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### Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

# Synthesis, crystal structure and redox properties of dihydropyrazole-bridged ferrocene-based derivatives

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#### HIGHLIGHTS

- ► Two dihydropyrazole-bridged ferrocenyl-substituted derivatives were synthesized in high yields.
- Ordered two-dimensional structure was promoted by weak hydrogen-bonding interactions and  $\pi$ - $\pi$  stacking interactions between neighboring molecules.
- DFT calculation results explain the electron transfer mechanism of typical compound.

#### ARTICLE INFO

Article history: Received 11 February 2012 Received in revised form 8 May 2012 Accepted 8 May 2012 Available online 16 May 2012

Keywords: Ferrocene (Fc) Dihydropyrazole (Pz) Crystal structure Cyclic voltammetry DFT

#### 1. Introduction

A B S T R A C T

Dihydropyrazole-bridged ferrocene-based derivatives were prepared by corresponding chalcones with hydrazine hydrate, then acylation with 3-(ethoxycarbonyl)propionyl chloride directly in high yields and purity. All of these compounds were characterized by MS, IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR and elemental analysis. The relationship between the structure and redox properties was investigated based on the results of single crystal X-ray structure determinations and cyclic voltammetry. The mechanism of the electron transfer for representative compound **4b** was verified by density functional theory (DFT) calculations. © 2012 Elsevier B.V. All rights reserved.

Recently, great interest has been generated in the synthesis and study of heterocyclic derivatives containing one or more ferrocenes, since these derivatives have potential applications as new functional materials in several areas [1–5]. It is well known that pyrazole derivatives have been arousing lots of interest for the construction of new heterocyclic compounds in which dihydropyrazole (Pz) composes the core structure of various compounds [6–11]. As a stable and readily oxidizable organometallic complex, ferrocene has been widely employed in multifunctional systems [12], which have exhibited potential utilizations in electrochemical sensors [13,14], molecular recognition [15,16] and highly efficient burning rate catalysts [17].

Combining the considerations above, we designed a simple and general approach to synthesis dihydropyrazole-bridged ferrocenyl-

substituted derivatives in high yields. The relationship between the structure and redox properties was investigated based on the results of single crystal X-ray structure determinations, electrochemical investigations and theoretical calculations (DFT). The mechanism of the electron transfer for typical compound **4b** was studied during the redox process [18].

#### 2. Experimental

#### 2.1. General

All experiments were carried out under an atmosphere of dry nitrogen. All solvents employed were dried by routine procedures. Melting points are uncorrected. NMR spectra were obtained on a Bruker AV600 spectrometer at ambient temperature in CDCl<sub>3</sub>. Infrared spectra were measured on a Spectrum 2000 FTIR spectrometer in KBr pellets and reported in cm<sup>-1</sup>. Electrospray ionization mass spectrometry (ESI-MS) was performed using an X7 ICP-MS instrument. 1-Aryl-3-ferrocenyl-2-propen-1-on (**2**) was prepared according to the previously reported methods [17,19].



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X-ray structural measurements were made using a Rigaku RAX-IS-IV CCD diffractometer with graphite-monochromated Mo K $\alpha$ radiation ( $\lambda$  = 0.071073 nm) at 293(2) K. All diffraction data were collected by scanning in a certain mode and refined in Lp factor. The structures were solved by the direct method and refined by the full-matrix least-squares method on  $F^2$  using the SHELX-97 program suite [20].

Cyclic voltammetry (CV) was performed with a CHI620C electrochemical workstation in a conventional three-electrode electrochemical cell using glassy carbon as the working electrode, platinum electrode as counter electrode, and Ag/AgCl (3.0 M KCl) as reference electrode at room temperature. The bare glassy carbon electrode was polished successively with 0.3 and 0.05  $\mu$ m  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> slurry on emery paper and rinsed with doubly distilled water. Acetonitrile containing [*n*-Bu<sub>4</sub>N] PF<sub>6</sub> (*c* = 0.10 M) was applied as a supporting electrolyte. Before each electrochemical measurement, the experimental solution in the cell was purged with highly purified nitrogen gas for at least 10 min to remove dissolved oxygen and then a nitrogen atmosphere was kept over the solution during measurements.

Theoretical calculations were performed at the DFT level using the B3LYP functional [21–23]. Geometry optimization of the singlet ground state was calculated using the 6–31G(d,p) basis set for H C N O atoms and the ECP Lanl2dz basis set for the Fe atom [24–26]. Vibrational frequency calculations were performed at the same level of theory to verify the nature of the stationary points. The DFT calculations were carried out with the Gaussian 03 program package [27].

## 2.2. Synthesis of the 5-aryl-1-(3-(ethoxycarbonyl)propionyl)-3-ferrocenyl-4,5-dihydro-1H-pyrazole derivatives

To a stirred solution of 3-(4-bromophenyl)-1-ferrocenyl-2-propen-1-on or 1,3-diferrocenyl-2-propen-1-on (2a or 2b, 2.4 mmol) in ethanol (10 mL), 98% hydrazine hydrate (100.0 mmol) was added at room temperature. After addition the reaction mixture was further stirred at 80 °C for 0.5 h. The solvent and excess hydrazine hydrate was evaporated under reduced pressure to give an orange viscous substance. The unstable compounds **3a** and **3b** were not purified but directly used for the following reaction. The orange viscous solid was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 mL), and a solution of 2.8 mmol 3-(ethoxycarbonyl)propionyl chloride of CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was added dropwise at room temperature. After addition, the mixture was further stirred for 10 min. The solution was poured into water (100 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub>  $(3 \times 10 \text{ mL})$ . Combined organic phases were dried with magnesium sulfate and evaporated. The product was purified by column chromatography.

#### 2.2.1. Synthesis of 5-(4-bromophenyl)-1-(3-

#### (ethoxycarbonyl)propionyl)-3-ferrocenyl-4,5-dihydro-1H-pyrazole (**4a**)

Elution of the chromatogram with 25% ethyl acetate in petroleum ether afforded 4a as a brown solid, 1.06 g (82.2%); m.p. 110–112 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.48 (2H, d, J = 7.7 Hz, Ph—H), 7.13 (2H, d, J = 7.6 Hz, Ph—H), 5.49 (1H, H<sub>x</sub>, dd, J<sub>XB</sub> = 11.2 Hz, J<sub>XA</sub> = 4.8 Hz, Pz—H), 4.67 (1H, s, Cp—H), 4.57 (1H, s, Cp-H), 4.42 (2H, s, Cp-H), 4.14 (5H, m, Cp-H), 3.65 (1H, H<sub>B</sub>, dd, J<sub>BA</sub> = 17.1 Hz, J<sub>BX</sub> = 11.2 Hz, Pz—H), 3.09 (2H, m,CH<sub>2</sub>), 2.94 (1H, H<sub>A</sub>, dd, J<sub>AB</sub> = 17.2 Hz, J<sub>AX</sub> = 4.8 Hz, Pz-H), 2.68 (2H, m, CH<sub>2</sub>), 2.63 (2H, m, CH<sub>2</sub>), 1.26 (3H, t, CH<sub>3</sub>). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  173.12 (C=0), 169.14 (C=0), 156.08 (Pz-C), 141.04 (Ph-C), 132.06 (Ph-C), 127.16 (Ph-C), 121.47 (Ph-C), 75.01 (Cp-C), 70.58 (Cp--C), 70.48 (Cp--C), 69.43 (Cp--C), 67.74 (Cp--C), 67.31 (Cp--C), 60.57 (Pz-C), 58.97 (-CH2-), 43.41 (Pz-C), 29.06 (-CH2-), 28.83 (-CH<sub>2</sub>-), 14.20 (-CH<sub>3</sub>), IR (KBr) v, cm<sup>-1</sup>: 2980, 1732, 1656, 1497, 1440, 1375, 1211, 1161, 820. MS (ESI) *m*/*z*: 537.16, [M + 1]<sup>+</sup> calcd. 537.23. Analysis (%): C, 55.72; H, 4.78; N, 5.41 (C<sub>25</sub>H<sub>25</sub>BrFeN<sub>2</sub>O<sub>3</sub> requires C, 55.89; H, 4.69; N, 5.21).

#### 2.2.2. Synthesis of 1-(3-(ethoxycarbonyl)propionyl)-3,5-diferrocenyl-4,5-dihydro-1H-pyrazole (**4b**)

Elution of the chromatogram with 25% ethyl acetate in petroleum ether afforded **4b** as a brown solid, 1.10 g (80.9%); m.p. 157–158 °C. <sup>1</sup>H NMR (600 MHz,CDCl<sub>3</sub>):  $\delta$  5.44 (1H, H<sub>x</sub>, dd, J<sub>XB</sub> = 11.2 Hz, J<sub>XA</sub> = 2.8 Hz, Pz—H), 4.68 (2H, d, Cp—H), 4.50 (1H, s, Cp-H), 4.44 (2H, s, Cp-H), 4.23 (5H, s, Cp-H), 4.18 (5H, m, Cp-H), 4.15 (2H, m, Cp-H), 4.05 (1H,s, Cp-H), 3.56 (1H, H<sub>B</sub>, dd,  $J_{BA} = 17.1 \text{ Hz}, J_{BX} = 11.2 \text{ Hz}, \text{ Pz-H}$ ), 3.32 (1H, H<sub>A</sub>, dd,  $J_{AB} = 17.2 \text{ Hz}$ , J<sub>AX</sub> = 2.8 Hz, Pz–H), 2.99 (2H, m,CH<sub>2</sub>), 2.68 (2H, m, CH<sub>2</sub>), 1.66 (2H, s, CH<sub>2</sub>), 1.26 (3H, t, CH<sub>3</sub>). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$ 173.24 (C=O), 168.99 (C=O), 155.95 (Pz-C), 87.69 (Cp-C), 75.58 (Cp-C), 70.39 (Cp-C), 69.50 (Cp-C), 68.68 (Cp-C), 68.20 (Cp-C), 67.56 (Cp-C), 65.22 (Cp-C), 60.44 (Pz-C), 54.99 (-CH<sub>2</sub>-), 40.93 (Pz-C), 29.22 (-CH<sub>2</sub>-), 29.03 (-CH<sub>2</sub>-), 14.23 (-CH<sub>3</sub>). IR (KBr) v, cm<sup>-1</sup>: 3098, 2920, 1732, 1656, 1425, 1166, 1105, 858, 823. MS (ESI) *m*/*z*: 567.11,[M + 1]<sup>+</sup> calcd. 566.25. Analysis (%): C, 61.39; H, 5.41; N, 5.02 (C<sub>29</sub>H<sub>30</sub>Fe<sub>2</sub>N<sub>2</sub>O<sub>3</sub> requires C, 61.51; H, 5.34; N, 4.95).

#### 3. Results and discussion

#### 3.1. Synthesis and characterization

The strategy (Scheme 1) for the preparation of compounds **3a** and **3b** was the cyclization reaction of  $\alpha$ , $\beta$ -unsaturated ketones with hydrazine hydrate [28]. Such cyclization is well documented for the synthesis of **3a** and **3b**, which were unstable and could not



*Reaction conditions:* (i) 4-bromobenzaldehyde or ferrocenecarboxaldehyde, NaOH, 40°C; (ii) NH<sub>2</sub>NH<sub>2</sub>·H<sub>2</sub>O, 80 °C; (iii) 3-(ethoxycarbonyl)propionyl chloride, CH<sub>2</sub>Cl<sub>2</sub>.



**4b** R = \* - CH<sub>2</sub>CH<sub>2</sub>COOEt

Scheme 2. Electron transfer mechanism of 4b.



Fig. 1. Molecular structure of compounds 4a and 4b.

be purified by conventional methods. The initial substances were directly acylated for the formation of the desired compounds **4a** and **4b** in high yield 82.2%, 80.9%, respectively.

The structures of **4a** and **4b** were characterized by IR, <sup>1</sup>H, and <sup>13</sup>C NMR spectral data. In the IR spectrum, the ester carbonyl absorptions were seen at 1732 cm<sup>-1</sup>. The strong bands at 1656 cm<sup>-1</sup> of all the compounds can be attributable to the carbonyl group stretching vibrations. The NMR spectra also confirmed the structures of compounds **4a** and **4b** (Fig. 1). The signals of unsubstituted cyclopentadiene (Cp) ring protons of both **4a** and

**4b** have approximated position in <sup>1</sup>H NMR spectra [29]. We concentrate our attention on  $\delta$ : 5.49–5.44 ppm (–CH– of the 4,5-dihydropyrazole ring) and  $\delta$ : 3.65–2.94 ppm (–CH<sub>2</sub>– of the 4,5-dihydropyrazole ring), which belong to the characteristic ABX proton spin systems. The presence of the 4-bromophenyl substituent at position 5 of the dihydropyrazole ring **4a** is typical of the pronounced upfield shift of the H(A) proton ( $\delta$ : 2.94 ppm), the difference ( $\delta_{H(B)} - \delta_{H(A)}$ ) being equal to 0.71 ppm. In the spectra of dihydropyrazole **4b** with the ferrocenyl group at position 5, the H(A) proton was present at lower fields ( $\delta$ : 3.32 ppm).

Analysis of the <sup>13</sup>C NMR spectra of compounds **4a** and **4b** (see Supporting information) also allows one to reveal characteristic differences for 3-ferrocenyl and 3,5-diferrocenyl-substituted pyrazoline. Thus signal for  $C_{ipso}$ —Fc of **4a** are located at 75.01 ppm while **4b** contains two types of signals for  $C_{ipso}$ —Fc, viz.  $\delta$ : 75.58 and 87.69 ppm, respectively [29].

#### 3.2. Crystal structure

Brown crystals of **4a** and **4b** suitable for X-ray single crystals analysis were crystallized by slow diffusion of petroleum ether into a solution of **4a** or **4b** in acetonitrile. The molecular structures of **4a** and **4b** are showed in Fig. 2. A summary of the key crystallographic information of **4a** and **4b** are given in Table 1. The selected bond distances and bond angles are given in Tables 2 and 3, respectively.

Two conformations in the crystal structure of compound **4a** have been defined with respect to the flexible aliphatic chain (Fig. 2a). The two cyclopentadienyl rings of the ferrocene moiety are parallel in both crystal structures. Interestingly, the Cp ring of Fc<sup>1</sup> is almost coplanar with the pyrazoline ring with a dihedral angle of  $13.24^{\circ}$ , while the Cp ring of Fc<sup>II</sup> is nearly orthogonal to the pyrazoline ring with a dihedral angle 88.30° in the crystal



Fig. 2. (a) The molecular structure of 4a. (b) The molecular structure of 4b.

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Table 1					
Crystallographic data and structure	e refinement	details	for <b>4a</b>	and	4b.

Compound	4a	4b
Empirical formula	C25H25BrFeN2O3	$C_{29}H_{30}Fe_2N_2O_3$
Crystal size (mm)	$0.20\times0.20\times0.20$	$0.20\times0.20\times0.20$
Formula weight	537.22	566.25
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	P(-1)	P(-1)
a (Å)	10.909(4)	10.387(2)
b (Å)	11.491(4)	10.813(2)
<i>c</i> (Å)	20.917(9)	13.215(3)
α (°)	93.531(13)	95.03(3)
β (°)	97.845(16)	106.25(3)
γ (°)	112.977(12)	117.20(3)
$V(Å^3)$	2372.5(15)	1226.4(4)
Ζ	4	2
$D_{\text{calc}}$ (g/cm <sup>3</sup> )	1.504	1.533
Absorption coefficient (mm <sup>-1</sup> )	2.349	1.218
F(000)	1096	720
Index ranges	$-14 \leqslant h \leqslant 14$	$-12 \leqslant h \leqslant 13$
	$-17 \leqslant k \leqslant 17$	$-14 \leqslant k \leqslant 13$
	$-27 \leqslant l \leqslant 27$	$-17 \leqslant l \leqslant 12$
Reflections collected	22,833	10,313
Independent reflections	10,580 R <sub>All</sub> = 0.0419	5415 R <sub>All</sub> = 0.0353
Completeness to $\theta$ = 27.50°	97.5%	96.2%
Absorption correction	Multi-scan	Multi-scan
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0672$ ,	$R_1 = 0.0537$ ,
	$wR_2 = 0.1771$	$wR_2 = 0.1613$
R indices (all data)	$R_1 = 0.1290$ ,	$R_1 = 0.0651$ ,
	$wR_2 = 0.2095$	$wR_2 = 0.1878$
Goodness-of-fit on F <sup>2</sup>	1.013	0.921

structure of compound **4b**. The bond length (**4b**) of N(2)–C(24) is 1.358 Å, which is shorter than the N(2)–C(13) single bond distance (1.475 Å) and longer than the N(1)=C(11) double bond distance (1.296 Å), at the same time the N(1)–N(2) distance (1.402 Å) is shorter than the corresponding N–N single bond (1.460 Å). Similarity, the C(9)–C(11) distance is 1.465 Å shorter than the length of C(13)–C(14) (1.507 Å).Thus, it can indicate that there is a conjugated system in **4b** between the C(24), N(2), N(1), C(11) and the Cp ring of Fc<sup>I</sup>, owing to the strong electron-withdrawing carbonyl group has a greater effect on Fc<sup>I</sup> than on Fc<sup>II</sup>.

Crystal packing of **4b** is shown in Fig. 3b. It can be seen that the adjacent molecules are stacked along the *c* axis through the edgeto-face interactions (the distance of C—H··· $\pi$  is 2.703 Å) and the weak hydrogen bond of C(2)—H(2)···O(2) (the length of H(2)···O(2) is 2.493 Å). Meanwhile **4b** is self-assembled by the offset face-to-face interactions between C(10) and C(11) of neighboring molecules (the distance of C(10)···C(11) is 3.284 Å) to form 2D supramolecular structure along the *a* axis. A similar structural arrangement of **4a** was seen in Fig. 3a, the adjacent molecules are held together by the hydrogen bond of C(19)—H(19)···O(4) or C(44)—H(44)···O(1) (the length of H(19)···O(4) and H(44)···O(1) is 2.461 Å, 2.504 Å, respectively) and the  $\pi \cdots \pi$  stacking interaction (the distance of Pz···Cp is 3.365 Å).

#### 3.3. Electrochemistry and quantum-chemical calculations

The electrochemical behaviors of compounds **4a** (see Supporting information) and **4b** ( $c = 10^{-3}$  M) were investigated by the cyclic voltammetric technique in acetonitrile containing [n-Bu<sub>4</sub>N]PF<sub>6</sub> (c = 0.10 M) as a supporting electrolyte at 25 °C. In order to explain the two redox processes of compound **4b**, we focused our attention on its electrochemical behaviors (Scheme 2).

Ta	ble	2	

Selected bond lengths (Å) and angles (°) for compound 4a.

Bond	Dist.	Bond	Dist.
Br(1) - C(17)	1.896(6)	Br(2) - C(42)	1.891(4)
N(1)-C(11)	1.288(5)	Fe(2)-C(28)	2.054(6)
N(1)-N(2)	1.402(5)	Fe(2)-C(28)	2.054(6)
N(2)-C(20)	1.342(6)	Fe(2)-C(28)	2.054(6)
N(1)-C(3)	2.060(6)	Fe(2)-C(28)	2.054(6)
O(1) - C(11)	1.296(5)	N(1)-N(2)	1.402(4)
O(3)-C(27)	1.328(5)	O(3)-C(28)	1.444(5)
N(2)-C(24)	1.358(5)	N(2)-C(13)	1.475(5)
O(1)-C(24)	1.223(5)	O(2)-C(27)	1.191(6)
C(9)-C(11)	1.464(5)	C(11)-C(12)	1.496(5)
C(12)-C(13)	1.532(5)	C(13)-C(14)	1.507(5)
Angles	(°)	Angles	(°)
C(18) - C(17) - Br(1)	121.0(6)	C(43) - C(42) - Br(2)	120.2(3)
C(16) - C(17) - Br(1)	117.8(6)	C(41) - C(42) - Br(2)	118.6(4)
C(20) - N(1) - N(2)	122.2(4)	C(36)-N(3)-N(4)	107.4(3)
C(20) - N(2) - C(13)	125.5(4)	C(45) - N(4) - N(3)	122.7(4)
N(1)-N(2)-C(13)	112.3(4)	C(45)-N(4)-C(38)	125.6(4)
C(11) - N(1) - N(2)	107.3(4)	N(3)-N(4)-C(38)	111.6(3)
C(23)-O(2)-C(24)	118.9(5)	C(48)-O(5)-C(49)	116.8(6)
N(1)-C(11)-C(1)	123.0(4)	N(3)-C(36)-C(26)	122.6(4)
N(1)-C(11)-C(12)	113.2(4)	N(3)-C(36)-C(37)	113.2(4)
C(1)-C(11)-C(12)	123.8(4)	C(26)-C(36)-C(37)	124.1(4)
C(11)-C(12)-C(13)	102.1(4)	C(36)-C(37)-C(38)	101.9(3)
N(2)-C(13)-C(14)	111.6(4)	N(4)-C(38)-C(39)	110.7(4)
N(2)-C(13)-C(12)	99.7(4)	N(4)-C(38)-C(37)	100.4(3)
C(14)-C(13)-C(12)	110.9(4)	C(39)-C(38)-C(37)	111.7(4)
O(1)-C(20)-N(2)	120.3(4)	O(4)-C(45)-N(4)	120.2(4)
O(1)-C(20)-C(21)	122.6(4)	O(4) - C(45) - C(46)	124.2(4)
N(2)-C(20)-C(21)	117.1(4)	N(4) - C(45) - C(46)	115.6(4)
C(22)-C(21)-C(20)	113.0(4)	C(45) - C(46) - C(47)	111.9(4)
C(21)-C(22)-C(23)	113.1(4)	C(48)-C(47)-C(46)	113.8(5)
O(3)-C(23)-O(2)	123.7(5)	O(6)-C(48)-O(5)	122.8(6)
O(3)-C(23)-C(22)	125.5(5)	O(6)-C(48)-C(47)	126.2(5)
O(2) - C(23) - C(22)	110.8(5)	O(5)-C(48)-C(47)	111.0(5)
C(24)-C(25)-O(2)	112.4(4)	C(50)-C(49)-O(5)	114.3(8)

Table 3		
Selected bond lengths (Å) ar	d angles (°) for	compound 4h

Bond	Dist.	Bond	Dist.
N(1)-C(11)	1.296(5)	N(1)-N(2)	1.402(4)
O(3)-C(27)	1.328(5)	O(3)-C(28)	1.444(5)
N(2)-C(24)	1.358(5)	N(2)-C(13)	1.475(5)
O(1)-C(24)	1.223(5)	O(2)-C(27)	1.191(6)
C(9)—C(11)	1.464(5)	C(11)-C(12)	1.496(5)
C(12)-C(13)	1.532(5)	C(13)-C(14)	1.507(5)
Angles	(°)	Angles	(°)
C(11) - N(1) - N(2)	106.2(3)	C(27)-O(3)-C(28)	115.8(4)
C(24)-N(2)-N(1)	122.2(3)	C(24)-N(2)-C(13)	125.3(3)
N(1)-N(2)-C(13)	112.2(3)	N(1)-C(11)-C(9)	122.4(3)
N(1)-C(11)-C(12)	114.4(3)	C(9) - C(11) - C(12)	123.3(3)
C(11)-C(12)-C(13)	101.1(3)	N(2) - C(13) - C(14)	110.6(3)
N(2) - C(13) - C(12)	100.2(3)	C(14)-C(13)-C(12)	110.4(3)
O(1)-C(24)-N(2)	121.0(4)	O(1)-C(24)-C(25)	123.1(4)
N(2) - C(24) - C(25)	115.9(4)	C(24) - C(25) - C(26)	111.6(4)
C(27)-C(26)-C(25)	112.8(4)	O(2)-C(27)-O(3)	122.6(5)
O(2)-C(27)-C(26)	125.4(4)	O(3)-C(27)-C(26)	112.0(4)
O(3)-C(28)-C(29)	107.1(4)		

As it can be seen from Fig. 4 and Table 4, the redox potentials of **4b** were slightly influenced by the scan rate in a range from 0.1 to 0.8 V/s. The cyclic voltammogram of compound **4b** shows two quasi-reversible oxidation waves at  $E_{1/2}^{II}$  of 0.472 V and  $E_{1/2}^{I}$  of 0.605 V. The first one-electron wave  $(E_{1/2}^{II})$  corresponds to Fe<sup>II</sup>(II)  $\leftrightarrow$  Fe<sup>II</sup>(III) oxidation and the second one-electron wave  $(E_{1/2}^{II})$  to Fe<sup>II</sup>(II)  $\leftrightarrow$  Fe<sup>II</sup>(III) oxidation. The difference between the values of these two potentials is arising from the strong electron-withdrawing effect of the carbonyl group.



Fig. 3. (a) Cell packing diagram of 4a (viewed down the *a* axis). (b) Cell packing diagram of 4b (viewed down the *c* axis).



Fig. 4. Cyclic voltammetry of compound 4b at different scan rates (0.1, 0.2, 0.4, 0.6, 0.8 V/s) in acetonitrile.

DFT computational studies were performed to verify the electron transfer mechanism of **4b** (Fig. 5a). The schematic

 Table 4

 The electrochemical data at the scan rate of 0.1 V/s.

Compound		$E_{\mathrm{pa}}^{a}(\mathrm{V})$	$E_{\rm pc}^{\ b}(V)$	$E_{1/2}^{c}(V)$	$\Delta E_{\rm p}^{\rm d}({\rm V})$	$\Delta E_{1/2}^{e}$ (V)
Fc		0.517	0.404	0.461	0.113	
4a		0.652	0.579	0.616	0.073	
4b	I	0.641	0.569	0.605	0.072	0.133
	П	0.507	0.437	0.472	0.070	

<sup>a</sup> *E*<sub>pa</sub>: anodic oxidation potential.

 $^{\circ} E_{\rm pc}$ : cathodic reduction potential.

 $E_{1/2}$ : half-wave potential,  $E_{1/2} = (E_{pa} + E_{pc})/2$ .

$${}^{e} \Delta E_{1/2} = E_{1/2}^{I} - E_{1/2}^{II}.$$

representation of the molecular frontier orbitals of **4b** was exhibited in Fig. 5b. From Fig. 5b, we can see that the HOMO (-5.34 eV) and HOMO-1 (-5.36 eV) of **4b** are dominated by the ferrocene unit **II**, while the HOMO-2 (-5.68 eV) and HOMO-3 (-5.81 eV) consist of orbitals on the ferrocene unit **I** moiety. These results conform to the electrochemical behavior of **4b**.

In addition, the effect of scan rate was investigated (Fig. 4), both the anodic and cathodic peak currents are linear to the square root of scan rates ( $v^{1/2}$ ) in the range of 0.1–0.8 V/s, which indicating a diffusion-controlled process [30].



Fig. 5. (a) The structure of compound 4b optimized by theoretical calculations. (b) Energy diagram of the first four HOMOs of compound 4b (B3LYP/LANL2DZ).

#### 4. Conclusion

Two dihydropyrazole-bridged ferrocenyl-substituted derivatives were successfully synthesized in high yields. The crystal arrangements of title compounds were promoted by weak hydrogen-bonding interactions and  $\pi$ – $\pi$  stacking interactions between neighboring molecules to form 2D supramolecular structure. Furthermore, electrochemical investigations showed that two quasi-reversible oxidation waves were controlled by diffusion. The difference between the values of two potentials in compound **4b** is arising from the strong electron-withdrawing effect of the carbonyl group. DFT calculation results explain the electron transfer mechanism of typical compound **4b**.

#### Acknowledgments

We are grateful for the financial support from the National Natural Science Foundation of China (No. 21172036), the Research Fund for the Doctoral Program of Higher Education of China (No. 20113514110002), the Natural Science Foundation of Fujian Province (No. 2009J05028, 2010J01036) and the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry (No. 20111568).

#### Appendix A. Supplementary material

General experimental procedure and spectroscopic data for the synthesized compounds see Supporting Information. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC 853434 and 800388 for compounds **4a** and **4b**, respectively. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam. ac.uk). Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j. molstruc.2012.05.026.

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