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A novel ferrocenic copper(II) complex Salen-like, derived from 5-chloromethyl-2-hydroxyacetophenone and *N*-ferrocenmethylaniline: Design, spectral approach and solvent effect towards electrochemical behavior of Fc^{+}/Fc redox couple

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Please cite this article as: Y. Ouennoughi, H. Eddine Karce, D. Aggoun, T. Lanez, R. Ruiz-Rosas, B. Bouzerafa, A. Ourari, E. Morallon, A novel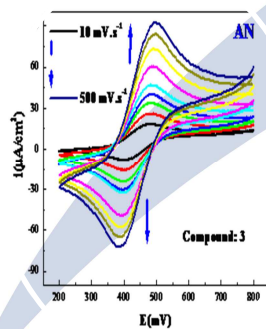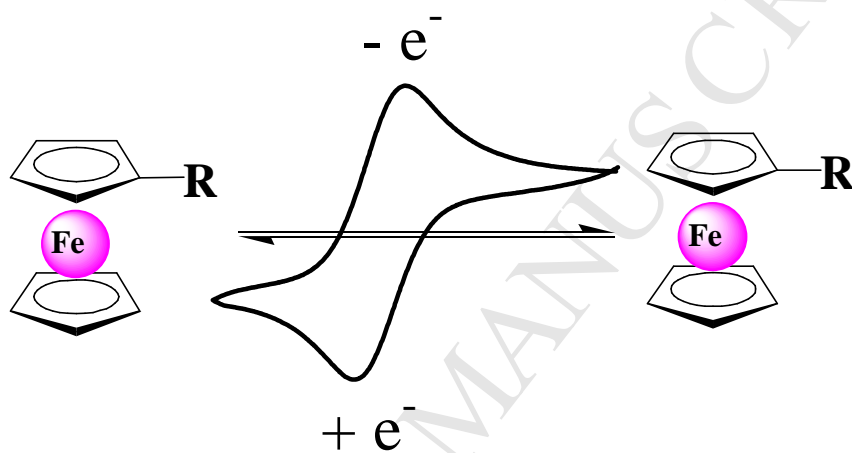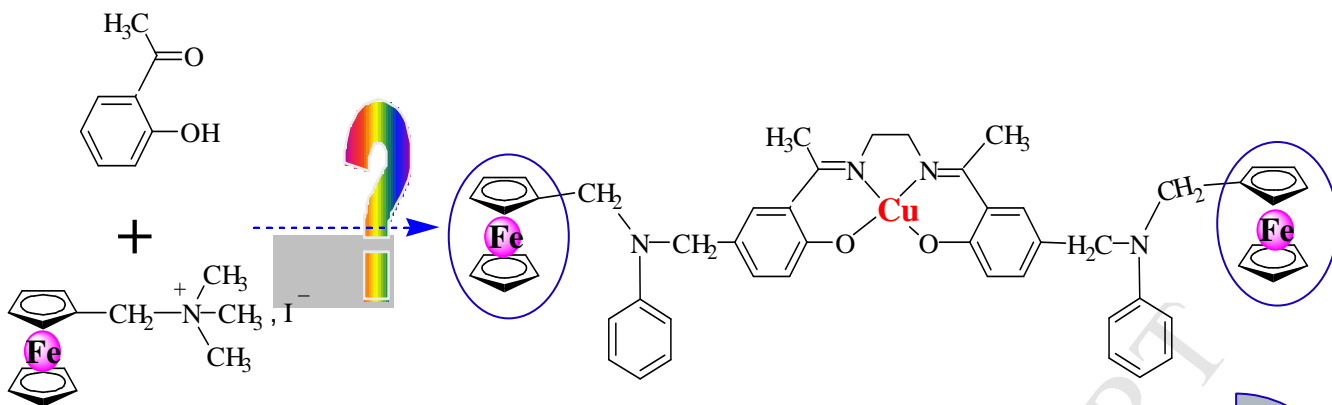 ferrocenic copper(II) complex Salen-like, derived from 5-chloromethyl-2-hydroxyacetophenone and *N*-ferrocenmethylaniline: Design, spectral approach and solvent effect towards electrochemical behavior of Fc^{+}/Fc redox couple, *Journal of Organometallic Chemistry* (2017), doi: 10.1016/j.jorganchem.2017.08.016.

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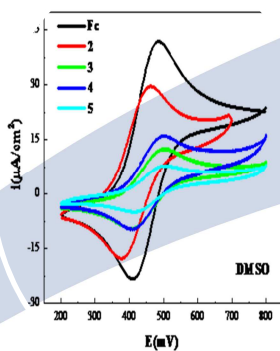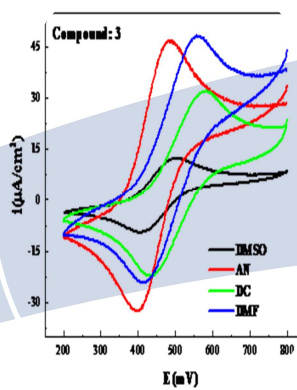
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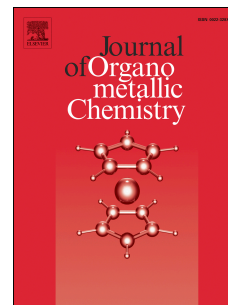
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A Novel Ferrocenic Copper^{II} Complex Salen-Like, Derived from 5-Chloromethyl-2-hydroxyacetophenone and N-Ferrocenmethylaniline: Design, Spectral Approach and Solvent Effect towards Electrochemical Behavior of Fc^{+}/Fc Redox Couple.

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Abstract

This paper reports the synthesis, spectroscopic characterizations and electrochemical behavior of the obtained tetradentate copper(II)-Schiff base complex with its two wings as ferrocenylaniline moieties. This new ferrocenic derivative with two ferrocenylaniline entities surrounding the copper(II)-Salen complex (**5**) was synthesized by reacting N-ferrocenmethyl-N-phenyl-5-aminomethyl-2-hydroxyacetophenone (**3**) with one half equivalent of 1,2-diaminoethane in absolute ethanol. As for the intermediates involved in this synthetic sequence, the compound (**3**) was prepared in tetrahydrofuran (THF) by reacting N-ferrocenmethylaniline (**2**) with 5-chloromethyl-2-hydroxyacetophenone (**1**) in presence of sodium hydrogenocarbonate (NaHCO$_3$). The compound (**3**) condensed on the diamine yields the Schiff base ligand (**4**). Under a nitrogen atmosphere and stirring at 50 °C, the ligand dissolved in absolute ethanol with stoichiometric amount of copper acetate monohydrate (Cu(COOCH$_3$)$_2$ · H$_2$O) formed the expected tetradentate Cu(II)-Schiff base complex (**5**) after 6 hours of reaction. All these synthesized compounds gave yields varying from 50 to 90%. Their purities were estimated from elemental analysis while the molecular structures were elucidated with FT-IR, UV–Vis, ^{1}H- and ^{13}C- NMR. For the obtained copper complex, it is tetracoordinated in a distorted square planar environment with two nitrogen and two oxygen atoms as donor sites. The electrochemical behaviors of the synthesized compounds were explored using cyclic voltammetry. This investigation showed an important anodic shifting of the E_{pc} and E_{pa} potential waves for the Fc^{+}/Fc redox couple of compound (**3**) in dichloromethane (**DC**) medium, compared to other polar

media like acetonitrile (**AN**), dimethylformamide (**DMF**) and dimethylsulfoxide (**DMSO**). This behavior was also observed for the tetradentate copper(II)-Salen complex with its different metallic centers.

Key words: N-Ferrocenmethylaniline, 5-Chloromethyl-2-hydroxyacetophenone, Organometallic copper(II)-Salen, Cyclic voltammetry, Solvent effects.

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1. Introduction

In recent years, more consideration and a large number of papers have been published on the synthesis and characterization of substituted derivatives of ferrocene as typical organometallic species **[1-3]**. These kinds of compounds are currently receiving much consideration due to their increasing role in the rapid growing area of materials science. Therefore, the addition of cyclopentadienyl rings of ferrocene moiety into an organic compound, not only improves the electrochemical and spectroscopic behavior, but also increases the application range of these compounds **[4,5]**. This is due to the fact that ferrocenyl derivatives are stable compounds, nontoxic, and have useful redox properties. From a redox perspective, ferrocene derivatives are also interesting as monoelectronic reservoir complexes capable to act as mediators in the redox-catalytic reactions.

Ferrocenyl Schiff base ligand may also be considered as one of the potential precursors for the ferrocenic compounds that have been studied in this context **[6-9]**. Accordingly, several groups have reported diverse redox properties for various monoferrocenyl and diferrocenyl of bi-, tri- tetra- or polydentate Schiff bases ligands but most of them have essentially focused their efforts on the tetradentate Schiff base ligands **[10]**. These compounds display excellent biological activities in

which potent therapeutics applications were proved like those applied against cancer [11], antimicrobial [12], antibacterial [13], antifungal [14] and DNA photo-cleavage activity [15].

Schiff bases were found to have good coordinating properties to synthesize various complexes using transition metal ions. The electropolymerization of these molecular materials yield the expected redox polymers with an electronic acceptable conductivity. These materials, with their high potential in chemistry, biology and medicine, have been found to be useful in several applications in a wide range of applications such as biochemistry [16], electrochemistry [17], spectroscopy [18] and in the other fields of analytical [19], nonlinear optics (NLO) [20], catalysis [21] and electrocatalysis [22].

Our interest, in this subject, is to synthesize novel substituted ferrocene derivatives containing appropriate coordinating spheres which make them efficient Schiff base ligands leading easily to their corresponding complexes of transition metals, electropolymerizable with its aniline unit (**Scheme 1**). Thus, ferrocenylmethylation was recognized as a powerful method for the preparation of various ferrocene derivatives [23]. This reaction typically uses stable starting materials such as N-ferrocenmethylammonium salts [24,25] that are usually applied as alkylating agents for the introduction of ferrocenmethyl group into various substrates. The most often employed ferrocenylmethylation reagents are certainly ferrocenylmethylation of aniline [26].

As a continuation of our studies with iminic compounds and modified electrodes, a new N_2O_2 donor type Schiff base ligand like N,N-Bis[N-ferrocenmethyl-N-phenyl-5-aminomethylsalicylidynemethyl]-1,2-diimino ethane (**H$_2$L**) and its copper complex were prepared and characterized by routine NMR, FT-IR, UV–Vis absorption spectroscopy, CHN elemental analysis and cyclic voltammetry. The Cyclic voltammograms of the synthesized copper complex (**Cu(II)L**) were conducted in different solvents such as DMF, DMSO, AN and DC. In this case, it must be noted that the redox system of ferrocene was systematically observed in all cases as a rapid and very stable redox couple. As for the Cu^{II}/Cu^{I} redox system, it displays a quasi-reversible

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behavior in the same media. The electrochemical reactions involved in these media are expressed by

chemical equations illustrated below in the **Scheme 1**.
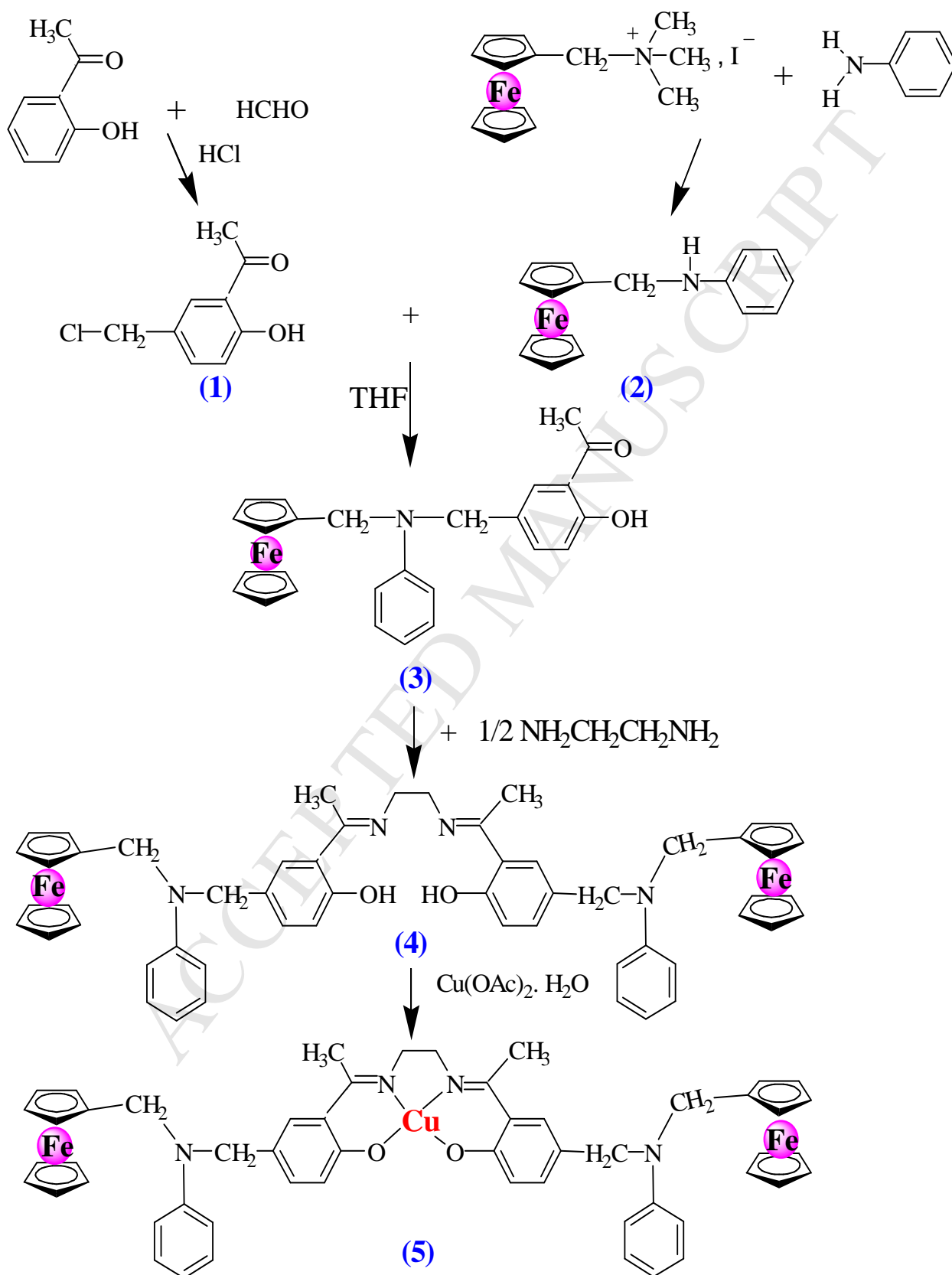
Scheme 1. Reaction pathways leading to the formation of the compounds: 1, 2, 3, 4 and 5.

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2. Experimental

2.1. Materials and physicochemical characterization

All reagents were obtained from commercial sources and were used as received without any further purification. The purity of the synthesized compound was checked by TLC using aluminum plates, precoated with silica gel (60F, Merck). FT-IR spectra were recorded as KBr disks on a PerkinElmer 1000 FTIR Spectrophotometer while the UV-Visible spectra were obtained on a UNICAM UV-300 spectrophotometer using DMF solutions (A cell length of 1 cm). The ^{1}HNMR spectra were recorded on a Bruker AC300 Y 400 at 25 °C using tetramethylsilane (TMS) as an internal reference. All chemical shifts ^{1}H are given in ppm using deuterated $CDCl_3$ and DMSO-d6 as solvents. The microanalysis was performed with LECO TruSpec Micro CHNS elemental micro analyzer. Cyclic voltammetry experiments were carried out in a Metrohm cell of 5 cm^3 using voltalab 40 (PGZ 301) potentiostat/galvanostat. A planar, circular glassy carbon (GC) electrode (3 mm in diameter) was employed as a working electrode, a platinum wire as an auxiliary electrode and a saturated calomel electrode (SCE) as a reference electrode. The ferrocene/ferricenium redox couple ($FcH^{0/+}$) was located at $E_{1/2}= 0.420$ V, where $E_{1/2}$ was calculated from the average of the oxidation and reduction peak potentials. This redox couple was also used as reference in this study. Tetra-n-butylammonium perchlorate (TBAP) was used as supporting electrolyte and dichloromethane (DC), acetonitrile (AN), dimethylformamide (DMF) and dimethylsulfoxyde (DMSO) as solvents in all electrochemical experiments. All solutions were nitrogen purged prior to and during the experiments.

2.2. Synthesis of starting materials

Compound 1: 5-Chloromethyl-2-hydroxyacetophenone (1)

This compound was synthesized according to the procedure described in the literature [27 a]. Briefly, 170 mg (0.125 mmol) of 2-hydroxyacetophenone were added to a mixture of 10 mL of concentrated hydrochloric acid containing 675 mg (0.225 mmol) of paraformaldehyde. The mixture was maintained at room temperature under stirring for 48 hours until a precipitate is formed. The solid product was collected by suction filtration, washed with a solution of sodium hydrogen carbonate ($NaHCO_3$, 50 %), then with water until neutrality, dried under vacuum and then recrystallized in a mixture of toluene and petroleum ether yielding 80 % of white crystals.

UV-Vis: $\lambda_{max(n)}$ (nm), $\varepsilon_{max(n)}$ [$M^{-1}.cm^{-1}$]: $\lambda_{max(1)}$ (265), $\varepsilon_{max(1)}$ [6030]; $\lambda_{max(2)}$ (327), $\varepsilon_{max(2)}$ [1139]. **^{1}H NMR** (CDCl$_3$): δ_H(ppm) = 12.33 (1H, s, OH), 7.37 (3H, m, Ar-H), 4.69 (2H, s, CH$_2$), 2.66 (3H, s,

CH$_3$). ^{13}**C NMR** (CDCl$_3$): δ$_C$(ppm) = 204.3 (1C, C=O), 161.1 (1C, C-O), 137.3, 132.3, 128.9, 120.8, 118.6 (5C, Aromatic carbons), 46.3 (1C, CH$_2$), 28.4 (1C, CH$_3$).

Compound 2: N-ferrocenmethylaniline (**2**)

This compound was also synthesized according the literature [27 b]. 40 g of ferrocenylmethyl trimethylammonium iodide (0.104 mol), in distilled water (300 mL) was added to a solution of aniline (55.6 g, 0.597 mol) in distilled water (300 mL). The mixed solution was stirred at reflux of water for 2 hours. Then, the product was extracted with toluene and recrystallized in a mixture of ethanol and water to give 20.09 g (0.069 mol) as yellow crystals (66 % yield).

UV-Vis (CH$_2$Cl$_2$): λ$_{max(n)}$ (nm), ε$_{max(n)}$ [M^{-1}.cm^{-1}]: λ$_{max(1)}$ (250), ε$_{max(1)}$ [15100]; λ$_{max(2)}$ (290), ε$_{max(2)}$ [4260]. ^{1}**H NMR** (CDCl$_3$): δ$_H$ (ppm) = 7.31(1H, s, H-N), 6.70-7.30 (5H, m, Ar-H), 4.33 (2H, s, C$_5$H$_4$ $_{(α,α')}$), 4.24 (5H, s, C$_5$H$_5$), 4.20 (2H, s, C$_5$H$_4$ $_{(β,β')}$), 4.01 (2H, s, CH$_2$); ^{13}**C NMR** (CDCl$_3$): δ$_C$(ppm) = 148.4 (1C, C$_{ph}$-N), 112.9, 117.6, 129.4 (5C, Aromatic carbons), 86.6 (1C, C$_5$H$_4$, ipso), 68.6 (5C, C$_5$H$_5$), 68.2 (2C, C$_5$H$_4$, C$_β$), 68.0 (2C, C$_5$H$_4$, C$_α$), 43.5 (1C, CH$_2$). **Microanalysis: Calc. (Found) (C$_{17}$H$_{17}$NFe): C**70.13% (69.80), **H** 5.88% (6.02), **N** 4.81% (5.32).

Compound 3: 5-(N-ferrocenylmethyl-N-phenyl)aminomethyl)-2-hydroxyacetophenone (**3**)

The 5-(N-ferrocenmethyl-N-phenyl)aminomethyl)-2-hydroxyacetophenone (**3**) was prepared according to the following experimental procedure: A mixture of 300 mg (0.257 mmole) of N-ferrocenmethylaniline (**2**) and one equivalent of NaHCO$_3$ (84 mg) in 6 mL of THF was placed in a three-necked flask surmounted by a condenser. To this mixture, 182 mg (0.257 mmole) of 5-Chloromethyl-2-hydroxyacetophenone (**1**), dissolved in 6 mL of THF, were added drop wisely. This mixture was then heated at 50 °C under stirring and nitrogen atmosphere for at least 6 hours. The resulting suspension containing NaCl was filtered, washed with diethyl ether and the solvents were removed under reduced pressure. The pale yellow solid obtained was recrystallized in a mixture of ethanol and petroleum ether to yield compound **3**. Its purity was checked by TLC using silica gel plates eluted with a combination of dichloromethane/heptane (8/2, v/v) as eluent. Yield 381 mg (79%).

UV-Vis (CH$_2$Cl$_2$): λ$_{max(n)}$ (nm), ε$_{max(n)}$ [M^{-1}.cm^{-1}]: λ$_{max(1)}$ (255), ε$_{max(1)}$ [2140]; λ$_{max(2)}$ (307), ε$_{max(2)}$ [304]; λ$_{max(3)}$ (337), ε$_{max(3)}$ [285]. ^{1}**H NMR** (DMSO-d6): δ$_H$ (ppm) = 11.75 (1H, s, OH), 7.80-6.50 (m, 8H, Ar-H), 4.48 (2H, s, N-CH$_2$-Ph), 4.41 (2H, s, N-CH$_2$-Fc), 4.26 (2H, t, C$_5$H$_{4(α,α')}$), 4.18 (5H, s, C$_5$H$_5$), 4.09 (2H, t, C$_5$H$_4$ $_{(β,β')}$), 3.32 (3H, s, CH$_3$). ^{13}**C NMR** (DMSO-d6): δ$_C$(ppm) = 204.9 (1C, C=O), 160.4 (1C, C-O), 148.8 (1C, C$_{ph}$-N), 135.6, 130.6, 130.2, 129.8, 121.1, 118.4, 117.0, 113.7 (10C, Aromatic carbons), 85.4 (1C, C$_5$H$_4$, ipso), 69.9 (5C, C$_5$H$_5$), 69.4 (2C, C$_5$H$_4$, C$_β$), 68.4 (2C,

C_5H_4, C_α), 53.3 (1C, CH_2), 50.8 (1C, CH_2), 28.6 (1C, CH_3). **Microanalysis: Calc. (Found) ($C_{26}H_{25}O_2NFe$): C**71.08 % (71.53), **H** 5.74% (5.59), **N** 3.19% (2.52).

Compound 4: N,N-Bis[(N-Ferrocenemethyl-N-phenyl)-5-aminomethylsalicylidynemethyl]-1,2-diiminoethane (**4**)

The tetradentate Schiff base ligand (**4**) was synthesized according to the literature [28]. Briefly, to a solution of 0.1 g (0.23 mmole) of 5-(N-Ferrocenmethyl-N-phenyl)aminomethyl-2-hydroxyacetophenone (**3**) in 7 mL of absolute methanol, placed in a 100 mL three-necked flask surmounted with a condenser, was slowly added a solution of 0.067 g (0.23 mmole) of 1,2-diaminoethane in 8 mL of the same solvent. This mixture was heated to 65 °C under stirring and nitrogen atmosphere for 4 hours. The precipitate obtained was filtered, washed with diethyl ether and dried under reduced pressure to afford 80 mg of compound **4** as a yellow solid. Its yield was estimated to 78% and the purity was checked by silica gel TLC plates using only dichloromethane as unique eluent.

UV-Vis: $\lambda_{max(n)}$ (nm), $\varepsilon_{max(n)}$ [$M^{-1}.cm^{-1}$]: $\lambda_{max(1)}$ (255), $\varepsilon_{max(1)}$ [22550], $\lambda_{max(2)}$ (310), $\varepsilon_{max(2)}$ [3970], $\lambda_{max(3)}$ (335), $\varepsilon_{max(3)}$ [3190], $\lambda_{max(4)}$ (405), $\varepsilon_{max(4)}$ [410]. **^{1}H NMR** (DMSO-d6): δ_H(ppm) = 15.67 (2H, s, 2OH), 7.50-6.50 (m, 16H), 4.48 (4H, s, N-CH_2-Ph), 4.42 (4H, s, N-CH_2-Fc), 4.28 (4H, t, C_5H_4 $_{(\alpha,\alpha')}$), 4.21 (10H, s, C_5H_5), 4.12 (4H, t, C_5H_4 $_{(\beta,\beta')}$), 3.38 (6H, s, 2CH_3), 2.32 (4H, t, 2CH_2). **^{13}C NMR** (DMSO-d6): δ_C(ppm) = 172.9 (2C, C=N), 161.7 (2C, C-O), 148.0 (2C, C_{ph}-N), 134.6, 130.8, 129.7, 128.8, 127.1, 118.7, 117.6, 115.9, 112.7 (20C, Aromatic carbons), 84.6 (2C, C_5H_4, ipso), 69.0 (10C, C_5H_5), 68.5 (4C, C_5H_4, C_β), 67.5 (4C, C_5H_4, C_α), 52.7 (2C, CH_2), 49.8 (2C, CH_2), 27.7 (2C, CH_2). 14.7 (2C, CH_3). **Microanalysis: Calc. (Found) ($C_{54}H_{50}$ $Fe_2N_4O_2$· 3H_2O): C**68.08 % (67.90), **H** 5.92% (5.57), **N** 5.88% (6.02).

Compound 5: Copper complex **Cu(II)L (5)**

Following the same way, a methanolic solution (5 mL) containing 33.8 mg of copper acetate monohydrate ($Cu(CH_3COO)_2$·H_2O) salt (0.17 mmol) was added slowly drop wise to a solution (5 mL) of 124.8 mg (0.34 mmol) of the ligand (**H_2L**) (**4**) placed in a 50 mL three-necked flask surmounted by a condenser. The mixture was then heated to reflux, under nitrogen atmosphere and stirring for at least 6 hours. The mixture was cooled to room temperature and the solvent was reduced under vacuum, the resulting precipitate was filtered, washed with diethylether and air-dried providing 98 mg (yield 62 %) of the copper complex.

UV-Vis: $\lambda_{max(n)}$ (nm), $\varepsilon_{max(n)}$ [M^{-1}.cm^{-1}]: $\lambda_{max(1)}$ (255), $\varepsilon_{max(1)}$ [23450]; $\lambda_{max(2)}$ (310), $\varepsilon_{max(2)}$ [3650]; $\lambda_{max(3)}$ (372), $\varepsilon_{max(3)}$ [1650]. **Microanalysis: Calc. (Found) ($C_{54}H_{48}Fe_2N_4O_2Cu$): C** 67.54% (67.87), **H** 5.04% (5.40), **N** 5.83% (5.65).

3. Results and discussion

3.1. Physicochemical and analytical characterization

Microanalysis data obtained for the copper complex confirmed that it is a mononuclear complex. Therefore, the ligand:metal ratio was found to be 1:1 and the resulting copper complex can be formulated as **Cu(II)L (5)** (See **Scheme 1**). The ligand with its copper complex seems to be stable at room temperature and they are also soluble in common organic solvents such as DC, MeOH, EtOH, DMF and DMSO. The synthesis of compounds (**1-4**) including the copper complex (compound **5)** was carried out through known chemical reactions as shown in **Scheme 1**. Regarding the compound **1**, it was prepared according to a recently published procedure involving the chloromethylation reaction of 2-hydroxyacetophenone. On the other hand, compound **2** was prepared by reacting aniline with (ferrocenmethyl)trimethylammonium iodide. As for compound (**3**), it was also synthesized *via* an alkylation of N-ferrocenmethylaniline (**2**) method with compound **1**. Thus, compound **3** reacted with ethylenediamine to afford the expected ligand as tetradentate Schiff base **H$_2$L** (**4**) which, upon treatment with copper acetate salt yielded its corresponding copper complex. The structures of these synthesized compounds were confirmed by different spectroscopic techniques such as UV-Vis, FT-IR and NMR spectral data. Additionally, the elemental analysis data were found to be in good agreement with the proposed structures. Details of some spectral data are given below.

3.2. Spectroscopic characterization

❖ *FT-IR spectra*

The FT-IR spectra of the starting products, the free ligand as well as its copper complex are listed in **Table 1**, together with assignments of most of the major bands. Generally, in order to study the binding modes of the Schiff base ligand to the metal ions in their complexes form, the FT-IR spectrum of the free ligand was compared to the spectrum of its corresponding copper complex.

As it can be seen, the FT-IR data of all compounds exhibit similar features indicating the analogy of their molecular structures. All these synthesized compounds, except compound **2** and the

copper complex, show a broad absorption band in the 3200-3800 cm^{-1} range which may be ascribed to the O–H groups (intramolecular hydrogen bonding). The spectra of all synthesized compounds are also dominated by bands between 3100–3050 cm^{-1} as ν (Aromatic, C-H) and 2950–2840 cm^{-1} for the ν (Aliphatic, C-H) stretching vibrations. The absorption bands observed at 1640 and 1637 cm^{-1} were attributed to the C=O stretching vibrations for compounds **1** and **3**, respectively. Also, the spectrum of **3** showed an absorption band at 1313 cm^{-1} due to the newly formed CH$_2$-N group **[28]**. As for the tetradentate Schiff base ligand **4**, its FT-IR spectrum displayed a characteristic band at 1618 cm^{-1} indicating the formation of an iminic function, currently known as azomethine group or Schiff base (HC=N). The characteristic frequencies of this group exhibit an obvious shifting to lower wave numbers (1598 cm^{-1}) in the spectrum of its Cu(II) complex. This bathochromic effect could be explained by an increase in the electronic delocalization through the metal centre, newly coordinated yielding the copper complex. Additional data supporting the formation of this complex was further provided by the appearance of other new indicative bands between 410-430 cm^{-1} and 510-520 cm^{-1} that are assignable to ν (N-Cu) and ν (O-Cu), respectively. The remaining characteristic band at 478 cm^{-1} in the free ligand could be assigned to the Fe–Cp stretching frequency. For the copper complex, no significant changes were observed including its ferrocenic moieties for which the two cyclopentadienyl rings were coordinated to the bivalent iron ion via their five molecular orbitals **[12,14]**.

Table 1 Characteristic FT-IR bands (4000–400 cm^{-1}) of 1, 2, 3, 4 and 5.

Compounds	ν(O-H)	ν(C-H) (arom.)	ν(C-H) (aliph.)	ν(C=O)	ν(C=N)	ν(CH$_2$-N)	ν(C-H)$_{(Cp)}$	ν(Fe-Cp)	ν (M-O)	ν (M-N)
1	3426	3013	2951	1640	-	-	-	-	-	-
2	-	3089	2920	-	-	-	753	490	-	-
3	3450	3085	2927	1637	-	1310	819	478	-	-
4	3430	3090	2920	-	1618	1380	819	478	-	-
5	-	3098	2925	-	1598	1381	820	477	503	422

❖ **Spectroscopic UV-Vis characterization**

The electronic spectra were recorded using freshly prepared solutions in DC at a concentration of 10^{-4} M. The common band, seen in the spectrum of the derivative **2** and in all the synthesized compounds, was observed at higher energy (200–300 nm) and it was attributed to π-π* transitions associated to the benzene ring (intraligand charge transfer ILCT). While the weaker one, appeared at lower energy (300–400 nm) in the spectra of compounds **2** and **3**. This band is probably related to n-

π^* transitions, implicated in the promotion of the lone pair electron of the carbonyl oxygen atom to the anti-bonding π orbital [29]. Moreover, a novel band, appearing at 375 nm in the spectrum of the copper complex, could be ascribed to LMCT and MLCT charge transfer (**See Fig. 1**).
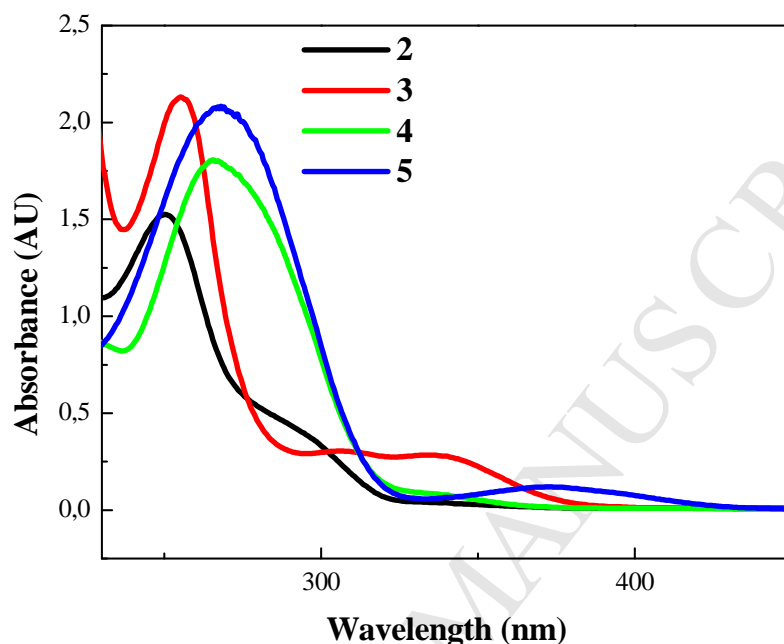

Fig. 1. UV-Vis spectra of the synthesized compounds: 2, 3, 4 and 5.

❖ ^{1}H and ^{13}C NMR characterization

The ^{1}H and ^{13}C NMR chemical shifts of the synthesized compounds with suggestible assignments have been listed in the experimental section in which the required evidences confirmed the proposed structures shown in **Scheme 1**. The ^{1}H NMR and ^{13}C NMR spectra of the ferrocenyl derivative (**3**) have been illustrated in **Fig. S1**.

The ^{1}H NMR spectrum of compound **3** was recorded in DMSO-d_6 at room temperature using TMS as internal standard (**Fig. S1A**). As it can be seen, the integral intensities of each signal were found to be in good agreement with the number of different types of protons of the studied structure. The most important peak of this compound was attributed to the singlet centered at 11.75 ppm confirming the presence of the phenolic (O-H) protons. In the case of the ligand **4**, these phenolic protons appear at 15.67 ppm. This deshielding effect is imputable to the formation of strongest intramolecular hydrogen bonds [30].

As for the aromatic protons, they resonate as multiplet between 6.50 and 7.80 ppm. The resonances appearing at 4.40 and 4.47 ppm were assigned to the aliphatic protons of the two methylene (N–CH$_2$) groups. The ferrocenyl entities exhibit three signals in the range 4.00-4.30 ppm which are assigned to the free C$_5$H$_5$ ring, with its two types of protons H$_\alpha$ and H$_\beta$ of the substituted cyclopentadienyl ring (C$_5$H$_4$). The singlet observed at 4.18 ppm was ascribed to the five protons of free cyclpentadienyl ring whereas the two distinct signals, respectively located at 4.26 (triplet: H$_{\alpha,\alpha'}$) and 4.09 ppm (triplet: H$_{\beta,\beta'}$), were attributed to the substituted ring. These assignments are consistent with those recently reported in the literature [6] for similar ferrocenyl derivatives. All of these assignments are in good accordance with almost the same chemical shifts in the case of the Schiff base ligand (compound **4**). As for the singlet observed at 3.32 ppm, it was attributed to the methyl protons directly linked to the carbonyl function (O=C–CH$_3$). The singlet observed at 3.38 ppm for the ligand and its chemical shift is due to the azomethine function (N=C–CH$_3$) linked to its methyl group. A new signal of both methylene groups, bonded to two azomethine linkage (C=N-CH$_2$-CH$_2$-N=C), was observed as triplet at 2.32 ppm in the free ligand.

The proton decoupled ^{13}C NMR spectrum of compound **3** seems to be in good accordance with ^{1}H NMR data above mentioned and confirming its structure by chemical shifts clearly shown by its spectrum. This structure has been confirmed by 18 observed resonances (See **Fig. S1B**) where carbon atoms resonances seen between 204.9–148.8 ppm are associated to carbonyl, phenoxy, and anilinic groups. As for the aromatic carbon atoms (C$_{sp2}$), they resonate in the 135.6–113.7 ppm range. In the spectrum of compound **3**, signals of the aliphatic carbon atoms (C$_{sp3}$), appear in the region of stronger fields between 53.3–28.6 ppm. The ferrocenyl carbon atoms were located in the region δ 86.0 to δ 67.0. As for the carbon atoms of unsubstituted cyclopentadienyl ring (C$_5$H$_5$), they appeared as a strong peak at δ 69.9 while other ferrocenyl peaks such as those of *α,α'* and *β,β'* carbons founded in the same ring (C$_5$H$_4$), produced rather chemical shifts at δ 68.4 and δ 69.4, respectively. The *ipso* carbon of the substituted cyclopentadienyl ring appears at δ 85.4. Aromatic and aliphatic carbon atoms resonate at almost the same chemical shifts for the same carbon atoms of compounds **3** and **4** but, in case of ligand (**4**), it displays a novel peak located at 14.72 ppm which is due to the methylene group. These results are in good accordance with the spectra of similar structures reported in literature [31].

3.3. Electrochemical characterization

Due to its well defined reversible system, experimentally obtained at the accessible potentials, the ferrocenium/ferrocene redox couple Fc^+/Fc ($Fc = Fe(C_5H_5)_2$) has been established as one of the internal standards for calibration of electrochemical measurements and extensively investigated as an interesting redox mediator currently involved in the electrochemical studies [32-34].

In this study, we have explored the changes in the oxidation potential of ferrocenium/ferrocene redox couple using cyclic voltammetry (CV). All the synthesized derivatives were studied in the presence of tetra-n-butylammonium perchlorate (TBAP) as a supporting electrolyte with the use of four aprotic organic solvents commonly utilized in the electrochemical measurements: dichloromethane (DC), acetonitrile (AN), *N*,*N*-dimethylformamide (DMF) and dimethylsulfoxide (DMSO). Therefore, this study was restricted to the use of only three solvents (DMF, DMSO and DC) for the Schiff base ligand (**4**) and its copper complex because of the low solubility of these compounds in acetonitrile medium.

➢ *Cyclic voltammetry characterization of Ferrocenyl derivatives*

The electrochemical properties of the synthesized compounds were studied by cyclic voltammetry 10^{-1} M TBAP and 2.10^{-3} M of each sample in different solvents using a glassy carbon electrode.

The potential was scanned within the potential range of +1.6 to -2.2 V at 100 mV/s. Cyclic voltammograms of all studied compounds showed reversible redox couples of Fc^+/Fc at about $E_{1/2} \approx$ 0.45 V. In the next step, the CV was also adopted to investigate the electrochemical response of this system (Fc^+/Fc) for all compounds between 0.2 and 0.8 V using various scan rates (**Figure S2**). This redox couple was systematically observed in all voltammograms, recorded in the following pure solvents DC, AN, DMF and DMSO. The electrochemical data for these compounds are summarized in **Table S1**. The main values shown in this table are i_{pa}/i_{pc} ratios, the peak-to-peak separation ΔEp (*Epa* and *Epc)* for various scan rates and $E_{1/2}$ as the half-wave potential values ($E_{1/2} = (Epa+Epc)/2$). As it can be seen in **Table S1**, the peak current ratio (i_{pa}/i_{pc}) seems to converge rapidly to unity and it is therefore independent of the scan rate in all the explored media. The values of ΔEp are higher than the ideal value of 60 mV for the Nernstian monoelectronic and reversible process system indicating some irreversibility of this process. As expected, the ΔEp value seems to be sensibly increased in DMSO producing a well defined redox system. The values of the half-wave potential ($E_{1/2}$) were also found to be significantly shifted to the more anodic potentials and are also independent of the scan rate.

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> *Effect of scan rates*

Figure 2A, recorded in acetonitrile medium, showed that the redox peak currents of the ferrocenic system (i_{pa}, i_{pc}) of compound **3** increase with increasing the scan rate. Their two anodic (E_{pa}) and cathodic (E_{pc}) potential waves also displayed an obvious shifting to the positive and negative potentials respectively as the scan rate increases. The peak to peak separation seems to be greater than 60 mV in all voltammograms even, at higher scan rates, which is an indication of fundamental slowness of the electron-transfer process. In addition, it was found that the obtained peak currents present a linear dependence versus the square root of the scan rate (**Fig. 2B**) as it is expected for a controlled diffusion process. The linear dependency of the anodic peak current with $v^{1/2}$ was also studied with all the synthesized compounds in different media as presented in figure S3.
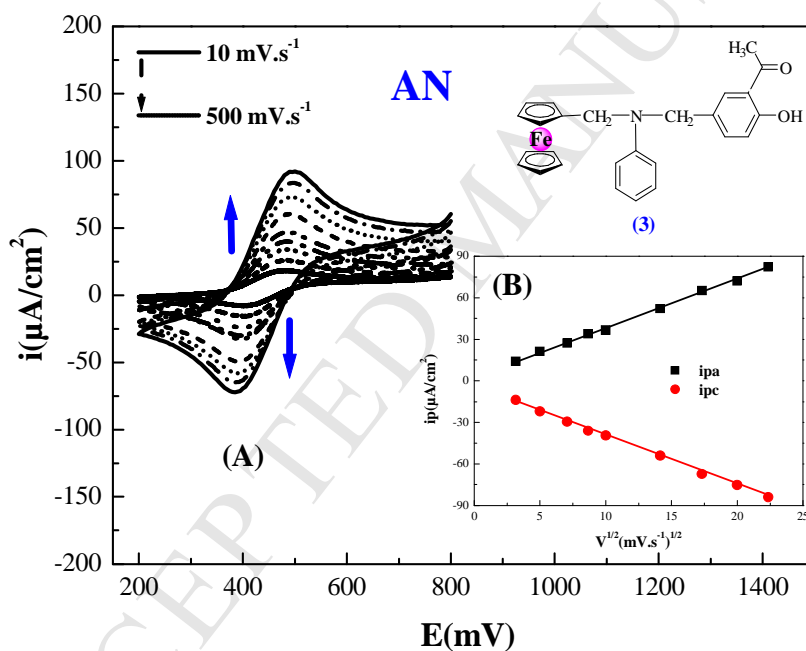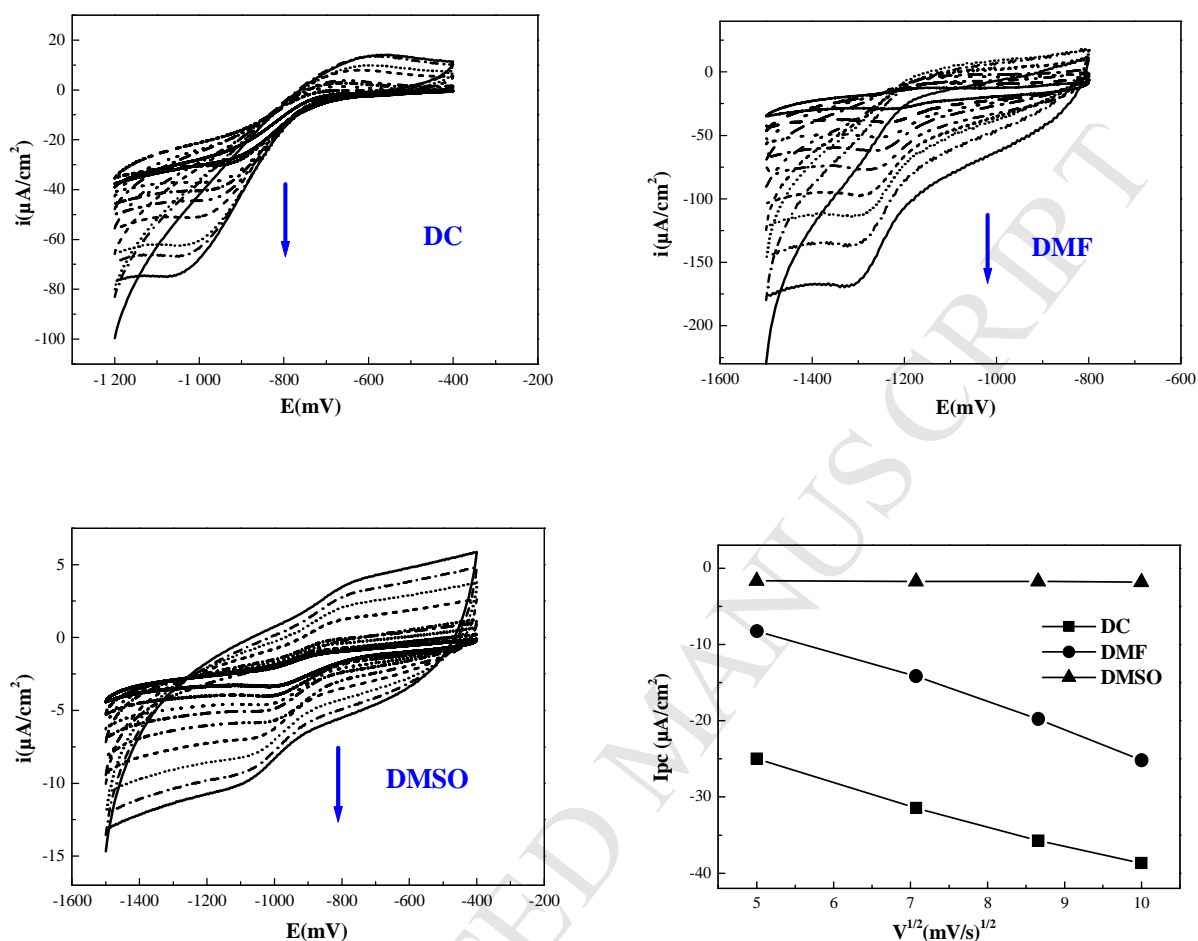

Fig. 2(A) Cyclic voltammograms recorded on glassy carbon electrode with 2.10^{-3} mol/L compound III and 10^{-1} mol/L TBAP in acetonitrile solution, (B) Anodic and the cathodic peak currents as function of square root of scan rate.

Detailed study of this effect for the copper complex is illustrated in **Fig. 3**. The voltammograms, recorded for the copper complex in the range between -0.4 and -1.5 V, indicate the presence of quasi-reversible process for the Cu(II)/Cu(I) system. This figure shows that each peak

position is not merely dependent on the scan rate but they are all critically dependent on solvent nature.

Fig. 3 Cyclic voltammograms, recorded on glassy carbon electrode, showing the effect of the scan rate and the cathodic peak heights as function of the square root of the scan rate for copper complex in various media (2.10^{-3} mol/L) (10^{-1} mol/L TBAP).

➢ *Effect of the Solvent on the Electrochemical Behaviour of Compound 3*

Cyclic voltammograms of compound **3** recorded in various solvent are shown in **Fig. 4**. It has been demonstrated that $E_{1/2}$ shifts towards the more anodic potentials according to the following order: AN<DC<DMF<DMSO. This order indicates that the oxidation reaction of ferrocene derivative to its ferrocenium cation is more and more difficult to be done from AN to DMSO.

In the present system, the electrochemical oxidation of ferrocene derivative corresponds to a reversible change between the neutral reduced form and the oxidized cationic form. The oxidized form is more sensitive to the interactions with the solvent molecules than the reduced neutral form.

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Therefore, the power of such interactions, involved between the cation and solvent molecules could be strongly influenced by the redox properties (donor number) of the solvent medium. As consequence, this behavior provides a strong electronic contribution from the solvent molecules influencing the oxidation reaction to yield the ferrocenic cations with an important increase of their $E_{1/2}$ values [35-37].
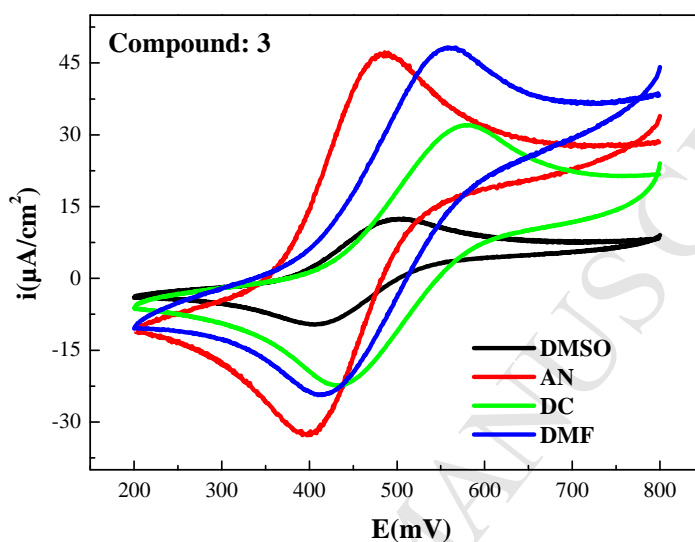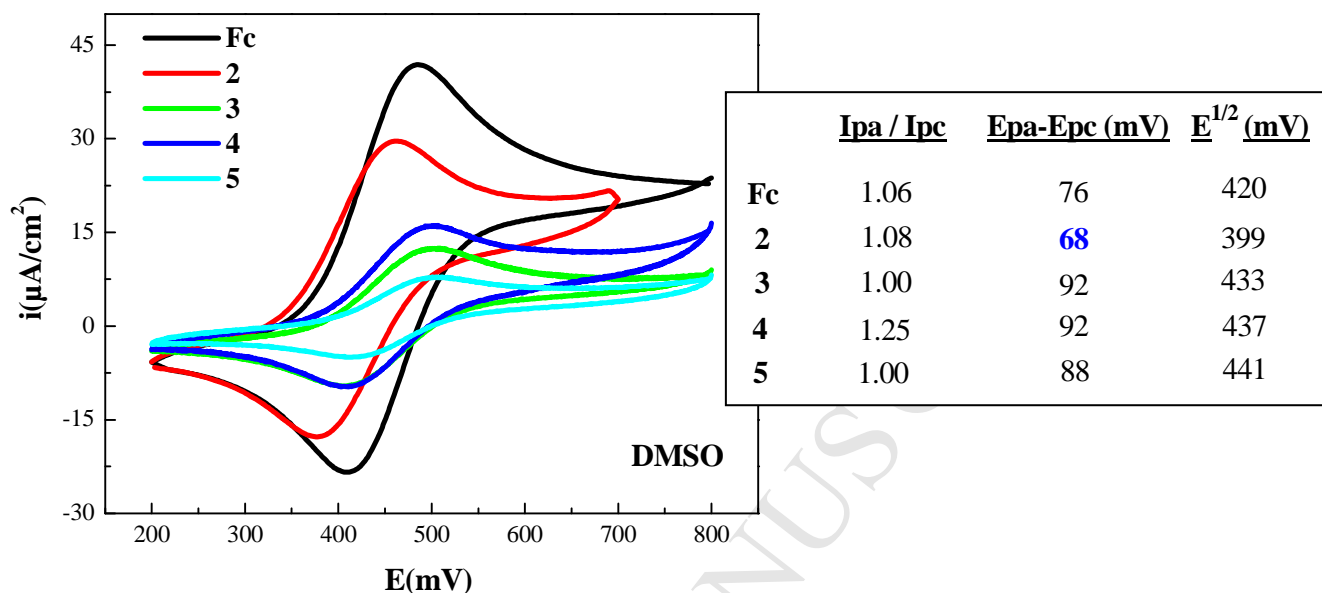

Fig.4 Cyclic voltammograms, recorded on glassy carbon electrode, showing the effect of the solvent medium on the electrochemistry of compound 3 (2.10^{-3} mol/L) (10^{-1} mol/L TBAP) using 100 mV.s^{-1} as scan rate.

➢ ***Effect of the Nature of Ferrocenyl derivatives on the Electrochemistry of Fc^+/Fc System in DMSO Medium***

Representative cyclic voltammograms of Fc$^+$/Fc in DMSO medium at 100 mV/s showing the effect of radical nature (**Fc-R**), are shown in **Fig. 5**. Ferrocenyl system exhibits reversible oxidation with all the synthesized ferrocenic compounds **2**, **3**, **4** and **5**. This reversibility exhibits some slight changes according to the nature of the studied compound. The anodic and cathodic peak separation (ΔEp) of these compounds was found to be variable in the range between 76 and 88 mV. The ΔEp value of compound **2** is in good accordance with Nernstian system. This observation indicates one-electron step oxidation and suggests an easy electron transfer as it was previously reported in similar studies [38]. The high ΔEp values, determined for other compounds can be attributed to the uncompensated resistance effect [39]. It was also observed that the peak currents ratio is near to the unity ($i_{pa}/i_{pc} = 1.0$) namely for the copper complex and also for some others like compound **3**. The

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difference in the half-wave potentials of ferrocene and its substituted derivatives could be explained based on the electron-withdrawing inductive effect of the substituents **[40]**.

	Ipa / Ipc	Epa-Epc (mV)	$E^{1/2}$ (mV)
Fc	1.06	76	420
2	1.08	**68**	399
3	1.00	92	433
4	1.25	92	437
5	1.00	88	441

Fig.5 Cyclic voltammograms, recorded on glassy carbon electrode, showing the effect of the Ferrocenyl derivative nature on the cyclic voltammetry of Fc^+/Fc system in DMSO medium (2.10^{-3} mol/L) (10^{-1} mol/L TBAP)) using 100 mV.s^{-1} as scan rate.

4. Conclusion

The ferrocenmethylaniline with other starting materials were successfully synthesized. So, four ferrocenyl derivatives were obtained via reactions sequence leading to the Schiff base ligand with its mononuclear copper complex. These resulting compounds were characterized by the usual physicochemical methods, such as elemental analysis, UV-Vis, FT-IR, and ^1H and ^{13}C NMR. The stoichiometry of the synthesized copper complex has been proposed based on elemental analysis data. The electrochemical behaviors of all the synthesized compounds were investigated by cyclic voltammetry using glassy carbon electrode in different solvents as dichloromethane, acetonitrile, dimethylformamide and dimethylsulfoxide. The redox couple Fc^+/Fc of these compounds **2**, **3**, **4** and **5**, show a reversible and a well defined monoelectronic system particularly in DMSO solvent compared to other solvents. Their half wave potentials ($E_{1/2}$) exhibit a good stability. This indicates that the ferrocenic couple could be used as an electrochemical reference avoiding any use of classical

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electrode materials. All the anilinic derivatives, synthesized in this study, may also be considered as electropolymerizable monomers which could be used in the fabrication of modified electrodes with their polyanilinic redox polymers.

Acknowledgement

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Highlights

- New ferrocenic compounds derived from Ferrocenmethylaniline and Cu-Salen.

- UV-Vis, FT-IR, Elemental analysis, NMR and Cyclic voltammetry.

- Studied of Fc^+/Fc redox couple using four aprotic organic solvents.

- Redox properties of ferrocenyl derivatives and their effect on the Fc^+/Fc system.