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The synthesis, X-ray crystal structure and optical properties of novel 1-ferrocenyl-2-(3-phenyl-1*H*-1,2,4-triazol-5-ylthio)ethanone derivatives

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ABSTRACT

A series of novel 1-ferrocenyl-2-(3-phenyl-1*H*-1,2,4-triazol-5-ylthio)ethanone derivatives was synthesized by the reaction of 3-substituted-1*H*-1,2,4-triazole-5-thiol and chloroacetyl ferrocene in the presence of sodium hydride and potassium iodide at reflux. The structures of the new compounds were determined by IR and ^{1}H NMR spectroscopy and HRMS. The structure of compound **5c** was established by X-ray crystallography. UV–vis absorption and fluorescence spectra were recorded in ethanol and dichloromethane. The results showed that compounds **5a–g** display similar absorptions ranging from 300 to 500 nm and maximal emission bands are about 566 nm. The intensity of fluorescence and maximal emission bands are dependent on the groups bonded to triazole rings.

1. Introduction

1,2,4-Triazoles and their condensed derivatives constitute an important class of organic compounds with bioactivities such as analgesic–anti-inflammatory [1], antimicrobial [2,3], anticancer [4,5], antifungal [6], antigenotoxic [7], herbicidal [8], and insecticidal activities [9]. In addition, 1,2,4-triazole and, in particular, its derivatives are very interesting as ligands [10–12], which have the potential possibility of coordinating with metal ions to fulfill the coordination requirements of clusters. In recent years, 1,2,4-triazole and its derivatives have been paid great attention in the field of electroluminescence [13–17]. The design and synthesis of fluorescent chemosensors 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 [18].

Incorporation of a ferrocene fragment into a molecule of an organic compound often obtained unexpected biological activity, which is rationalized as being due to their different membrane permeation properties and anomalous metabolism. The integration of one or more ferrocene units into a heterocyclic ring molecule has been recognized as an attractive way to endow a novel molecule functionally [19–21]. In the electroluminescence research, ferrocene derivatives have also attracted much attention with respect to their high degree of chemical and thermal stabilities, electrochemical, electronic, and magnetic properties [22–26].

To date there have been relatively few studies on the cellular localization of agents in which a small molecule is linked to a fluorophore, such as coumarin [27,28]. Thus, in continuation of our efforts in synthesizing various bioactive molecules [29–32], we would like to synthesize novel small molecules with both potential bioactivity and fluorescent property. We report, herein, the synthesis, X-ray crystal structure and optical properties of novel 1-ferrocenyl-2-(3-phenyl-1*H*-1,2,4-triazol-5-ylthio)ethanone.

2. Materials and methods

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 $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. Melting points were determined on an XD-4 digital micromelting point apparatus. IR spectra were recorded with an IR spectrophotometer VERTEX 70 FT-IR (Bruker Optics). HRMS spectra were recorded on a Q-

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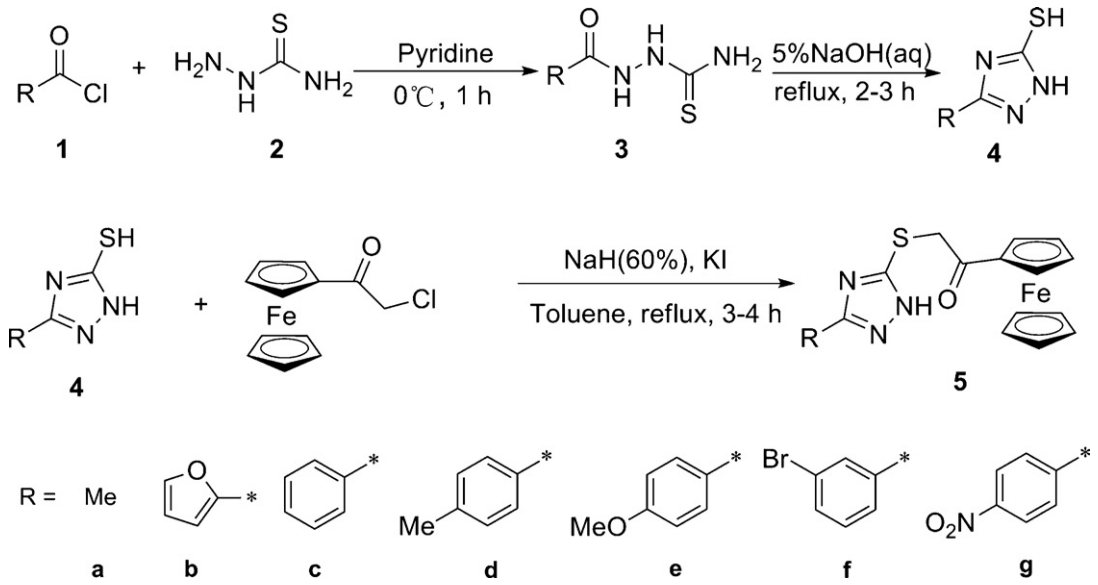

Fig. 1. Synthesis of 1-ferrocenyl-2-(3-substituted-1*H*-1,2,4-triazol-5-ylthio)ethanone.

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-substituted-1H-1,2,4-triazole-5-thiol (**4a–g**)*

As shown in Fig. 1, compound **4** was synthesized according to the literature method [33,34]. 2-(Acetyl)hydrazinecarbothioamide or 2-(4-aroyl)hydrazinecarbothioamide (**3**) (10 mmol) and 5% sodium hydroxide aqueous (40 mL) were added to a three-necked round-bottomed flask. The mixture was refluxed for 2–3 h, and then it was cooled to room temperature. The mixture was acidified with acetic acid to about pH 5. After filtration, the solid was washed with cold water and dried to afford 3-substituted-1*H*-1,2,4-triazole-5-thiol (**4**) in 77–90% yield.

*2.3. General procedure for the synthesis of 1-ferrocenyl-2-(3-substituted-1H-1,2,4-triazol-5-ylthio)ethanone (**5a–f**)*

To a round-bottomed flask 3-substituted-1*H*-1,2,4-triazole-5-thiol (**4**) (1.25 mmol), sodium hydride (60% dispersion in mineral oil, 120 mg, 2.85 mmol), potassium iodide (190 mg, 1.14 mmol), chloroacetyl ferrocene (300 mg, 1.14 mmol) and toluene (30 mL) were added and the mixture was refluxed for 3–4 h. The reaction mixture was cooled and poured into cold water (25 mL). The mixture was extracted with ethyl acetate (3× 30 mL), and then the combined extraction was dried over anhydrous magnesium sulfate. After filtration, the solvent was removed under reduced pressure in a rotary evaporator. The crude residue was purified by column chromatography on silica gel to afford compound **5a–f** in 57–87% yield.

*2.4. Data of compounds **5***

*2.4.1. 1-Ferrocenyl-2-(3-methyl-1H-1,2,4-triazol-5-ylthio)ethanone (**5a**)*

Dark brown solid, yield 85%; mp 124–128 °C; IR (KBr, cm^{-1}): 3228, 1664; ^1H NMR ($CDCl_3$, 400 MHz), δ: 11.22 (s, 1H, NH triazole), 4.85 (s, 2H, Cp), 4.60 (s, 2H, Cp), 4.26 (s, 7H, Cp and $COCH_2S$), 2.45 (s, 3H, CH_3); HRESIMS calcd for $[M+H]^+$ $C_{15}H_{16}FeN_3OS$: 342.0363, found: 342.0355.

*2.4.2. 1-Ferrocenyl-2-(3-(furan-2-yl)-1H-1,2,4-triazol-5-ylthio)ethanone (**5b**)*

Orange solid, yield 73%; mp 139–142 °C; IR (KBr, cm^{-1}): 3245, 1662; ^1H NMR($CDCl_3$, 400 MHz), δ: 11.73 (s, 1H, NH triazole), 7.52 (s, 1H, furan), 7.01 (d, J = 3.3 Hz, 1H, furan), 6.51 (t, J = 1.4 Hz, 1H, furan), 4.87 (t, J = 1.7 Hz, 2H, Cp), 4.64 (d, J = 1.7 Hz, 2H, Cp), 4.28 (s, 7H, Cp and $COCH_2S$); HRESIMS calcd for $[M+H]^+$ $C_{18}H_{16}FeN_3O_2S$: 394.0313, found: 394.0303.

*2.4.3. 1-Ferrocenyl-2-(3-phenyl-1H-1,2,4-triazol-5-ylthio)ethanone (**5c**)*

Orange solid, yield 57%; mp 156–159 °C; IR (KBr, cm^{-1}): 3226, 1666; ^1H NMR ($CDCl_3$, 400 MHz), δ: 11.84 (s, 1H, NH triazole), 8.04 (s, 2H, Ar), 7.42 (s, 3H, Ar), 4.88 (s, 2H, Cp), 4.65 (s, 2H, Cp), 4.27 (s, 7H, Cp and $COCH_2S$); HRESIMS calcd for $[M+H]^+$ $C_{20}H_{18}FeN_3OS$: 404.0520, found: 404.0513.

*2.4.4. 1-Ferrocenyl-2-(3-p-tolyl-1H-1,2,4-triazol-5-ylthio)ethanone (**5d**)*

Brown solid, yield 73%; mp 178–182 °C; IR (KBr, cm^{-1}): 3163, 1656; ^1H NMR ($CDCl_3$, 400 MHz), δ: 11.99 (s, 1H, NH triazole), 7.91 (d, J = 7.8 Hz, 2H, Ar), 7.23 (d, J = 7.8 Hz, 2H, Ar), 4.87 (s, 2H, Cp), 4.62 (s, 2H, Cp), 4.30 (s, 2H, $COCH_2S$), 4.26 (s, 5H, Cp), 2.38 (s, 3H, CH_3); HRESIMS calcd for $[M+H]^+$ $C_{21}H_{20}FeN_3OS$: 418.0677, found: 418.0643.

*2.4.5. 1-Ferrocenyl-2-(3-(4-methoxyphenyl)-1H-1,2,4-triazol-5-ylthio)ethanone (**5e**)*

Red brown solid, yield 87%; mp 175–178 °C; IR (KBr, cm^{-1}): 3184, 1653; ^1H NMR($CDCl_3$, 400 MHz), 11.85 (s, 1H, NH triazole), δ: 7.95 (d, J = 6.0 Hz, 2H, Ar), 6.95 (d, J = 7.1 Hz, 2H, Ar), 4.87 (s, 2H, Cp), 4.63 (s, 2H, Cp), 4.29 (s, 2H, $COCH_2S$), 4.26 (s, 5H, Cp), 3.84 (s, 3H, CH_3); HRESIMS calcd for $[M+H]^+$ $C_{21}H_{20}FeN_3O_2S$: 434.0626, found: 434.0613.

*2.4.6. 1-Ferrocenyl-2-(3-(3-bromophenyl)-1H-1,2,4-triazol-5-ylthio)ethanone (**5f**)*

Yellow solid, yield 80%; mp 154–156 °C; IR (KBr, cm^{-1}): 3247, 1665; ^1H NMR ($CDCl_3$, 400 MHz), δ: 12.12 (s, 1H, NH triazole), 8.25 (s, 1H, Ar), 8.00 (d, J = 6.1 Hz, 1H, Ar), 7.52 (d, J = 7.4 Hz, 1H, Ar), 7.30 (t, J = 6.9 Hz, 1H, Ar), 4.88 (s, 2H, Cp), 4.68 (s, 2H, Cp), 4.27 (s, 5H, Cp), 4.22 (s, 2H, $COCH_2S$); HRESIMS calcd for $[M+H]^+$ $C_{20}H_{17}BrFeN_3OS$: 481.9625, found: 481.9611.

*2.4.7. 1-Ferrocenyl-2-(3-(4-nitrophenyl)-1H-1,2,4-triazol-5-ylthio)ethanone (**5g**)*

A 100 mL, three-necked, round-bottomed flask was fitted with a magnetic stir bar. Under nitrogen, the flask is charged with 3-(4-nitrophenyl)-1*H*-1,2,4-triazole-5-thiol (4 g) (279 mg, 1.25 mmol), sodium hydride (60% dispersion in mineral oil, 120 mg, 2.85 mmol), potassium iodide (190 mg, 1.14 mmol), chloroacetyl ferrocene (300 mg, 1.14 mmol), toluene (30 mL) and DMF (6 mL). The mixture was stirred and refluxed for 2 h. The reaction mixture was cooled to room temperature, and poured into water (25 mL). The mixture was extracted with ethyl acetate (3× 30 mL), and then the combined extraction was dried over anhydrous magnesium sulfate. After filtration, the solvent was removed under reduced pressure in a rotary evaporator. The crude residue was purified by column chromatography (silica gel; 1:2 petroleum ether—ethyl acetate) to afford brown solid (121 mg), yield 24%; mp 189–192 °C; IR (KBr, cm^{-1}): 3348, 3099, 3086, 1651; ^1H NMR ($CDCl_3$, 400 MHz), δ: 12.29 (s, 1H, NH triazole), 8.28 (s, 4H, Ar), 4.88 (s, 2H, Cp), 4.71 (s, 2H, Cp), 4.28 (s, 5H, Cp), 4.19 (s, 2H, $COCH_2S$); HRESIMS calcd for $[M+H]^+$ $C_{20}H_{17}FeN_4O_3S$: 449.0371, found: 449.0360.

2.5. X-ray crystallography

Suitable single crystals of **5c** for X-ray structural analysis were obtained by slow evaporation of a solution of the solid in acetone. The diffraction data for structure was collected with a Bruker SMART CCD diffractometer using a graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at 298(2) K. The structure was 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 nonhydrogen 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 $U_{iso}(H) = 1.5\,U_{eq}(C)$. 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 $U_{iso}(H) = 1.2U_{eq}(C)$.

3. Result and discussion

3.1. Synthesis

The synthetic approach for the preparation of 1-ferrocenyl-2-(3-substituted-1*H*-1,2,4-triazol-5-ylthio)ethanone derivatives is shown in Fig. 1. Firstly, the acyl thiosemicarbazide **3** was obtained by the reaction of acetyl chloride or aroyl chloride **1** and thiosemicarbazide **2**, which are readily available, in the presence of pyridine at 0 °C [34]. Compound **3** was cyclized with 5% aqueous sodium hydroxide to afford 3-substituted-1*H*-1,2,4-triazole-5-thiol 4 in good yield after work-up. Finally compound **4** reacted with chloroacetyl ferrocene in toluene in the presence of sodium hydride and potassium iodide at reflux for 3–4 h to furnish 1-ferrocenyl-2-(3-substituted-1*H*-1,2,4-triazol-5-ylthio)ethanone **5** in 24–87% yield.

3.2. Structure characterization

The structures of the products **5** were determined by the analyses of their spectral data including IR, ^1H NMR and HRMS. The IR spectra of all the compounds **5a–g** showed ν(C=O) stretch at 1651–1666 cm^{-1} consisting with carbonyl. In the ^1H NMR spectra, the signal of a proton in triazole moiety appeared at the range of δ 11.22–12.29 ppm and it was downfield as increase of electron-withdrawing in the benzene moiety. Four protons in monosubstituted Cp of Fc moiety peaks appeared around 4.87 and 4.65 ppm as singlet that maybe results from resolving power of instrument in present conditions except **5b** for which a triplet and a doublet peaks were observed as normal monosubstituted Cp ring. Five protons of unsubstituted Cp appeared around 4.27 ppm as singlet peak. Two methylene protons appeared around 4.20–4.30 ppm as singlet peak. It is interesting that the signal of methylene protons was upfield when benzene moiety possesses electron-withdrawing substituent, whereas it was downfield in the case of electron-donating substituent, comparing the signal of unsubstituted Cp.

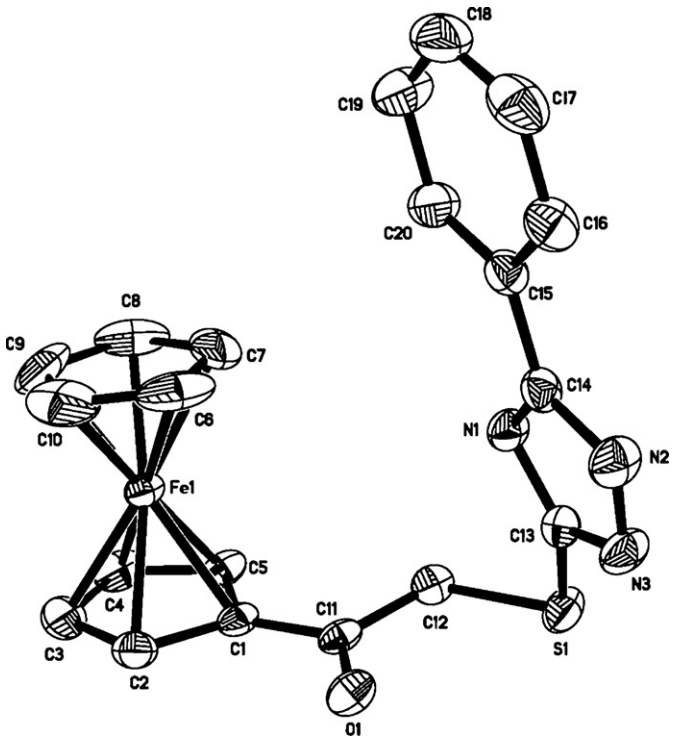

Fig. 2. The molecular structure of compound **5c**, with displacement ellipsoids drawn at the 50% probability level and H atoms omitted.

3.3. X-ray crystallography

The spatial structure of compound **5c** was determined by using X-ray diffraction analysis. Crystals suitable for X-ray diffraction were obtained by slow evaporation of a solution of the solid in acetone at room temperature for 7 days. The molecular view of **5c** is shown in Fig. 2. A summary of crystallographic data collection parameters and refinement parameters for **5c** are compiled in Table 1.

Fig. 2 shows that compound **5c** contains a phenyl ring bonded to the triazole ring which links a ferrocenyl group by a flexible S–C–C=O chain. In the ferrocenyl moiety, the cyclopentadienyl (Cp) rings are perfectly planar but deviate slightly from being parallel, that is, the angle between the planes is 2.9(4)°, and two Cp rings twist from the eclipsed conformation by 27.23–28.50°. The angle Cg1–Fe1–Cg2 is 176.52(13)°. Cg1 and Cg2 is the centroid of unsubstituted Cp ring and substituted Cp ring, respectively. The distances Cg1–Fe and Cg2–Fe are 1.647(3) and 1.642(2) Å. The C–C bond lengths and C–C–C angles in the cyclopentadienyl rings show electronic overlap of the p-system-induced variations. The triazole ring makes dihedral angles of 3.6(3)° and 77.8(3)° with the bonded phenyl ring and the substituted Cp ring, respectively. In the crystal, molecules are connected *via* pairs of intermolecular N3–H1...O1 hydrogen bonds into inversion dimers and further assembled into (0 0 1) layers *via* stacking interactions between the phenyl ring and the triazole ring [interplanar distance = 3.642(3) Å] (Table 2). Furthermore, the crystal is consolidated by another intermolecular

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

	5c
Empirical formula	$C_{20}H_{17}FeN_3OS$
Formula weight	403.28
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	*P*-1
Unit cell dimensions	$a = 9.755(4)$ Å, $\alpha = 104.142(6)^\circ$ $b = 10.347(4)$ Å, $\beta = 101.256(6)^\circ$ $c = 10.744(4)$ Å, $\gamma = 116.811(6)^\circ$
Volume	878.2(6) A^3
Z	2
Calculated density	1.525 Mg/m^3
Absorption coefficient	0.992 mm^{-1}
F(0 0 0)	416
Crystal size	0.21 mm × 0.18 mm × 0.16 mm
θ range for data collection	2.09–25.05°
Limiting indices	$-11 \le h \le 8$, $-11 \le k \le 12$, $-12 \le l \le 11$
Reflections collected/unique	4482/3085 [R(int) = 0.0354]
Completeness to $\theta = 25.05^\circ$	98.8%
Absorption correction	None
Max. and min. transmission	0.8575 and 0.8188
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3085/0/235
Goodness-of-fit on F^2	1.050
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0533$, $wR_2 = 0.1372$
R indices (all data)	$R_1 = 0.0691$, $wR_2 = 0.1497$
Largest diff. peak and hole	0.826 and −0.668e $Å^{-3}$

C4–H4...N2 hydrogen bonds and a significant C–H...π interaction between the phenyl ring hydrogen (C18–H18) and Cg1. The S1/C12/C11/O1/C1 fragment is almost planar as revealed by the corresponding S1–C12–C11–O1 torsion of 1.7(5)° and S1–C12–C11–C1 torsion of −177.7(3)°. The dihedral angles of the S1/C12/C11/O1/C1 plane with the triazole ring and the substituted Cp ring are 83.1(2)° and 6.5(2)°, respectively.

Table 2
Hydrogen bond geometry (Å,°).

D–H...A[a]	D–H	H...A	D...A	D–H...A
N3–H1...O1[i]	0.86	2.11	2.935(5)	159
C4–H4...N2[ii]	0.98	2.45	3.408(6)	166
C18–H18...Cg1[iii]	0.93	2.86	3.777(7)	167

D and A are the hydrogen bond donor and acceptor, respectively.
[a] Symmetry code: (i) $1-x, 1-y, -z$; (ii) $1+x, 1+y, 1+z$; (iii) $1-x, -y, 1-z$.

3.4. Absorption spectral characteristics of the compounds ***5a–g***

The UV–vis spectrum of the compounds **5a–g** in ethanol and dichloromethane are shown in Figs. 3 and 4, respectively, and the optical characteristics are summarized in Table 3. The results show that **5a–g** display similar absorptions ranging from 300 to 500 nm and the absorption maximum are about 340 and 460–470 nm (Table 3).

The absorptions in the range of 260–280 nm in ethanol are attributed to the π–π* transitions arising probably from 3-aryl-1,2,4-triazole moiety, whereas the longer wavelength region absorptions between 310 and 380 nm are attributed to the π–π* transitions of the cyclopentadienyl rings. The absorption bands between 420 and 500 nm 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 [35,36].

The data indicated that, when electron-withdrawing substituent, such as a nitro group, is located on the phenyl ring at position 3, the absorption peaks assigned to π–π* transitions of the cyclopentadienyl rings of **5g** are at shorter wavelengths (306 and 305 nm) than those of other compounds in ethanol or dichloromethane, respectively. But the absorption intensity of **5g** is stronger than that of other compounds. By contrast, the electron-donating substituent located on the phenyl ring at position 3 could not obviously affect the absorption spectra of **5**.

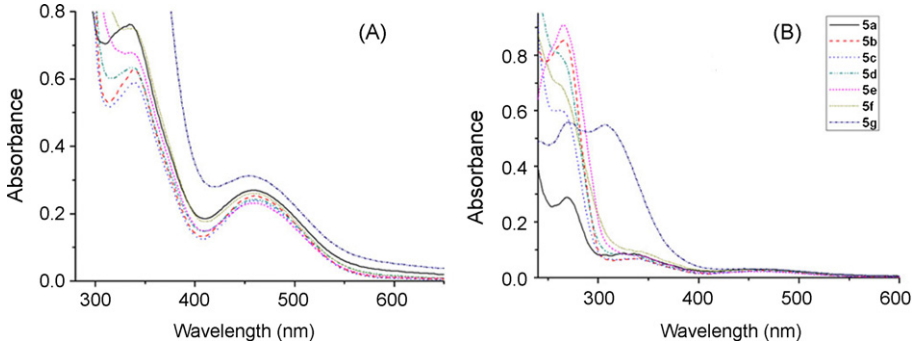

Fig. 3. UV–vis absorption spectra of compounds **5a–g** taken in ethanol at 4×10^{-4} M (A) and 4×10^{-5} M (B), respectively.

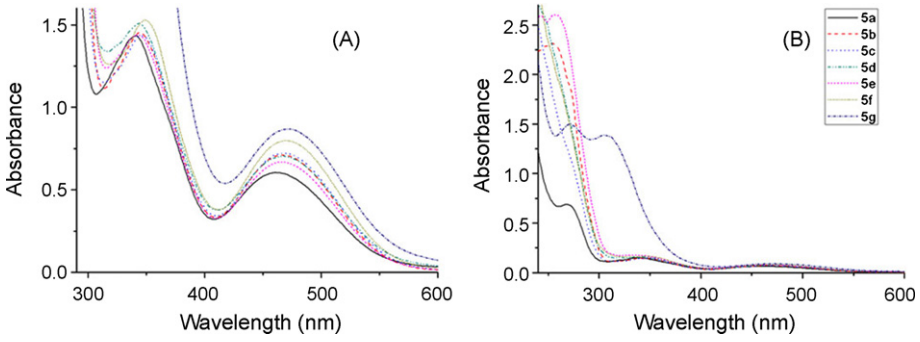

Fig. 4. UV–vis absorption spectra of compounds **5a–g** taken in dichloromethane at 10^{-3} M (A) and 10^{-4} M (B), respectively.

Table 3
The optical characteristics of compounds **5a–g**.

Compounds **5a–g**	λ_{max} (nm)					ε_{max} ($L\,mol^{-1}\,cm^{-1}$)				
	EtOH			CH_2Cl_2		EtOH			CH_2Cl_2	
5a	460	335	269	460	341	638	1687	7275	605	1435
5b	460	341	266	468	344	616	1484	21563	710	1452
5c	460	340	266	469	348	589	1450	14256	723	1430
5d	460	339	270	468	344	600	1510	16259	702	1506
5e	460	339	268	464	341	580	1586	22937	664	1415
5f	460	349	262	471	349	633	1710	15697	796	1517
5g	454	306	271	471	305	749	13413	14199	862	13019

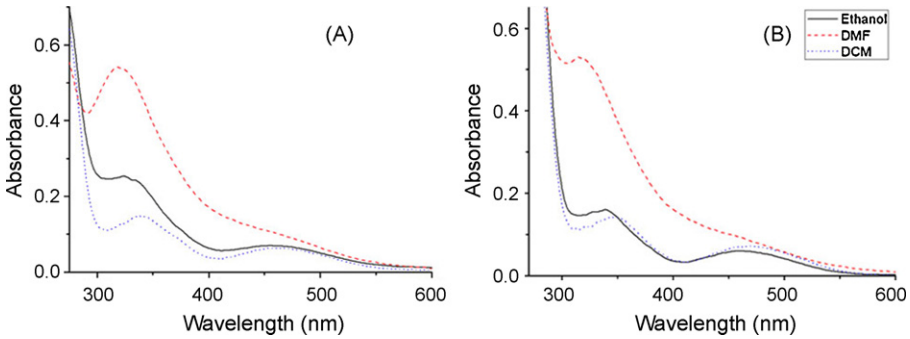

Fig. 5. UV-vis absorption spectra of compounds **5a** (A) and **5c** (B) taken at 10^{-4} M taken in ethanol, DMF and DCM, respectively.

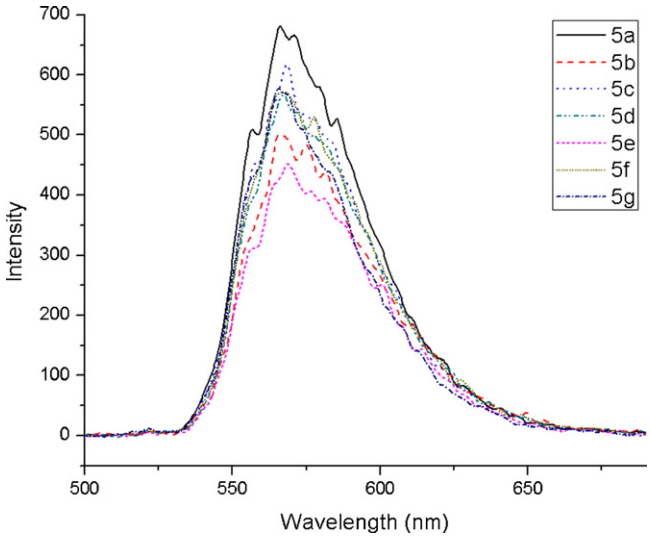

Fig. 6. Emission spectra of **5a–g** in ethanol at 10^{-6} M and at 265, 260, 263, 263, 261, 264 and 261 nm excitation wavelengths, respectively.

Possible influence of the solvent on the absorption behavior is investigated. Weak solvatochromism is observed in the absorption bands for all compounds as shown in Table 3. The hypsochromic shifts take place when the solvent is changed from dichloromethane to ethanol. Furthermore, the absorption spectra of **5a** and **5c**, as examples, in three different solvents, EtOH, CH_2Cl_2 and DMF, at a concentration of 10^{-4} M are shown in Fig. 5. It is noticed that there is obvious difference in maximum absorption wavelength and hypsochromic shifts is observed as polarity increasing of solvents.

Table 4
Data of fluorescence spectra of compounds **5a–g** at 10^{-6} M in ethanol.

Compounds **5a–g**	λ_{ex} (nm)	λ_{em} (nm)	Stoke's shift (nm)
5a	265	566	301
5b	260	566	306
5c	263	568	305
5d	263	567	304
5e	261	568	307
5f	264	566	302
5g	261	566	305

3.5. *Fluorescence spectral characteristics*

The maximum excitation wavelengths of **5a–g** were 265, 260, 263, 263, 261, 264 and 261 nm respectively, and the emission spectra were taken at the maximum excitation wavelengths in ethanol at 10^{-6} M as shown in Fig. 6. It can be found that the emission spectra with maximum emission 566–568 nm for compounds **5a–g** are almost identical except difference in intensity (Table 4).

4. Conclusion

A series of novel ferrocene-containing 1,2,4-triazole derivatives was synthesized by the reaction of 3-substituted-1*H*-1,2,4-triazole-5-thiol with chloroacetyl ferrocene in the presence of sodium hydride and potassium iodide. The structures of compounds obtained were determined by IR, ^{1}H NMR and HRMS spectra, typically, the spatial structure of compound **5c** was determined by using X-ray diffraction analysis. Absorption and fluorescence spectral characteristics of the compounds were investigated in ethanol and dichloromethane by UV–vis absorption and emission spectra. The absorption spectra and fluorescence characteristics were correlated with substituent on triazole rings.

Supplementary materials

CCDC 749530 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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