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ORIGINAL PAPER

The Synthesis, X-ray Crystal Structure and Optical Properties of Novel 5-aryl-3-ferrocenyl-1-pyridazinyl-pyrazoline Derivatives

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Abstract A series of novel 5-aryl-3-ferrocenyl-1-pyridazinyl pyrazoline derivatives was synthesized by the reaction of ferrocenyl chalcone and 3-chloro-6-hydrazinylpyridazine in 10–65% yields. The compounds were characterized using IR, ^{1}H NMR, HRMS spectroscopic techniques and representative compounds **3c** and **4c** were assigned based on the X-ray crystallographic structure. The absorption and fluorescence characteristics of the compounds were investigated in chloroform, tetrahydrofuran and acetonitrile, respectively. The results showed that the absorption maxima of the compounds varied from 323 to 327 nm depending on the groups bonded to benzene and pyridazine ring. The maximum emission spectra of compounds in $CHCl_3$ were dependent on groups in pyridazine ring in which a strong donating-electron group such as propoxyl group on pyridazine ring in N-1 position of pyrazoline made the emission wavelength of **4a-4e** small red shifte than that of compounds **3a-3e** with chlorine group. The intensity of absorption and fluorescence was also correlated with substituent on aryl ring in C-5 position of pyrazoline. In addition, the absorption spectra of these compounds changed very little, but the fluorescence spectra had much change with increasing solvent polarity.

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Introduction

Pyrazolines are important nitrogen containing 5-membered heterocyclic compounds and have received considerable attention. It is worthy of note that pyrazoline derivatives have been reported to show a wide range of biological activity, including antimicrobial [1–3], antiamoebic [4, 5], antinociceptive [6], anticancer [7], antidepressant [8] and anti-inflammatory [9–13]. Of particular interest is the use of pyrazolines in electroluminescence fields, such as organic light-emitting diodes [14–16], due to their blue light emission with high fluorescence quantum yield [17, 18]. Attempts have been made to synthesize and elucidate the effects of substituent on the absorption and fluorescence properties of this class of compounds [19–29].

The design and synthesis of fluorescent small molecules with desirable properties is of considerable current interest in biology research. The advent of sensitive fluorescence detectors has enabled advances in biological imaging and the emergence of the field of single molecule spectroscopy [30, 31]. Recently, it is reported that pyrazoline derivatives can be used as DNA probe [32]. To date there have been relatively few studies on the cellular localization of agents in which small molecule linked to a fluorophore, such as coumarin [33, 34]. Thus, in continuation of our efforts in synthesizing various bioactive molecules [35–40], we attempt to synthesize novel small molecules with both potential bioactivity and fluorescent property. In our previous paper, we reported that the synthesis and optical

properties of 1,3,5-triaryl pyrazoline derivatives [41]. In light of few report concerning ferrocenyl pyrazoline [42, 43], herein, we would like to report the synthesis, X-ray crystal structure and optical properties of novel 5-aryl-3-ferrocenyl-1-pyridazinyl-pyrazoline derivatives.

Experimental

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 $CDCl_3$ 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). Fluorescent measurements were recorded on ISS K2 (ISS Inc) Time-resolved Fluorescence Spectrometer.

General Procedure for the Synthesis of Compound 3 and 4

To a stirred solution of substituted chalcone (**1**) (1.0 mmol) in *n*-propanol (15 mL) was added 3-chloro-6-hydrazinyl-pyridazine (**2**) (1.5 mmol) and NaOH (2.5 mmol) and the reaction mixture was refluxed at 97 °C for 4–6 h. The progress of the reaction was monitored by TLC. After completion, the reaction mixture was cooled to room temperature and the precipitate was filtered, washed with water and ethanol, and then dried to give the mixture of products **3** and **4**. After chromatography on silica gel (petroleum ether/ethyl acetate/dichloromethane = 5/1/2) compounds **3a-e** and **4a-e** were obtained in 28–55% and 10–28% yields, respectively (Fig. 1).

The Spectroscopic Data of Compounds 3 and 4

*3-Chloro-6-(5-phenyl-3-ferrocenyl-4,5-dihydro-1H-pyrazol-1-yl)pyridazine (**3a**)* Orange red solid, yield 52%; mp 187–189 °C; IR (KBr, cm^{-1}): 2955.4, 2922.1, 2851.4, 1574.5, 1534.6, 1491.6, 1447.2, 1096.9, 836.8, 816.2; ^{1}HMNR ($CDCl_3$): δ 3.14 (dd, 1H, J=4.7, 17.2 Hz, 4-H_{trans}), 3.78 (dd, 1H, J=12.0, 17.2 Hz, 4-H_{cis}), 4.13 (s, 5H, ferrocene-H), 4.41 (s, 2H, ferrocene-H), 4.55 (s, 1H, ferrocene-H), 4.69 (s, 1H, ferrocene-H), 5.79 (dd, 1H, J=4.7, 12.0 Hz, 5-H of pyrazoline), 7.21 (d, 1H, J=9.4 Hz, pyridazine-H), 7.22–7.31 (m, 5H, Ar-H), 7.63 (d, 1H, J=9.4 Hz, pyridazine-H). HRMS: calcd for $[M+H]^+$ $C_{23}H_{20}ClFeN_4$: 443.0720; found: 443.0723.

*3-Chloro-6-(5-(2-chlorophenyl)-3-ferrocenyl-4,5-dihydro-1H-pyrazol-1-yl)pyridazine (**3b**)* Orange yellow solid, yield 28%; decomposed at 230 °C; IR (KBr, cm^{-1}): 2958.6, 2925.7, 2852.6, 1575.4, 1535.3, 1489.8, 1446.1, 1100.3, 1009.9, 835.7; ^{1}HMNR($CDCl_3$): δ 2.97 (dd, 1H, J=5.1, 17.2 Hz, 4-H_{trans}), 3.82 (dd, 1H, J=12.8, 17.2 Hz, 4-H_{cis}), 4.14 (s, 5H, ferrocene-H), 4.48 (s, 2H, ferrocene-H), 4.64 (s, 1H, ferrocene-H), 4.77 (s, 1H, ferrocene-H), 6.14 (dd, 1H, J= 5.1, 12.8 Hz, 5-H of pyrazoline), 7.03 (d, 1H, J=7.3 Hz, Ar-H), 7.13 (t, J=7.4 Hz, 1H, Ar-H), 7.18 (t, J=7.4, 1H, Ar-H), 7.24 (d, 1H, J=9.2 Hz, pyridazine-H), 7.42 (d, 1H, J=7.5 Hz, Ar-H), 7.64 (d, 1H, J=9.2 Hz, pyridazine-H). HRMS: calcd for $[M+H]^+$ $C_{23}H_{19}Cl_2FeN_4$: 477.0331; found: 477.0306.

*3-Chloro-6-(5-(2,4-dichlorophenyl)-3-ferrocenyl-4,5-dihydro-1H-pyrazol-1-yl)pyridazine (**3c**)* Orange yellow solid, yield 28%; mp 234–236 °C; IR (KBr, cm^{-1}): 1641.4, 1575.6, 1535.2, 1487.0, 1437.2, 1101.4, 832.7; ^{1}HMNR ($CDCl_3$): δ 2.99 (dd, 1H, J=5.2, 17.2 Hz, 4-H_{trans}), 3.85 (dd, 1H, J= 11.9, 17.2 Hz, 4-H_{cis}), 4.11 (s, 5H, ferrocene-H), 4.42 (s, 2H, ferrocene-H), 4.58 (s, 1H, ferrocene-H), 4.67 (s, 1H, ferrocene-H), 6.02 (dd, 1H, J=5.2, 11.9 Hz, 5-H of pyrazoline), 7.01 (d, 1H, J=8.4 Hz, Ar-H), 7.13 (dd, 1H, J=1.4, 8.4 Hz, Ar-H), 7.27 (d, 1H, J=9.2 Hz, pyridazine-

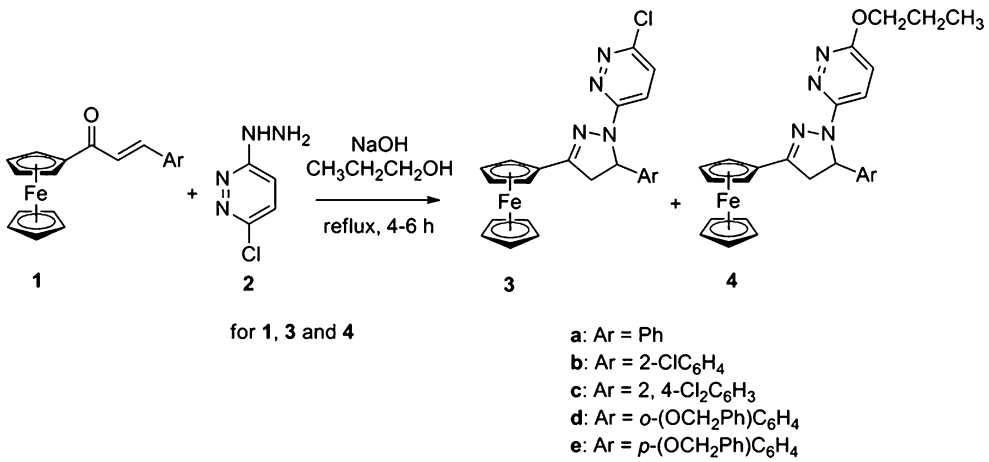

Fig. 1 Synthesis of 5-aryl-3-ferrocenyl-1-pyridazinyl-pyrazoline derivatives

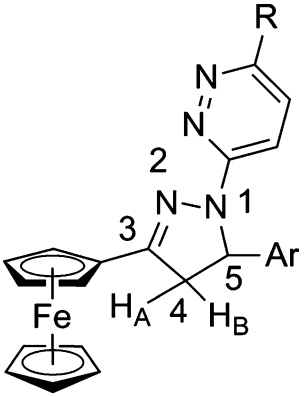

Fig. 2 Structure of compounds **3** and **4**

H), 7.44 (d, 1H, *J*=1.4 Hz, Ar-H), 7.66 (d, 1H, *J*=9.2 Hz, pyridazine-H). HRMS: calcd for $[M+H]^+$ $C_{23}H_{18}Cl_3FeN_4$: 510.9941; found: 510.9889.

*3-(5-(2-(Benzyloxy)phenyl)-3-ferrocenyl-4,5-dihydro-1H-pyrazol-1-yl)-6-chloropyridazine (***3d***)* Orange yellow solid, yield 31%; mp 207–208 °C; IR (KBr, cm^{-1}): 2921.5, 2852.8, 1582.9, 1535.9, 1492.5, 1454.3, 1248.3, 1105.9, 1014.2, 753.2; ^{1}HMNR ($CDCl_3$): δ 3.00 (dd, 1H, *J*=4.5, 17.2 Hz, 4-H_{trans}), 3.73 (dd, 1H, *J*=11.8, 17.2 Hz, 4-H_{cis}), 4.04 (s, 5H, ferrocene-H), 4.36 (s, 2H, ferrocene-H), 4.52 (s, 1H, ferrocene-H), 4.64 (s, 1H, ferrocene-H), 5.20 (s, 2H, OCH_2Ar), 6.16 (dd, 1H, *J*=4.5, 11.8 Hz, 5-H of pyrazoline), 6.84 (t, 1H, *J*=7.4 Hz, Ar-H), 6.99 (d, 2H, *J*=6.4 Hz, Ar-H), 7.18 (t, 1H, *J*=7.4 Hz, Ar-H), 7.22 (d, 1H, *J*=9.3 Hz, pyridazine-H), 7.34 (t, 1H, *J*=7.2 Hz, Ar-H), 7.42 (t, 2H, *J*=7.2 Hz, Ar-H), 7.52 (d, 2H, *J*=7.2 Hz, Ar-H), 7.65 (d, 1H, *J*=9.3 Hz, pyridazine-H). HRMS: calcd for $[M+H]^+$ $C_{30}H_{26}ClFeN_4O$: 549.1139; found: 549.1137.

*3-(5-(4-(Benzyloxy)phenyl)-3-ferrocenyl-4,5-dihydro-1H-pyrazol-1-yl)-6-chloropyridazine (***3e***)* Orange red solid, yield 55%; mp 160–161 °C; IR (KBr, cm^{-1}): 2922.6, 2852.3, 1610.1, 1580.6, 1512.2, 1450.3, 1242.3, 819.2, 730.3; ^{1}HMNR ($CDCl_3$): δ 3.12 (dd, 1H, *J*=4.8, 17.2 Hz, 4-H_{trans}), 3.75 (dd, 1H, *J*=11.8, 17.2 Hz, 4-H_{cis}), 4.14 (s, 5H, ferrocene-H), 4.41 (s, 2H, ferrocene-H), 4.56 (s, 1H,

Table 1 Summary of crystallographic data and structure refinement details for **3c** and **4c**

	3c	4c
Empirical formula	$C_{23}H_{17}Cl_3FeN_4$	$C_{26}H_{26}Cl_2FeN_4O$
Formula weight	511.61	537.26
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/n$	$P2_12_12_1$
Unit cell dimensions	a=10.753 (2) Å, α=90.00°	a=10.416(2) Å, α=90.00°
	b=11.099(2) Å, β=90.030(3)°	b=11.014(2) Å, β=90.00°
	c=17.826(3) Å, γ=90.00°	c=21.296(3) Å, γ=90.00°
Volume	2126.2(6) A^3	2443.1(7) A^3
Z	4	4
Calculated density	1.598 Mg/m^3	1.461 Mg/m^3
Absorption coefficient	1.106 mm^{-1}	0.863 mm^{-1}
F(000)	1,040	1,112
Crystal size	0.10×0.10×0.10 mm	0.15×0.10×0.10 mm
θ range for data collection	2.16 to 24.55°	2.08 to 23.30°
Limiting indices	−10≤h≤12, −12≤k≤12, −20≤l≤17	−11≤h≤11, −12≤k≤11, −13≤l≤23
Reflections collected/unique	9912/3540 [R(int) = 0.0369]	10441/3515 [R(int) = 0.0378]
Completeness to θ=25.05°	99.6%	99.7%
Absorption correction	Multi-scan	Multi-scan
Max. and min. transmission	0.8975 and 0.8975	0.8814 and 0.9186
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3540/0/280	3515/0/367
Goodness-of-fit on F^2	1.072	0.944
Final *R* indices [$I>2\sigma(I)$]	R_1=0.0426, wR_2=0.1145	R_1=0.0315, wR_2=0.0683
R indices (all data)	R_1=0.0692, wR_2=0.1385	R_1=0.0411, wR_2=0.0733
Largest diff. peak and hole	0.611 and −0.394 e. $Å^{-3}$	0.231 and −0.167 e. $Å^{-3}$
Bjvioet pairs	none	1492
Flack parameter	none	−0.019(18)

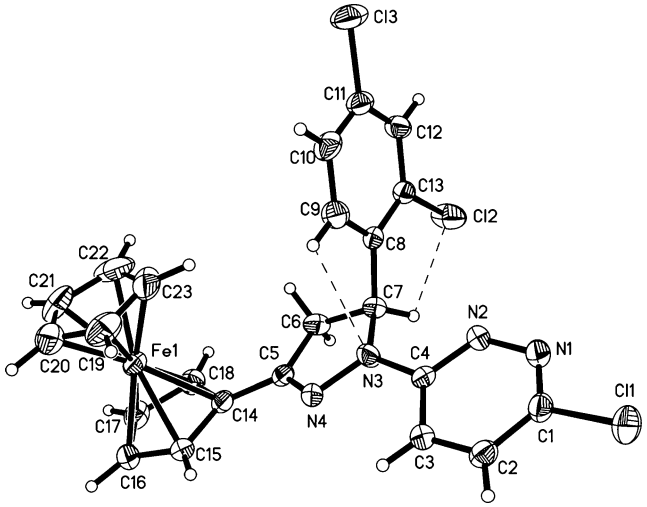

Fig. 3 Structure of compound **3c** with displacement ellipsoids drawn at the 30% probability level

ferrocene-H), 4.68 (s, 1H, ferrocene-H), 5.00 (s, 2H, OCH_2Ar), 5.74 (dd, 1H, J=4.8, 11.8 Hz, 5-H of pyrazoline), 6.91 (d, 2H, J=8.7 Hz, Ar-H), 7.20 (d, 1H, J=9.4 Hz, pyridazine-H), 7.23 (d, 2H, J=8.7 Hz, Ar-H), 7.27–7.39 (m, 5H, Ar-H), 7.60 (d, 1H, J=9.4 Hz, pyridazine-H). HRMS: calcd for $[M+H]^+$ $C_{30}H_{26}ClFeN_4O$: 549.1139; found: 549.1131.

*3-Chloro-6-(5-phenyl-3-ferrocenyl-4,5-dihydro-1H-pyrazol-1-yl)pyridazine (***4a***)* Orange red solid, yield 10%; mp 174–175 °C; IR (KBr, cm^{-1}): 2955.1, 2923.1, 2852.3, 1612.5, 1588.7, 1547.8, 1496.9, 1463.2, 1001.5; ^{1}HMNR ($CDCl_3$): δ 0.98 (t, 3H, J=7.4 Hz, CH_3), 1.73–1.78 (m, 2H, CH_2), 3.06 (dd, 1H, J=5.8, 17.0 Hz, 4-H_{trans}), 3.74 (dd, 1H, J=12.0, 17.0 Hz, 4-H_{cis}), 4.11 (s, 5H, ferrocene-H), 4.25–4.32 (m, 2H, OCH_2), 4.36 (s, 2H, ferrocene-H), 4.52 (s, 1H, ferrocene-H), 4.67(s, 1H, ferrocene-H), 5.76 (dd, 1H, J=5.8, 12.0 Hz, 5-H of pyrazoline), 6.85 (d, 1H, J=9.5 Hz, pyridazine-H), 7.19–7.34 (m, 5H, Ar-H), 7.70 (d, 1H, J=9.5 Hz, pyridazine-H). HRMS: calcd for $[M+H]^+$ $C_{26}H_{27}FeN_4O$: 467.1529; found: 467.1532.

*3-(5-(2-Chlorophenyl)-3-ferrocenyl-4,5-dihydro-1H-pyrazol-1-yl)-6-propoxypyridazine (***4b***)* Orange red solid, yield 22%; mp 208–209 °C; IR (KBr, cm^{-1}): 2963.1, 2930.7, 2876.4, 1608.6, 1547.6, 1460.4, 1281.4, 1106.8, 977.9; ^{1}HMNR ($CDCl_3$): δ 0.98 (t, 3H, J=7.4 Hz, CH_3), 1.72–1.80 (m, 2H, CH_2), 2.97 (dd, 1H, J=4.5, 17.1 Hz, 4-H_{trans}), 3.87 (dd, 1H, J=11.9, 17.1 Hz, 4-H_{cis}), 4.05 (s, 5H, ferrocene-H), 4.25–4.32 (m, 2H, OCH_2), 4.36 (s, 2H, ferrocene-H), 4.54 (s, 1H, ferrocene-H), 4.66 (s, 1H, ferrocene-H), 6.11 (dd, 1H, J=4.5, 11.9 Hz, 5-H of pyrazoline), 6.91 (d, 1H, J=9.3 Hz, pyridazine-H), 7.13–7.19 (m, 3H, Ar-H), 7.41 (d, 1H, J=7.3 Hz, Ar-H), 7.76 (d, 1H, J=9.3 Hz, pyridazine-H). HRMS: calcd for $[M+H]^+$ $C_{26}H_{26}ClFeN_4O$: 501.1139; found: 501.1119.

*3-(5-(2,4-Dichlorophenyl)-3-ferrocenyl-4,5-dihydro-1H-pyrazol-1-yl)-6-propoxypyridazine (***4c***)* Orange yellow solid, yield 26%; mp 155–157 °C; IR (KBr, cm^{-1}): 2952.4, 2922.9, 2878.0, 2851.4, 1603.7, 1588.4, 1551.7, 1452.7, 1283.7, 1106.2, 1003.9; ^{1}HMNR($CDCl_3$): δ 0.98 (t, 3H, J=7.3 Hz, CH_3), 1.74–1.78 (m, 2H, CH_2), 2.93 (dd, 1H, J=4.5, 16.8 Hz, 4-H_{trans}), 3.86 (dd, 1H, J=12.5, 16.8 Hz, 4-H_{cis}), 4.08 (s, 5H, ferrocene-H), 4.27–4.33 (m, 2H, OCH_2), 4.37 (s, 2H, ferrocene-H), 4.55 (s, 1H, ferrocene-H), 4.64 (s, 1H, ferrocene-H), 5.97 (dd, 1H, J=4.5, 12.5 Hz, 5-H of pyrazoline), 6.91 (d, 1H, J=9.1 Hz, pyridazine-H), 7.08 (d, 1H, J=8.2 Hz, Ar-H), 7.12 (d, 1H, J=8.2 Hz, Ar-H), 7.41 (s, 1H, Ar-H), 7.75 (d, 1H, J=9.1, pyridazine-H). HRMS: calcd for $[M+H]^+$ $C_{26}H_{25}Cl_2FeN_4O$: 535.0749; found: 535.0724.

*3-(5-(2-(Benzyloxy)phenyl)-3-ferrocenyl-4,5-dihydro-1H-pyrazol-1-yl)-6-propoxypyridazine (***4d***)* Orange yellow solid, yield 26%; mp 151–153 °C; IR (KBr, cm^{-1}): 2961.8, 2924.8, 2875.2, 1601.3, 1553.4, 1493.6, 1451.3, 1240.6, 1106.4; ^{1}HMNR ($CDCl_3$): δ 0.98 (t, 3H, J=7.1 Hz, CH_3), 1.74–1.79 (m, 2H, CH_2), 2.94 (dd, 1H, J=4.5, 16.2 Hz, 4-H_{trans}), 3.72 (dd, 1H, J=12.8, 16.2 Hz, 4-H_{cis}), 4.02 (s, 5H, ferrocene-H), 4.28–4.30 (m, 2H, OCH_2), 4.32 (s, 2H, ferrocene-H), 4.49 (s, 1H, ferrocene-H), 4.62 (s, 1H,

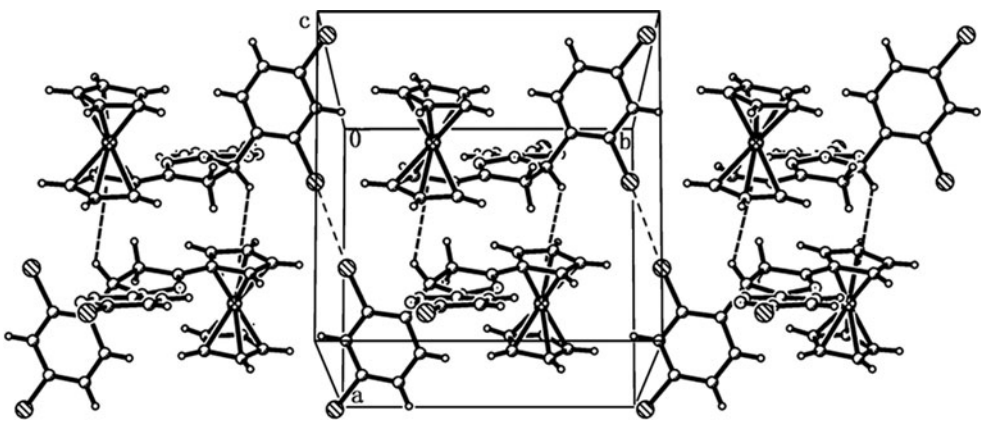

Fig. 4 Crystsl packing digram of **3c** along the *a*-axis

ferrocene-H),5.18 (s, 2H, OCH_2Ar), 6.10 (dd, 1H, J=4.5, 12.8 Hz, 5-H of pyrazoline), 6.84 (t, 1H, J=7.5 Hz, Ar-H), 6.88 (d, 1H, J=9.5 Hz, pyridazine-H), 6.97 (d, 1H, J= 7.8 Hz, Ar-H), 7.06 (d, 1H, J=6.5 Hz, Ar-H), 7.18 (t, 1H, J=7.2 Hz, Ar-H), 7.34 (t, 1H, J=7.0 Hz, Ar-H), 7.42 (t, 2H, J=7.0 Hz, Ar-H), 7.53 (d, 2H, J=7.0 Hz, Ar-H), 7.74 (d, 1H, J=9.5 Hz, pyridazine-H). HRMS: calcd for $[M+H]^+$ $C_{33}H_{33}FeN_4O_2$: 573.1947; found: 573.1920.

*3-(5-(4-(Benzyloxy)phenyl)-3-ferrocenyl-4,5-dihydro-1H-pyrazol-1-yl)-6-chloropyridazine (***4e***)* Orange yellow solid, yield 28%; mp 155–156 °C; IR (KBr, cm^{-1}): 2965.5, 2922.3, 2878.7, 2853.0, 1608.4, 1582.4, 1553.3, 1455.9, 1243.8, 1109.7; ^{1}HMNR ($CDCl_3$): δ 0.98 (t, 3H, J=7.4 Hz, CH_3), 1.72–1.81 (m, 2H, CH_2), 3.05 (dd, 1H, J=5.7, 17.1 Hz, 4-H_{trans}), 3.71 (dd, 1H, J=12.0, 17.1 Hz, 4-H_{cis}), 4.12 (s, 5H, ferrocene-H), 4.26–4.32 (m, 2H, OCH_2), 4.36 (s, 2H, ferrocene-H), 4.53 (s, 1H, ferrocene-H), 4.66 (s, 1H, ferrocene-H), 5.01 (s, 2H, OCH_2Ar), 5.72 (dd, 1H, J=5.7, 12.0 Hz, 5-H of pyrazoline), 6.84 (d, 1H, J=9.5 Hz, pyridazine-H), 6.91 (d, 2H, J=8.7 Hz, Ar-H), 7.27 (d, 2H, J=8.7 Hz, Ar-H), 7.29–7.40 (m, 5H, Ar-H), 7.68 (d, 1H, J= 9.5 Hz, pyridazine-H). HRMS: calcd for $[M+H]^+$ $C_{33}H_{33}FeN_4O_2$: 573.1947; found: 573.1954.

X-ray Crystallography

Suitable single crystals of **3c** and **4c** for X-ray structural analysis were obtained by slow evaporation of a solution of the solid in dichloromethane at room temperature for 7 days.

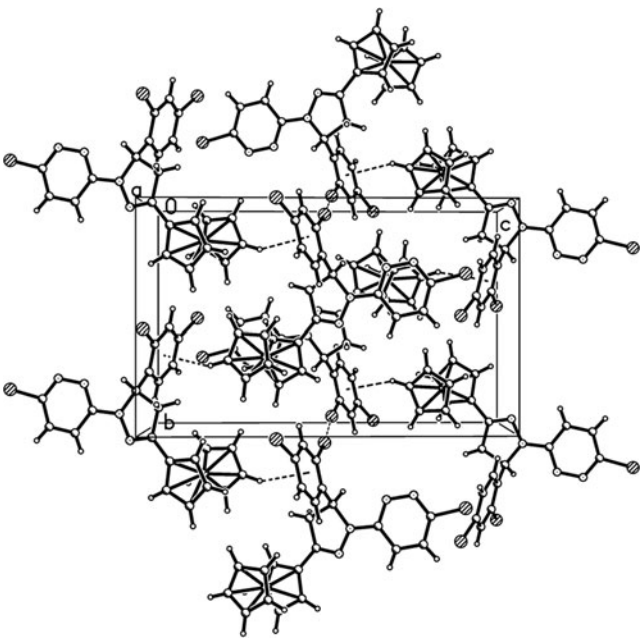

Fig. 5 Crystsl packing digram of **3c** along the *b*-axis

Table 2 Hydrogen-bonding geometry of compound **3c**

D—H···*A*[a]	*D*—H (Å)	H···*A* (Å)	*D*···*A* (Å)	*D*—H···*A* (°)
C7—H7···Cl2	0.98	2.55	3.017(4)	109
C9—H9···N3	0.93	2.61	2.921(5)	100
C7—H7···Cg3^{i}	0.98	2.93	3.699(5)	136
C21—H21···Cg4^{ii}	0.98	2.85	3.756(6)	154

[a] Symmetry code: (i) 2-x, -y, -z; (ii) 3/2-x, 1/2+y, 1/2-z. Cg3 and Cg4 are the centroids of the unsubstituted Cp ring and the benzene ring, respectively

The crystals with approximate dimensions of 0.10×0.10×0.10 mm for **3c** and 0.15×0.10×0.10 mm for **4c** were mounted on a Bruker Smart Apex II CCD equipped with a graphite monochromated MoKα radiation (λ=0.71073 Å) by using ϕ and ω scan modes and the data were collected at 293(2) K. The structures of the two crystals were 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=0.0426, wR2=0.1145 for **3c** and R1=0.0315, wR2=0.0683 for **4c**.

Results and Discussion

Synthesis of Compounds 3 and 4

The synthetic routes of the proposed compounds **3** and **4** are outlined in Fig. 1. Starting ferrocenyl chalcone **1** can be easily prepared by Claisen-Schmidt condensation between acetylferrocene and aromatic aldehyde in 86–92% yield by a mild, efficient, and solvent-free green

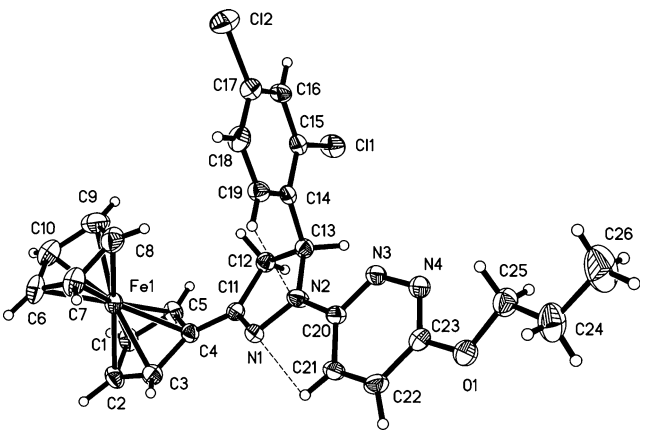

Fig. 6 The structure of compound **4c** with displacement ellipsoids drawn at the 30% probability level

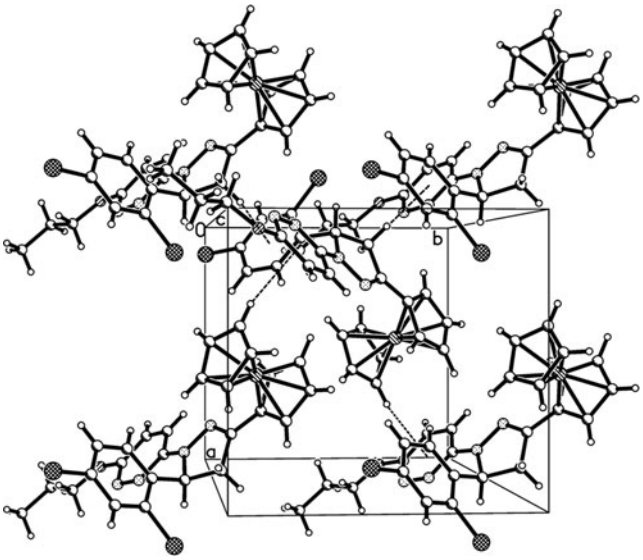

Fig. 7 Crystsl packing digram of **4c** along the *a*-axis

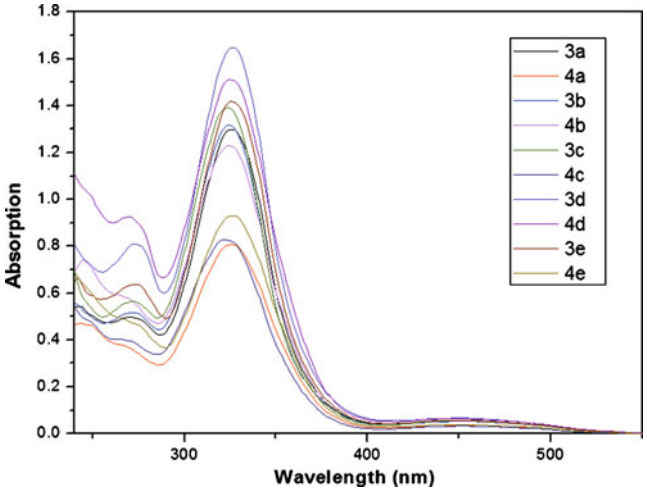

Fig. 8 The UV-Vis spectra of compounds **3a-e** and **4a-e** in chloroform (5×10^{-5} MolL^{-1})

procedure according to the literature [44]. These compounds can also be prepared by the reaction method in ethanol for 20 h and obtained in lower yields [45]. Thus, the solvent-free method is faster, easier and more environmentally friendly than that using an organic solvent. The pyrazoline derivatives **3a-e** and **4a-e** were obtained by the reaction of chalcone **1** with 3-chloro-6-hydrazinylpyridazine **2** in propanol at reflux in 28–55% and 10–28% yields, respectively. The formation of compound **4** should be due to the nucleophilic substitution reaction of compound **3** by propanol used as solvent. The structures of the products **3** and **4** were assigned by the analyses of their spectral data including ^{1}H NMR, IR and HRMS comparing with X-ray diffraction analysis.

Structure Characterization

The IR spectra of all the compounds **3a-e** showed ν (C=N) stretch at 1,574–1,582 cm^{-1} consisting with pyrazoline and pyridazine moiety, and compounds **4a-e**, ν (C=N) stretch appeared at 1,582–1,589 cm^{-1}. In the ^{1}H NMR spectra of pyrazoline moiety of compounds **3** and **4** that is shown in Fig. 2, protons H_A and H_B that are geminal protons at C4 carbon appeared in the region of 2.97–3.14 and 3.73–3.85 ppm as doublet of doublets for compounds **3**, and for compounds **4** that appeared in the region of 2.93–3.06 and 3.71–3.87 ppm. The CH proton at C5 also appeared as doublet of doublets in the region of 5.74–6.16 and 5.72–6.11 ppm due to vicinal coupling with two non–equivalent geminal protons of C4 carbon in compounds **3** and **4**, respectively. Two *ortho*-aromatic protons signals in chloropyridazine moiety appeared at the range of δ=7.20–7.27 and 7.60–7.66 ppm as doublet peaks (J=9.2–9.4 Hz) in compounds **3**, but for compounds **4** that appeared at the range of δ=6.84–6.91 and 7.68–7.76 ppm as doublet peaks (J=9.1–9.5 Hz). In the ^{1}H NMR spectra of ferrocene moiety of compounds **3** and **4**, four protons in mono-substituted Cp of Fc moiety appeared in the region of 4.32–

Table 3 Hydrogen-bonding geometry of compound **4c**

D—H···*A*[a]	*D*—H (Å)	H···*A* (Å)	*D*···*A* (Å)	*D*—H···*A* (°)
C19—H19···N2	0.93(3)	2.49(3)	2.861(5)	104(2)
C21—H21···N1	0.90(3)	2.56(3)	2.871(4)	101(2)
C6—H6···Cg1^{i}	0.90(4)	2.85(4)	3.639(5)	147(3)
C12—H12A···Cg2^{ii}	0.97(3)	2.90(3)	3.634(4)	134(2)

[a] Symmetry code: (i) 1-x, 1/2+y, 3/2-z; (ii) 2-x, 1/2+y, 3/2-z. Cg1 and Cg2 are the centroids of pyridazine and benzene ring, respectively

Table 4 The maximum wavelength of absorption and fluorescence spectra of compounds **3a-e** and **4a-e** in chloroform

Compound	λ_{max}^{abs} (nm)	ε_{max} (mol^{-1} cm^{-1})	λ_{max}^{ex} (nm)	λ_{max}^{em} (nm)	Stokes shift (nm)
3a	326	25984	298	410	112
4a	326	16146	301	410	109
3b	325	26318	332	381	49
4b	325	24614	331	383	52
3c	324	27816	300	399	99
4c	323	16536	303	406	103
3d	326	32980	298	407	109
4d	325	30202	300	410	110
3e	326	28336	301	398	97
4e	327	18620	300	408	108

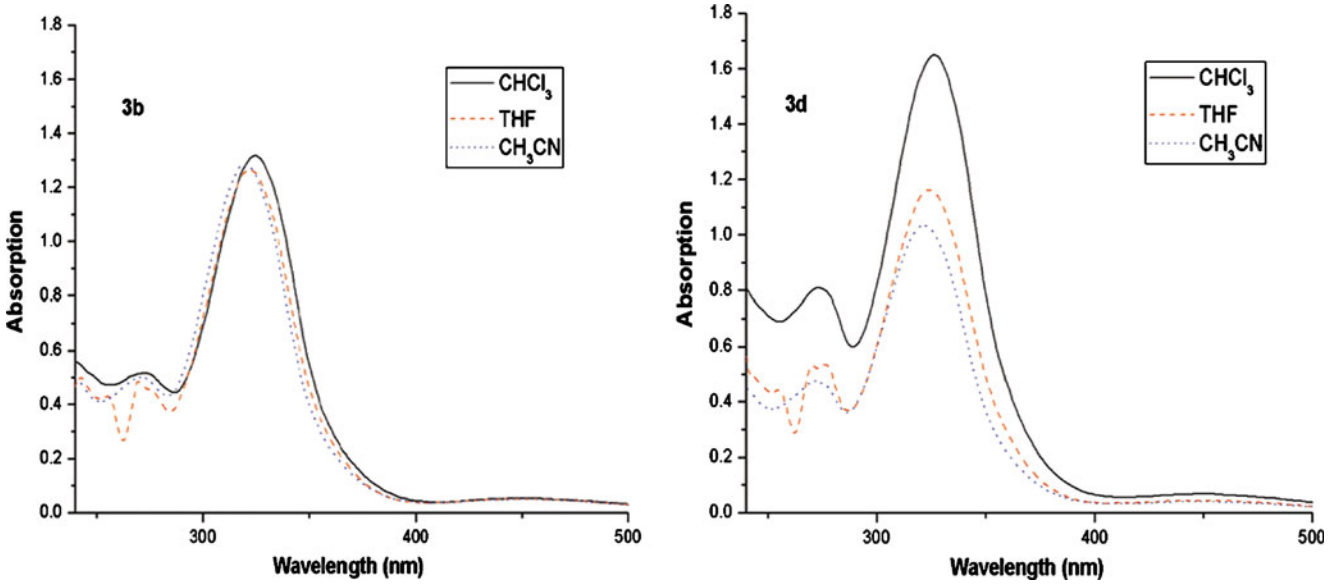

Fig. 9 The UV-Vis spectra of compounds **3b** and **3d** in chloroform, tetrahydrofuran and acetonitrile, respectively (5×10^{-5} MolL^{-1})

4.48, 4.49–4.64 and 4.62–4.77 ppm as three singlet peaks and five protons of unsubstituted Cp appeared in the region of 4.02–4.14 ppm as singlet peak. HRMS showed that found [M+H]-ion peak accorded with calculated value. Moreover, typically, the structures of compound **3c** and **4c** were confirmed by X-ray diffraction analysis.

X-ray Crystallography Analysis

The spatial structures of compounds **3c** and **4c** were determined by using X-ray diffraction analysis. A summary of crystallographic data collection parameters and refinement parameters for **3c** and **4c** are compiled in Table 1.

The single crystal structure and atomic numbering chosen for **3c** are shown in Fig. 3. The structure of compound **3c** is crystallized in monoclinic space group $P2_1/n$. The molecular conformation is stabilized by intramolecular C7—H7· · ·Cl2 and C9—H9· · ·N3 hydrogen bonds. In the ferrocenyl moiety, the Cp rings are perfectly planar but deviate slightly from being parallel being 1.6 (3)°, twisted from the eclipsed conformation by 1.8°–4.0°. In the asymmetry unit, the pyrazoline ring is almost planar, the maximum deviation from the least squares plane being 0.057(4) Å for atom C6. The pyrazoline ring makes dihedral angles with benzene and pyridazine ring of 81.6 (2)° and 17.2(2)°, respectively, while the dihedral angle between pyrazoline and substituted Cp ring is 6.0(2)°. In the crystal structure, the molecules are linked into zig-zag chains along the *b* axis by alternate intermolecular C—H···π (C7···Cg3 3.699(5) Å; Cg3 is the centroid of the unsubstituted Cp ring) interactions and Cl···Cl (3.243 Å) bonds (Fig. 4). The chains are further connected by C—H···π (C21···Cg4 3.756(6); Cg4 is the centroid of the benzene ring) interactions (Fig. 5 and Table 2).

The single crystal structure and atomic numbering chosen for **4c** are shown in Fig. 6. The structure of compound **4c** is crystallized in orthorhombic space group $P2_12_12_1$. The absolute structure parameter is −0.019(18) indicates the correct structure at position C13 is assigned as *S* configuration [46]. The torsion angle, 3.0°, defined as C

Table 5 The maximum wavelength of absorption of compounds **3b** and **3d** in $CHCl_3$, THF and CH_3CN, respectively (5×10^{-5} MolL^{-1})

Solvent	$CHCl_3$	THF	CH_3CN
λ_{max} ^{3b} (nm)	325	321	320
λ_{max} ^{3d} (nm)	326	323	321

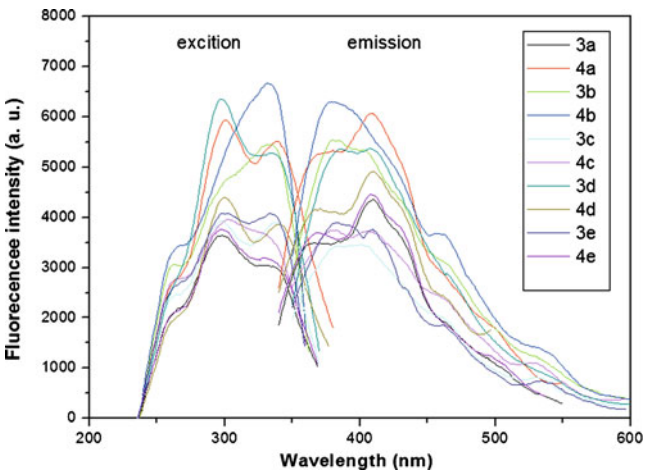

Fig. 10 The fluorescence excitation and emission spectra of compounds **3a-e** and **4a-e** in chloroform (1×10^{-5} MolL^{-1})

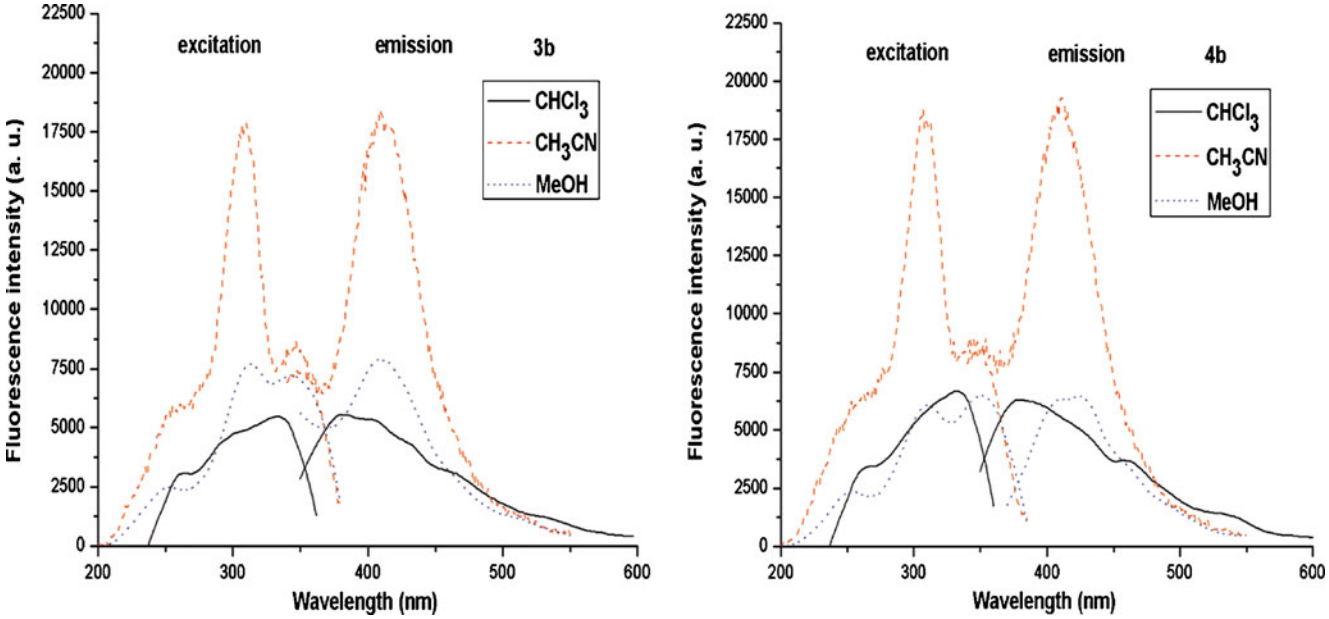

Fig. 11 The fluorescence excitation and emission spectra of compounds **3b** and **4b** in chloroform, acetonitrile and methanol, respectively (1×10^{-5} MolL^{-1})

(4)—C(centroid)—C(centroid)—C(8) indicates almost the eclipsed orientation of two cyclopentadienyl (Cp) rings. The pyrazoline ring adopts a flat-envelope conformation with atom C12 (at the flat) deviating by 0.166 Å from the mean plane of the remaining atoms. The dihedral angles of pyridazine and benzene rings with the substituted Cp ring are 21.3(2)° and 79.5(2)°. Regarding the crystal structure of **4c**, there are two significant intramolecular C19—H19···N2 and C21—H21···N1 hydrogen bonds forming corresponding pseudo five-membered rings. Instead of the intramolecular hydrogen bonds, the crystal packing is mainly stabilized by *van der Waals* interactions and further assigned into layers *via* C—H···π intermolecular hydrogen bonds (C6 ··· Cg1 3.639(5)Å; C12 ··· Cg2 3.634(4)Å; Cg1 and Cg2 are the centroids of pyridazine and benzene ring, respectively), wherein each molecule is connected to four neighboring molecules (Fig. 7 and Table 3).

Absorption Spectra

The UV–vis spectra of the compounds **3a-e** and **4a-e** measured in chloroform solutions are shown in Fig. 8 and the optical characteristics are summarized in Table 4. Compounds **3a-e** and **4a-e** display similar absorptions ranging from 323 to 327 nm that are attributed to π-π* transition of conjugate system. However, the absorption intensity is different depending on substitution, for example, molar absorptivity (ε_{max}) changes from 25,984 to 32,980 mol^{-1}cm^{-1} for compounds **3a-e** and from 16,146 to 30,202 for compounds **4a-e**. Interestingly, it can be found that absorption intensity of compounds **3a-e** is stronger than that of compounds **4a-e**. In addition, the absorption bands between 420 and 500 nm, although the absorbance are very less, are attributed to metal to ligand charge transfer (MLCT) transition from Fe to either the non-bonding or the antibonding orbitals of the cyclopentadienyl rings [47, 48].

Possible effect of the solvent on the absorption behavior was investigated. The absorption spectra of representative compounds **3b** and **3d** in different solvents with the concentration of 5×10^{-5} MolL^{-1} are presented in Fig. 9 and Table 5. The hypsochromic shifts take place as increasing solvent polarity and it consists with our previous observation [41]. Moreover, the effect of solvent on the absorption intensity is more obvious for compound **3d** with benzyloxy group in benzene moiety.

Fluorescence

The excitation and emission spectra of compounds **3a-e** and **4a-e** in chloroform are shown in Fig. 10 and Table 4. It can be found that their intensity of fluorescence differed from

Table 6 The maximum wavelength of excitation and emission spectra of compounds **3b** and **4b** in chloroform, acetonitrile and methanol, respectively (1×10^{-5} MolL^{-1})

Solvent	$CHCl_3$	CH_3CN	CH_3OH
λ_{ex} **3b** (nm)	332	310	313
λ_{em} **3b** (nm)	381	410	411
λ_{ex} **4b** (nm)	331	307	350
λ_{em} **4b** (nm)	378	409	424

each other. Interestingly, the fluorescence emission is almost the mirror image of excitation spectrum for all of compounds.

The effects of solvent on the fluorescence characteristics of the compounds **3b** and **4b** were studied, and it can be found that the emission wavelength of the compounds was red-shifted with the increase of solvent polarity (Fig. 11 and Table 6).

Conclusion

A series of novel 5-aryl-3-ferrocyl-1-pyridazinyl pyrazoline derivatives was synthesized and characterized. The study on absorption and fluorescence characteristics of the compounds in chloroform, tetrahydrofuran and acetonitrile showed that the absorption maxima of the compounds varied from 323 to 327 nm depending on the group bonded to benzene and pyridazine ring. The intensity of absorption and fluorescence was also correlated with substituent on aryl ring in C-5 position of pyrazoline. In addition, the absorption spectra of these compounds changed very little, but the fluorescence spectra had much change with increasing solvent polarity.

Supplementary Materials

CCDC 762264 and 762265 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: +44 1223 336033.

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