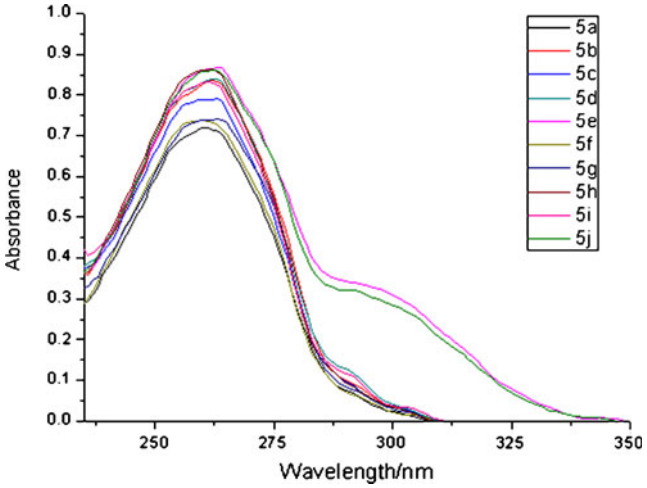

Fig. 4 UV–vis absorption spectra of **5a-5j** in dichloromethane (2×10^{-5} M)

X-ray crystallography analysis

The spatial structures of compounds **5c** and **5e** were determined by using X-ray diffraction analysis. A summary of crystallographic data collection parameters and refinement parameters for **5c** and **5e** are compiled in Table 1.

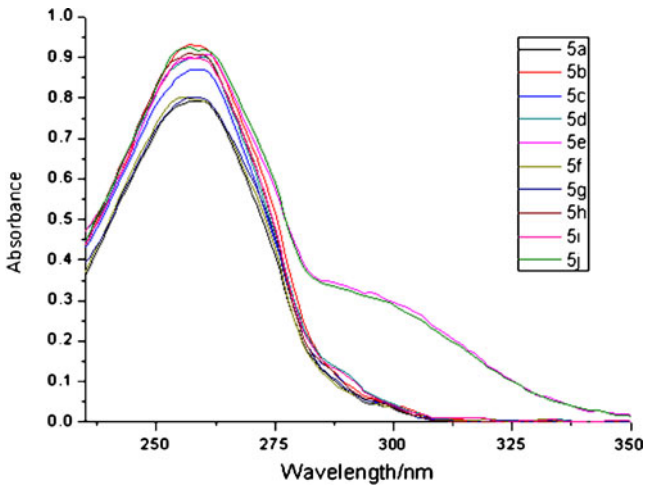

Fig. 5 UV–vis absorption spectra of **5a-5j** in acetonitrile (2×10^{-5} M)

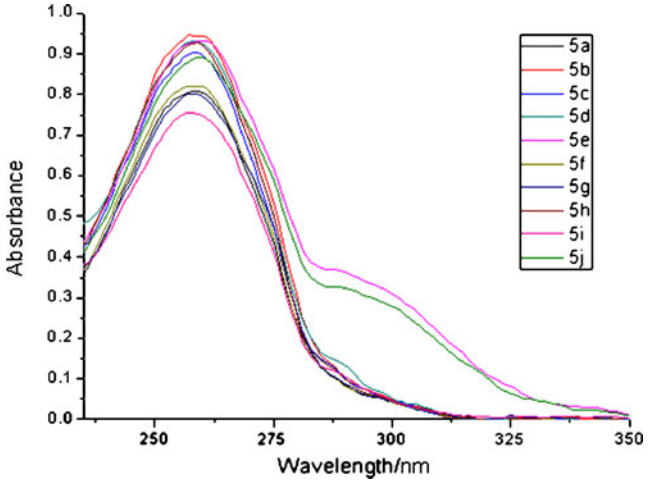

Fig. 6 UV–vis absorption spectra of **5a-5j** in ethanol solution (2×10^{-5} M)

The single crystal structure and atomic numbering chosen for **5c** are shown in Fig. 2. The dihedral angles between the pyrazole ring and the C4 phenyl or 1,3,4-oxadiazole ring are 7.9(3)° and 10.0(3)°, respectively. All the small dihedral angles above indicate that the pyrazole, C4 phenyl and oxadiazole rings in **5c** are nearly in the same plane and conjugated in which the bond lengths of C9–C10 and C4–C7 are 1.453(6) Å and 1.470(6) Å, respectively, and they have double-bond character. The bond length C9-C10 (1.453(6) Å) is similar to pyrazoly 1,3,4-oxadiazole derivatives (C9–C21 1.449 Å) we have reported [26]. The molecular conformation is stabilized by intramolecular C5–H5···N1 and C19–H19A···N3 hydrogen bonds (Fig. 2): C5–H5 0.94 Å, H5···N1 2.57 Å, C5···N1 2.875(7) Å and C5–H5···N1 100°; C19–H19A 0.97 Å, H19A···N3 2.50 Å, C19···N3 3.050(7) Å and C19–H19A···N3 116°. In the crystal structure, centrosymmetric dimers are formed by two intermolecular hydrogen bonds of the C12–H12B···N4 (C12–H12B 0.97 Å, H12B···N4 2.42 Å, C12···N4 3.377(7) Å and C12–H12B···N4 168°; Symmetry code: -x, 3-y, 1-z) resulting in a $R_2^2(8)$ descriptor on a unitary level (Fig. 3). The dimers are further connected to form a three-dimensional network by intermolecular C–H···π hydrogen bonds: C8–H8 0.93 Å, H8···Cg 2.89(4) Å, C8···Cg 3.805(6) Å, C8–H8···Cg 168(4)° and symmetry code: -x, 2-y, 1-z; C27–H27A 0.96 Å, H27A···Cg 2.96 Å, C27···Cg 3.880(11) Å, C8–H8···Cg 161° and symmetry code: -x, 2-y, 2-z (Cg is the centroid of the C20–C25 ring).

Absorption Spectra

The UV–vis absorption spectra of the compounds **5a-j** in dichloromethane, acetonitrile and ethanol at the concentration of 2×10^{-5} mol/L were given in Figs. 4, 5 and 6, respectively. The results were summarized in Table 2. These compounds displayed similar absorptions ranging from 256 to 263 nm that were attributed to π-π transition of conjugation system. Comparing with 5-aryl-2-(1-aryl-3-(4-chlorophenyl)-1*H*-pyrazol-5-yl)- 1,3,4-oxadiazole reported in previous paper [26], compounds **5a-j** have blue shift about 10 nm. It is easily understood that the aryloxy linked methylene in C5 cannot extend to the pi-conjugation system because they are blocked to π-system by methylene. It is also observed that the λ_{max} values of **5a-5j** changes with the polarity of solutions. Generally in different solvents, there is a consequence for the λ_{max} values of **5a-5e**: λ_{max} (DCM)>λ_{max} (CH_3CN)>λ_{max} (EtOH). However, for **5f-5j**, λ_{max} (DCM)>λ_{max} (EtOH)>λ_{max} (CH_3CN). In the same solvent, compounds **5a-5j** have the similar maximum absorption that means substituent R^1, R^2, R^3 and X has no significant impact to the absorption. The maximum molar extinction coefficients of **5a-5j** in dichloromethane, acetonitrile and ethanol are different, and although the difference is less, it can be observed that

Table 2 Maximum absorption wavelength (λ_{max}) and maximum molar extinction coefficients (ε_{max}) of 5a-j in dichloromethane, acetonitrile and ethanol

Compound	λ_{max} (nm)			ε ($mol^{-1}cm^{-1}L$)		
	DCM	CH_3CN	EtOH	DCM	CH_3CN	EtOH
5a	260	259	259	35950	39650	40300
5b	262	257	257	41800	46600	47300
5c	263	260	259	39600	43500	45250
5d	262	260	258	41950	45050	46600
5e	263	261	260	43450	45400	46650
5f	260	256	259	36950	40100	41000
5g	263	257	258	37000	40150	40150
5h	262	257	259	43150	45550	46450
5i	261	257	257	41650	45050	37750
5j	263	256	259	43050	46100	44550

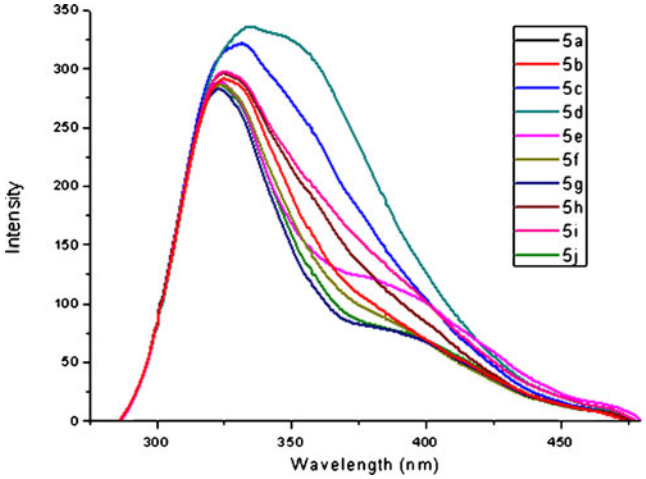

Fig. 7 Fluorescence spectra of the compounds **5a-5j** in hexane (10^{-7} M)

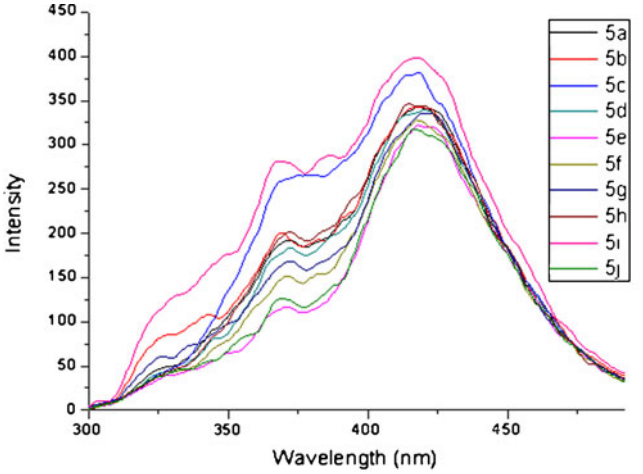

Fig. 9 Fluorescence spectra of the compounds **5a-5j** in acetonitrile (10^{-7} M)

the enhancement order is generally ε (DCM) <ε (CH_3CN) <ε (EtOH).

Fluorescence

The emission spectra of these compounds in hexane, dichloromethane and acetonitrile at the concentration of 10^{-7} mol/L were investigated as shown in Figs. 7, 8 and 9 respectively. Their excitation wavelengths were all fixed at 260 nm. It can be seen from Table 3 that the maximum emission wavelengths of **5a-5j** are different in three solvents. Taking **5a** as an example, its maximum emission wavelength is 308, 367 and 408 nm in hexane, dichloromethane and acetonitrile, respectively. The results indicate that the emission wavelengths red-shift with the increase of the solvent polarity. In addition, substituent groups in π-conjugation system influence maximal emission bands. For example, in hexane, the maximum emission wavelengths of **5c** and **5d** are red-shifted 9 nm and 25 nm comparing with **5 h** and **5i**. These differences might be attributed to substituted aryl groups in *N*-1 position. The maximum emission wavelengths of **5b**, **5e** and **5 g** in DCM have a little red shift comparing with other compounds. In CH_3CN, all the compounds have almost the same maximum emission wavelength. Interestingly, the effects of the solvents on the fluorescence intensities of **5a-5j** are obvious. Compounds **5a-5j** have similar fluorescence intensities in hexane and CH_3CN. However, they have significant differences in DCM. These results indicate that the molecules have strong coordination effects and the environment plays an important role in determining the fluorescence intensity of the compounds. The findings consist with the report on 1,3,4-oxadiazole derivatives [3].

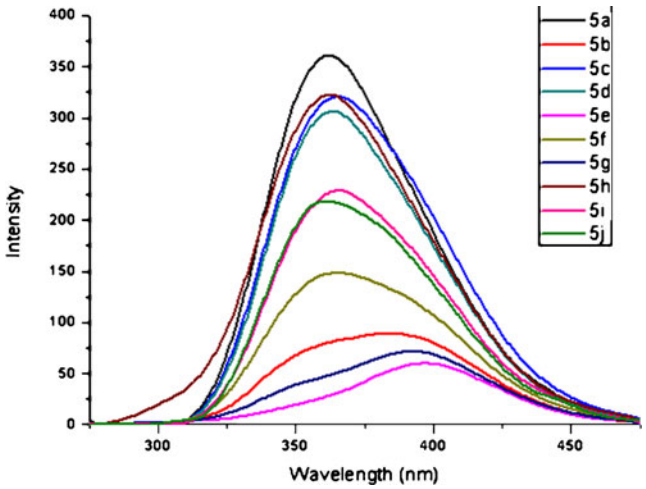

Fig. 8 Fluorescence spectra of the compounds **5a-5j** in dichloromethane (10^{-7} M)

Table 3 Maximum wavelength (nm) of excitement and emission of fluorescence of compounds 5a-j

Compound	λ_{ex} (nm)	λ_{em} (nm)		
		Hexane	DCM	CH_3CN
5a	260	308	367	408
5b	260	307	387	405
5c	260	316	364	406
5d	260	333	357	408
5e	260	308	393	406
5f	260	307	363	405
5g	260	306	392	409
5h	260	307	361	402
5i	260	308	361	405
5j	260	308	360	405

Conclusion

A series of novel 1,3,4-oxadiazole-based pyrazole derivatives have been synthesized and characterized by ^{1}H NMR, IR, HRMS spectra and X-ray analysis. Studies on the optical properties indicate that the polarity of solvent has no significant impact to the UV–vis absorption; however, the maximum emission wavelength of fluorescence changes significantly with the increase of solvent polarity. Contrasting previous report, present work provides small molecules with more interesting structure diversity and similar optical properties. Currently, investigations are underway to elucidate the bioactivity and localization of small molecule in cells and the results will be reported in due course.

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