

## Crystal Structure and Electrochemical Properties of 1-(4-bromophenyl)-ferrocene-prop-2-en-1-one and 1-(3-(4-bromophenyl)-5-(ferrocene)-4.5-dihydropyrazol-1-yl) ethenone

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Compounds having redox-active ferrocenyl groups have attracted considerable interest in several branches of Chemistry and Materials Science. Here we investigate a chalcone (compound I) having a ferrocenyl group which is further derivatized to pyrazoline to achieve a hybrid molecule having a ferrocenyl couple to a heterocyclic ring (compound II). These compounds were characterized using spectroscopic techniques including the (<sup>1</sup>H-NMR and <sup>13</sup>C-NMR), UV–Visible and infrared (FT-IR) studies to confirm the structures and investigate the electronic properties of I and II. Furthermore, we confirmed the three-dimensional structures and any relevant interactions among the molecules in their unit cells using single crystal X-ray diffraction analysis. The molecules of both compounds stabilized by the C-H...halogen interactions, where Br acts as a halogen atom. Finally, the redox properties of I and II were accessed by cyclic voltammetry experiments. It is observed that the chalcone derivative has larger oxidation potential than the pyrazoline derivative.

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**Keywords:** Synthesis, Ferrocene, Pyrazoline

### 1. INTRODUCTION

Pyrazolines molecules are valuable materials for the preparation of various biologically active heterocyclic compounds [1] such as catalyzing the reaction by clay-cop. Hybrid molecules containing pyrazolines and sulfonamide moieties have also been used as a potent anti-inflammatory and anti-cancer agents [2]. Novel pyrazolines compounds have also been investigated for their unique

photophysical properties [3] and derivatives having pyrazoline, sulfonamide and indolyl moieties have been investigated as lipoxygenase and cyclo-oxygenase inhibitors [4]. A report showed that new pyrazolines were formulated by the reactions of chalcones and hydrazines which were studied as anti-inflammatory, anti-tumor, and analgesic active reagents [5]. Taking the benefit of the double bond present in the cyclohexene of  $\alpha,\beta$ -unsaturated steroidal ketones, new pyrazolines were prepared and investigated for antimicrobial activities and docking studies were also carried out [6]. Some novel pyrazoline molecules were also detected as very good antioxidants [7]. Finally, pyrazolines having ferrocenyl group in them were investigated as fluorescent materials their optical activities were also measured [8].

Ferrocenyl-containing molecules are getting a lot of attention for their interesting electrochemical activities [9,10]. Coordination complexes containing ferrocenyl and pyridine groups have also been synthesized and their electrochemical properties were investigated by means of cyclic voltammetry (CV) and X-ray photoelectron spectroscopy (XPS) [11]. In our literature search, we observed that there is a limited number of reports showing the synthesis of molecules having both pyrazolines and ferrocenyl groups in the same molecule. There is one report showing the promising synthesis of such hybrid molecules with interesting antioxidant activities and the reaction mechanism, thermodynamics and kinetics results were supported by density functional theory [12].

All the above valuable investigations encourage us to investigate in more details hybrid molecules with ferrocenyl and pyrazoline moieties (compound I and II). Thus, we have prepared two molecules functionalized with the ferrocenyl unit [Scheme 1] and their characterization was also performed using the spectroscopic techniques like UV-Vis, IR, NMR and finally the structures were confirmed by single crystal X-ray diffraction analysis. The crystal structures of these molecules have never been reported yet. These molecules were also characterized by electrochemistry using cyclic voltammetry technique.

## 2. EXPERIMENTAL DETAILS

### 2.1. Materials and general chemical characterization

#### *Synthesis*

All reagents and solvents were purchased from Aldrich, TCI America, and VWR and they were used without further purification. The NMR spectra were recorded in solution of  $\text{CDCl}_3$  (chloroform-d) or  $\text{CD}_2\text{Cl}_2$  (dichloromethane-d<sub>2</sub>) on AVANCE-III 400 MHz instrument (Bruker, Fallanden, Switzerland) at 300 K. Abbreviations for signal coupling are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. UV-Vis spectra were recorded on Evolution 300UV/VIS spectrophotometer (Thermo Scientific). IR spectra were recorded on a Thermo Scientific NICOLET iS50 FT-IR spectrometer (Thermo Scientific, Madison, WI, USA).

*Synthesis of 1-(4-bromophenyl)-ferrocene-prop-2-en-1-one (I).* One half of a mixture of 4-bromoacetophenone (1.5g, 0.0079mol) and ferrocenecarboxaldehyde (1.69g, 0.0079mol) in ethanol was added to a 50% ethanolic solution (20 ml) of sodium hydroxide (0.5g, 0.0119mol). The mixture

was allowed to stir at room temperature for 30 mins followed by the addition of the remaining reactant portion. Stirring was continued for another 3 hours. The precipitate produced was filtered and washed with chloroform. The color: Burgundy. Yield 95.38%.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ ppm: 4.18(s, 5H, *Cp*-H), 4.55(d, 4H, *Cp*-H), 7.066(d, 1H, Ar-H,  $J = 15.6$  Hz), 7.63(d, 2H, Ar-H,  $J = 7.8$  Hz), 7.767(d, 1H, Ar-H,  $J = 15.6$  Hz), 7.846(d, 1H, Ar-H,  $J = 7.8$  Hz).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ ppm 69.11, 69.86, 71.60, 78.96, 118.42, 127.35, 129.88, 131.81, 137.36, 147.62, 188.62. I.R ( $\text{cm}^{-1}$ ): Ferrocene (487), C-Br (821), aromatic C-C stretching (1580), C=O (1653), Aromatic C-H (3085). U.V. (nm):  $\lambda_{\text{max}} = 302.5$ , Concentration =  $2.4 \times 10^{-5}$  mole. Mass: 395.071 g/mole.

*Synthesis of 1-(3-(4-bromophenyl)-5-(ferrocene)-4.5-dihydropyrazol-1-yl)ethenone (II).* The mixture of 1-(4-bromophenyl)(ferrocene)prop-2-en-1-one (compound 1) (0.5g, 0.0013mole), hydrazine hydrate (0.64g, 0.0013mole), and (20ml) acetic acid was refluxed under stirring for 9-10 hrs. On completion of the reaction the mixture was quenched with ice, then the solid filtered, washed with water and recrystallized from chloroform. The color: grey, Yield: 81.56,  $^1\text{H-NMR}$  ( $\text{CDCl}_3\text{-d}_6$ )  $\delta$ ppm 2.309 (s, 3H,  $\text{CH}_3$ ), 3.49 (dd, 1H, CH-methylene), 3.64 (m, 1H, CH-methylene), 3.98 (t, 1H, *Cp*-H), 4.13 (s, 5H, *Cp*-H), 4.17 (m, 1H, *Cp*-H), 4.34 (t, 1H, *Cp*-H), 4.49 (t, 1H, *Cp*-H), 5.51 (dd, 1H, Chiral-H), 7.57 (dd, 2H, Ar-H), 7.67 (d, 2H, Ar-H),  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ ppm 22.02, 39.38, 55.60, 65.48, 66.38, 68.27, 68.44, 68.59x5C, 69.04, 69.68, 70.34, 76.80, 77.01, 77.22, 77.75, 87.13, 127.13, 127.95, 131.84, 132.04, 168.89, **IR**( $\text{cm}^{-1}$ ): Ferrocene (482), C-Br (814), aromatic C-C stretching (1591), C=O (1656), Aromatic C-H (3091). **U.V**(nm):  $\lambda_{\text{max}} = 258$ , Concentration =  $1.7 \times 10^{-5}$  mole. **Mass**: 480.20 g/mole.

## 2.2. Crystallography

The structure of both compounds was determined using single crystal X-ray diffraction technique. As per our search from CCDC the crystal structures of these compounds have never been reported before this. The selection of suitable crystals was performed under a microscope followed by their fixing on the tip of thin glass fiber. The sample holder is a copper hollow rod with a magnetic base. This sample holder was mounted on Agilent SuperNova (Dual source) Agilent Technologies Diffractometer for each sample, equipped with microfocus Cu/Mo  $K\alpha$  radiation for data collection. The data collection was accomplished using CrysAlisPro software[13] at 296 K under the Cu  $K\alpha$  radiation. The structure solution was performed using SHELXS-16 method[14] and refined by full-matrix least-squares methods on  $F^2$  using SHELXL-16 method,[14] in-built with WinGX[15]. All non-hydrogen atoms were refined anisotropically by full-matrix least squares methods. The Figures were generated through PLATON[16], ORTEP[17] inbuilt with WinGX and Olex2[18]. All the C-H hydrogen atoms were positioned geometrically with  $C_{\text{aromatic-H}} = 0.93$  Å,  $C_{\text{methyl-H}} = 0.96$  Å,  $C_{\text{methylene-H}} = 0.97$  Å &  $C_{\text{chiral-H}} = 0.98$  Å and treated as riding atoms with Uiso(H) was set to 1.2 Ueq(C) for aromatic, methylene & chiral carbon atoms. Similarly, Uiso(H) was set to 1.5 Ueq(C) for methyl carbon atoms. The Crystal data were deposited at the Cambridge Crystallographic Data Centre and following deposition numbers have been assigned 1841629 and 1841630 which are known as CCDC number for molecules **I**, and **II** respectively. Crystal data can be received free of charge on

application to CCDC 12 Union Road, Cambridge CB21 EZ, UK. (Fax: (+44) 1223 336-033; e-mail: data\_request@ccdc.cam.ac.uk).

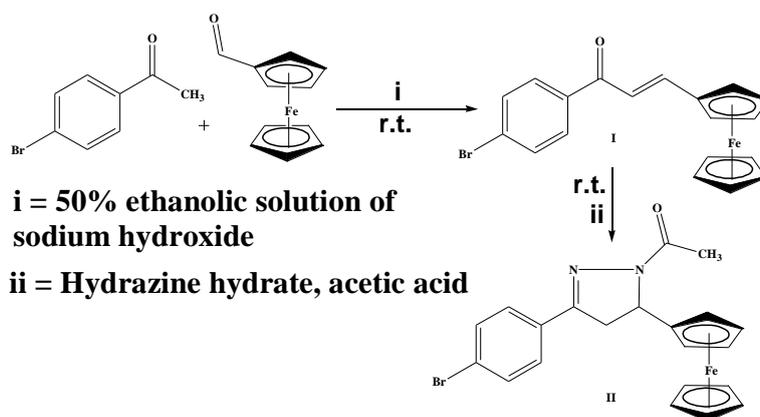
### 2.3. Electrochemistry

Electrochemical measurements were carried out using Epsilon Electrochemical Workstation equipped with BAS Epsilon software (Bioanalytical Systems, Inc., Lafayette, IN) in a 3-electrode cell configuration (VC-2 voltammetry cell), using 1.0 mm diameter glassy carbon working electrode, a Pt counter electrode, an Ag/AgCl reference electrode. Cyclic voltammetry measurements were performed in 0.1 M tetrabutylammonium hexafluorophosphate ( $\text{Bu}_4\text{N}^+\text{PF}_6^-$ ) acetonitrile solution at a scan rate of 100 mV/s.

## 3. RESULTS AND DISCUSSION

The preparation of the ferrocene-based chalcone and pyrazoline molecules for the present study was achieved following small variation of procedures described in our previous studies [19–22]. The first reaction in the present scheme is following the Claisen-Schmidt mechanism for the synthesis of chalcones [23, 24]. According to this mechanism in basic medium [25] active methylene group of ketonic compound reacts with the carbonyl group of aldehydes. In our case methylene group from 4-bromoacetophenone reacts with the carbonyl of ferrocenecarboxaldehyde to produce chalcone. The reaction yield was very promising for this target molecule. The obtained yield is 95% which is better than the yield of some similar compounds in other reports [26, 27]. This chalcone was further reacted with hydrazine hydrate in the presence of aliphatic acid [28], which is acetic acid in the current study. The acetyl group of acetic acid takes part in reaction and substitute a hydrogen atom of the one of the nitrogen atoms of hydrazine as a side chain to form the amide group. The workup yield is in comparison with already reported procedure [28].

The characterization was accomplished by nuclear magnetic resonance (NMR) spectroscopy along with UV/VIS and IR spectroscopic techniques. We have carried out  $^1\text{H}$ -NMR as well as  $^{13}\text{C}$ -NMR spectroscopy to identify the number of protons and carbon in the molecules along with their positions. These spectra are shown in Figures S1-S4.



**Scheme 1.** Synthesis of compounds I and II.

Compound I, i.e. the chalcone has only aromatic and *cp*(cyclopentadienyl)-protons along with the C=C ones. The aromatic protons are observed in the range of 7.05 – 7.85 ppm. There is a doublet with a  $J = 15.6$  Hz, at 7.07 ppm showing the presence of one proton. A doublet at 7.63 ppm with the  $J = 7.80$  Hz, showing the presence of two protons. The third doublet at 7.67 ppm with  $J = 15.60$  Hz, is indicating the presence of only one proton. The fourth doublet with  $J = 7.80$  Hz, at 7.84 ppm showing the presence of two protons. From the above values, we can conjecture that the protons at 7.63 and 7.84 ppm are those of the aromatic rings and the remaining two protons (at 7.07 and 7.67) belong to the double bond between the ferrocenyl and ketone functional groups. The data published by Attar et al [27] for 63 chalcones having ferrocenyl group in them shows that these protons appeared in the range of 6.61-8.69. The five *cp*-protons appeared at 4.19 ppm as a singlet and the remaining four *cp*-protons appeared as a doublet at 4.55 ppm Figure S1. The C-13 spectrum indicates that there are eleven peaks for the nineteen carbon atoms. A strong peak at 69.857 ppm represents the five-carbon atom of one of the cyclopentadienyl of the ferrocene ring. Two peaks at 69.11 and 71.60 ppm are associated to the four carbons of the other *cp*ferrocenyl ring. A peak at 78.96 ppm represents the presence of fifth carbon atom of *cp*ferrocenyl ring. The carbonyl carbon atom appeared at 188.62 ppm while all the other aromatic carbon atoms appeared in the range of 118.43- 147.96 ppm (see Figure S2).

Compound II, i.e. the pyrazoline derivative was also well characterized using the NMR spectroscopy. The methyl hydrogens appeared at 2.31 ppm as a singlet. There are nineteen protons in total for this molecule. The two hydrogens of the methylene group of the pyrazoline ring are located at 3.49 and 3.64 ppm as a doublet of doublet each while in literature we found that these protons appeared at 3.19 and 3.79 [29]. In a report from our group where we have published crystal structures of five pyrazolines, these methylene hydrogen atoms appeared in the range of 3.09-3.92 [30]. The chiral carbon of the pyrazoline ring is located at 5.51 ppm as doublet of doublet. The two protons of the aromatic ring are at 7.57 ppm as a doublet of doublet while other two hydrogens appeared at 7.67 ppm as a doublet. The ferrocenyl ring has nine protons, five from these appeared as singlet at 4.131 ppm while the other four appeared in separate four peaks. The peaks at 3.98, 4.17, 4.34 and 4.49 ppm indicate the presence of one proton atom of the *cp*-ring (Figure S3). The five carbon atoms of one of the *cp*-ring are located at 68.591 ppm while the other five carbon atoms occupy a different position, (see experimental section). The carbonyl carbon atom is located at 168.89 ppm. The peak at 22.027 ppm might be for the only methyl group present in the molecule. The other carbon atoms of the pyrazoline and aromatic rings are located in the expected regions (for details please see the experimental section, Figure S4). All these data confirm the identity of the two molecules.

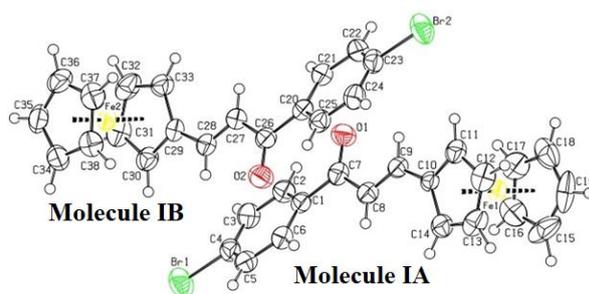
### 3.1. UV and IR Characterization

The Ultraviolet/Visible spectra of both molecules were measured in solution to access their maximum absorption ( $\lambda_{max}$ ) values. The solutions of I and II were prepared in methanol with concentrations of  $2.4 \times 10^{-5}$  and  $1.7 \times 10^{-5}$  M, respectively. Compound I has a more extended  $\pi$ -conjugation than the compound II, which resulted in a higher  $\lambda_{max}$  value for the former molecule ( $\lambda_{max} = 302.5$  nm for I and  $\lambda_{max} = 258$  nm for II). The UV/Vis  $\lambda_{max}$  values for five similar molecules were reported in the range of 263-311 nm and molecules in this report also have  $\lambda_{max}$  in the range [30]. This

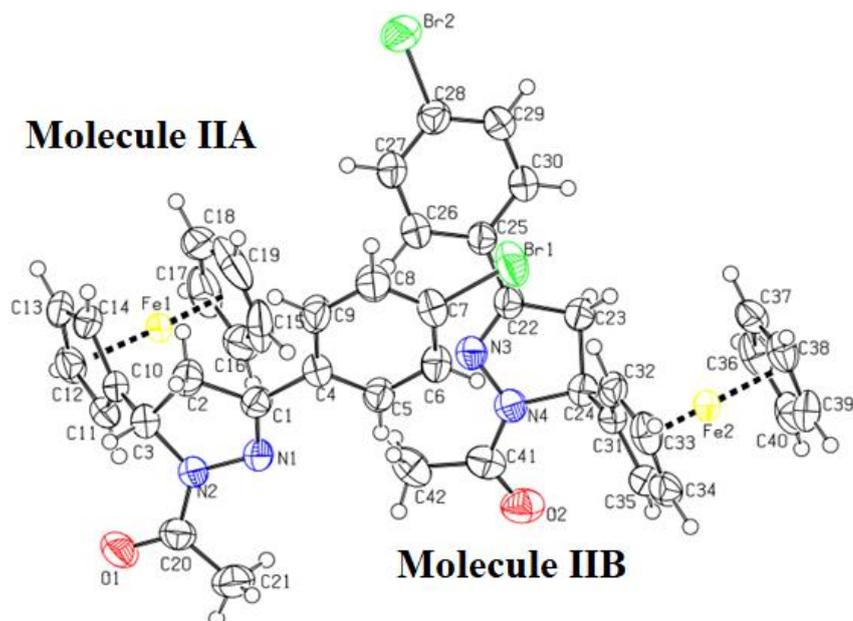
band corresponds to  $\pi$ - $\pi^*$  transition in both molecules (Figures S5-S6). The IR spectrum for both molecules was also recorded to determine the characteristic peaks of the different functional groups. The IR peaks for the ferrocene group appeared at 487 and 482  $\text{cm}^{-1}$  for the chalcone and pyrazoline derivatives, respectively, while the C-Br stretching were observed at 821 and 814  $\text{cm}^{-1}$  for the chalcone and pyrazoline derivatives respectively. Similar materials showed the frequencies range for C-Br bond as of 704-1050  $\text{cm}^{-1}$ , this means the values of molecules in the present study are in accordance with the literature [30]. The aromatic C-C stretching peaks detected at 1580 and 1591  $\text{cm}^{-1}$  are assigned to the chalcone and pyrazoline derivatives, respectively. The peaks at 1653 and 1656  $\text{cm}^{-1}$  showed the presence of carbonyl groups in both the molecules. Similarly, the aromatic C-H stretching appeared at 3085 and 3091 for the chalcone and pyrazoline derivatives, respectively (Figures S7-S8).

### 3.2. Crystal Structure Description

Both molecules belong to a series where firstly chalcone was prepared which further reacted with hydrazine hydrate in glacial acetic acid to produce the pyrazoline ring. The single crystal X-ray diffraction study confirmed the molecular structure of the proposed molecules. Compound I adopted an orthorhombic crystal system with a  $Pca2_1$  space group while II adjusted itself in monoclinic crystal system with a  $P21/a$  space group (Table 1). Bond lengths and bond angles for compounds I and II are collected in Tables S1 and S2 and these are in comparison with the reported crystal structures [30]. Both compounds have two independent molecules per their unit cells (Figures 1 and 2). In the compound I, the centroid distances between the planes of each  $cp$  rings are 3.311Å and 3.319Å for molecule Ia and Ib, respectively. Both the  $cp$  rings have stabilized themselves in an eclipsed conformation. The central backbone prop-2-en-1-one is attached to 4-bromophenyl ring on one side while ferrocenyl moiety on the other side. 4-Bromophenyl ring is twisted at a dihedral angle of 24.651 (4)° and 24.288 (4)° with respect to the plane produced from the atoms of prop-2-en-1-one in molecule IA and IB respectively. We have observed weak hydrogen bonding, where, bromine atom of molecule IA acts as acceptor and C38 of molecule IB acts as a hydrogen donor to form the dimers (Figure 3).

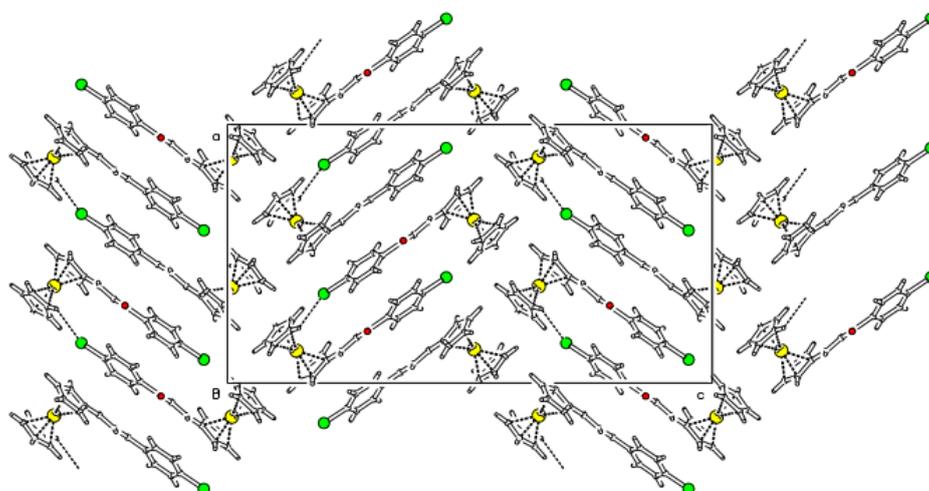


**Figure 1.** ORTEP labelled diagram of compound I, where thermal ellipsoids were drawn at 50% probability level.

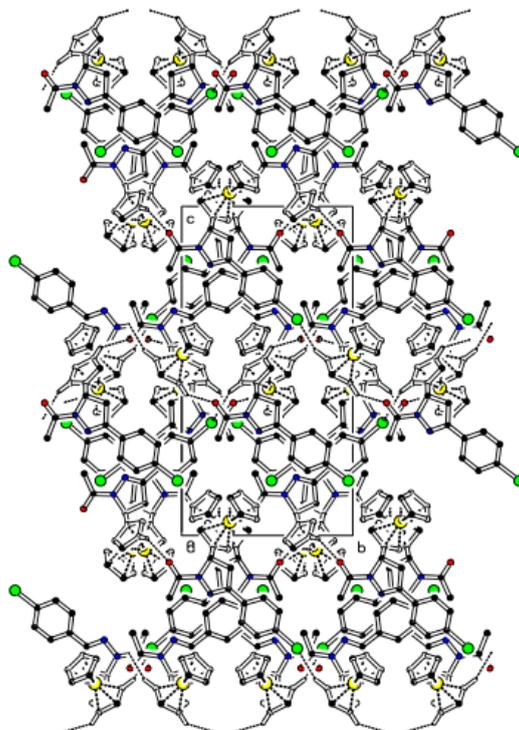


**Figure 2.** ORTEP labelled diagram of compound II, where thermal ellipsoids were drawn at 50% probability level.

In compound II, the central pyrazoline ring is connected to 4-bromophenyl ring, acetyl, and the ferrocenyl groups. The root mean square (r.m.s.) deviation for the pyrazoline rings in molecule IIA and IIB are  $0.0594\text{\AA}$  and  $0.0842\text{\AA}$ , respectively. In both molecules the pyrazoline ring adopted the envelope conformation where the atoms C2 and C3 are deviating by  $0.0717(2)\text{\AA}$  and  $-0.0800(2)\text{\AA}$  in molecule A while in molecule B the most deviations were shown by  $C23 = -0.1026(2)\text{\AA}$  and  $C24 = 0.1129(2)\text{\AA}$  from the mean plane produced from the remaining atoms.



**Figure 3.** A unit cell view along *ac*-planes showing the C-H...Br interaction in molecule I.

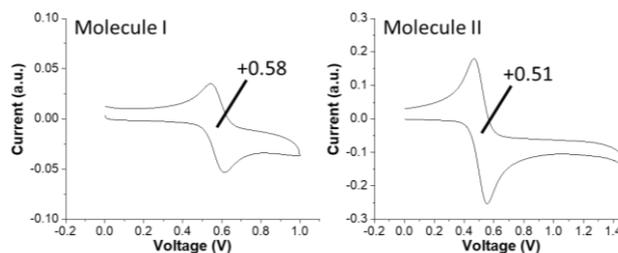


**Figure 4.** A unit cell molecular packing diagram showing a view along *bc* plane, in molecule II. Hydrogen bonding were shown using dashed lines.

The two *cp* rings adopted the eclipsed conformation in both the molecules. The dihedral angle between the pyrazoline and 4-bromophenyl ring are  $8.31(14)^\circ$  and  $7.107(17)^\circ$  in molecule IIA and IIB, respectively. The acetyl group is oriented at dihedral angle of  $18.48(25)^\circ$  and  $16.75(27)^\circ$  with the pyrazoline ring in molecule IIA and IIB, respectively. Atoms C13 and C33 in the reference molecule at  $(x, y, z)$  act as a hydrogen-bond donor *via* H13 and H33, to atoms O1 and O2 at  $(1/2-x, y+1/2, 1-z)$  and  $(1/2-x, y+1/2, 2-z)$  respectively, so connect the molecules in a zig-zag fashion to generate two different chains along the  $(0\ 0\ 1)$  base vector (Figures 4 and S9, Table 2). A C-H...Br type weak interaction connects these two chains along the *b*-axis and produces two-dimensional network along the *bc*-plane (Figures 4 and S9, Table 2).

### 3.3. Electrochemistry

It is well established that Ferrocene can easily undergo reversible one-electron oxidation to form ferricenium cation. Thus, we investigated the ferrocene electrochemical behaviors of compounds I and II in solution by cyclic voltammetry (CV) experiment. All experiments were carried out at a concentration of  $\sim 10^{-3}$  M in deoxygenated anhydrous acetonitrile using a glassy carbon working electrode, a Pt counter electrode, an Ag/AgCl reference electrode, and 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte. Each solution was scanned at scan rate equal to 100 mV/s.



**Figure 5.** Cyclic voltammograms (0.1 M  $\text{Bu}_4\text{N}^+\text{PF}_6^-$ , scan rate = 100  $\text{mV s}^{-1}$ ) of compounds I and II.

Representative CV curves and electrochemical parameters are shown in Figure 5, which clearly demonstrate characteristic reversible oxidation of ferrocene-containing molecules. Thus, molecule I exhibit anodic and cathodic redox processes at +0.545 and +0.613 V while those of molecule II occur at +0.465 and +0.555 V. The potential difference between the anodic and cathodic peaks, 0.073 and 0.090 V, are larger than the idea 0.059 V at room temperature, due to a slower than ideal electron transfer. For these data, the half-wave reversible oxidation potentials of compounds I and II are measured at +0.58 and +0.51 V, respectively. The larger oxidation potential of compound I is likely due to the conjugation with the electron-withdrawing C=O group, making the molecule harder to oxidize compared to II. However, both oxidation potentials are closed to that measured for ferrocene in our system (+0.46 V). Thus, attachment of the Fc unit to both the keto and pyrazoline functionalities does not substantially affect the redox properties of the ferrocenyl group.

#### 4. CONCLUSIONS

We investigated chalcone and pyrazoline compounds functionalized with a redox-active ferrocenyl unit. These molecules were characterized using several techniques and their molecular structure accessed by single crystal X-ray diffraction technique and discussed geometry and packing characteristics. The structures are stabilized by the non-classical symmetry related hydrogen bonding interactions which form dimers in the structure of compound I and generate two-dimensional network for compound II. Finally, the electrochemical properties of both systems were studied by cyclic voltammetry demonstrating the redox-active ferrocenyl group preserves its electrochemical characteristics when incorporated into these molecules.

SUPPORTING MATERIAL:

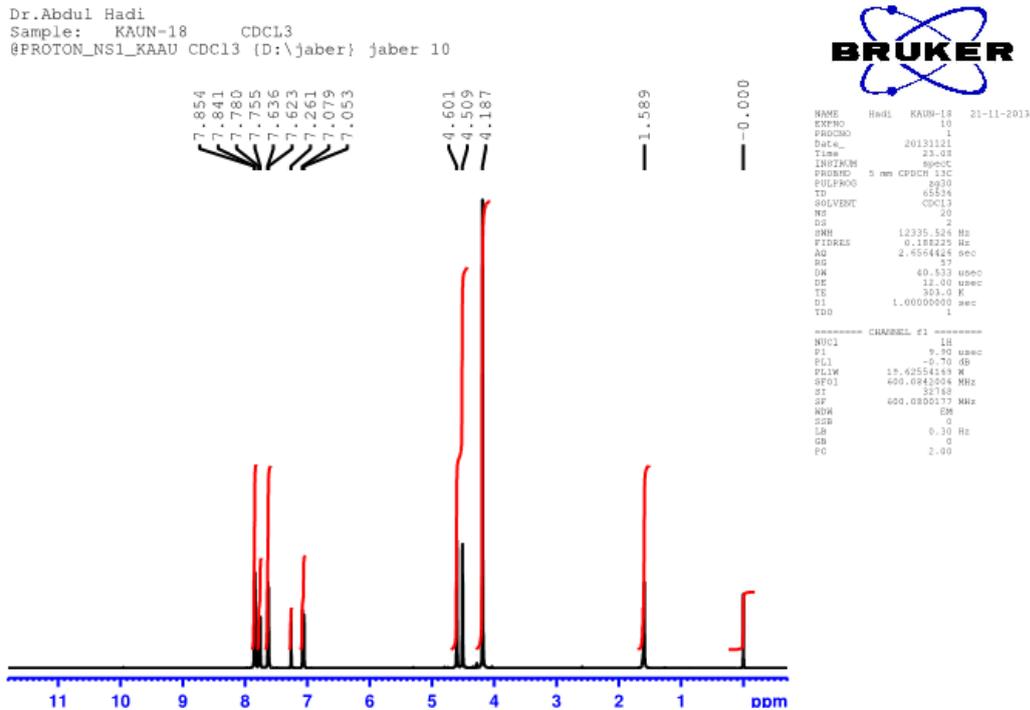


Figure S1: <sup>1</sup>H-NMR of Chalcone

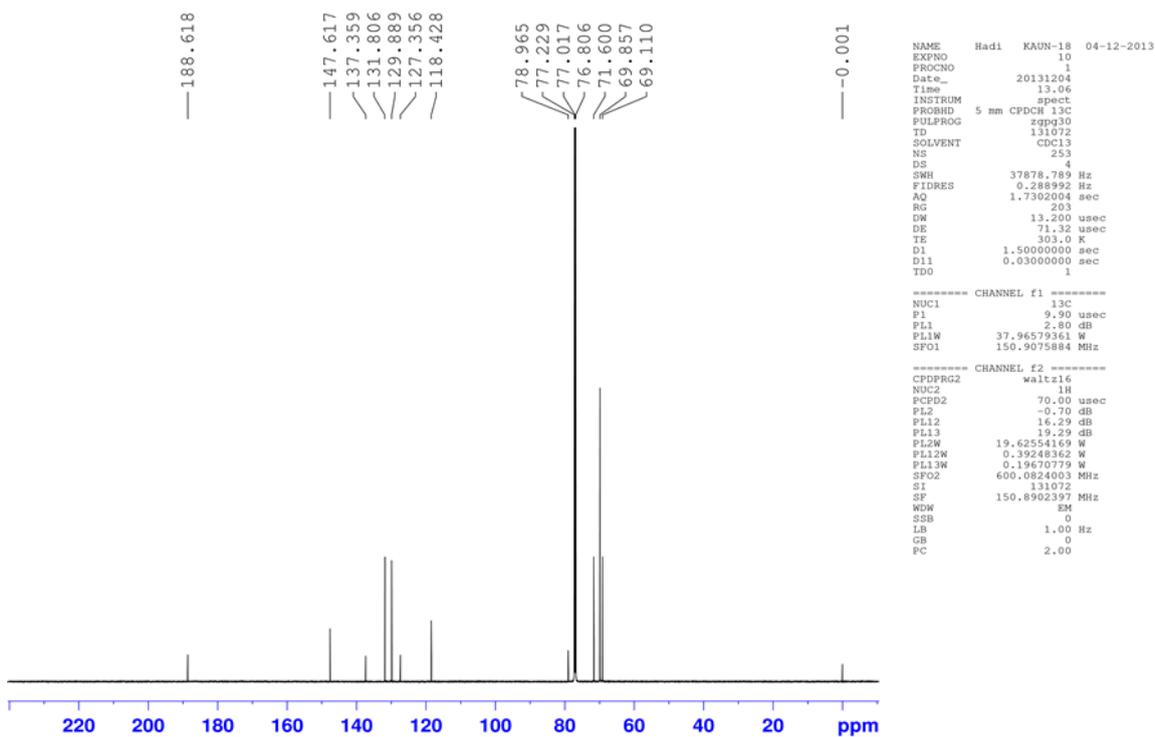


Figure S2: <sup>13</sup>C-NMR of Chalcone

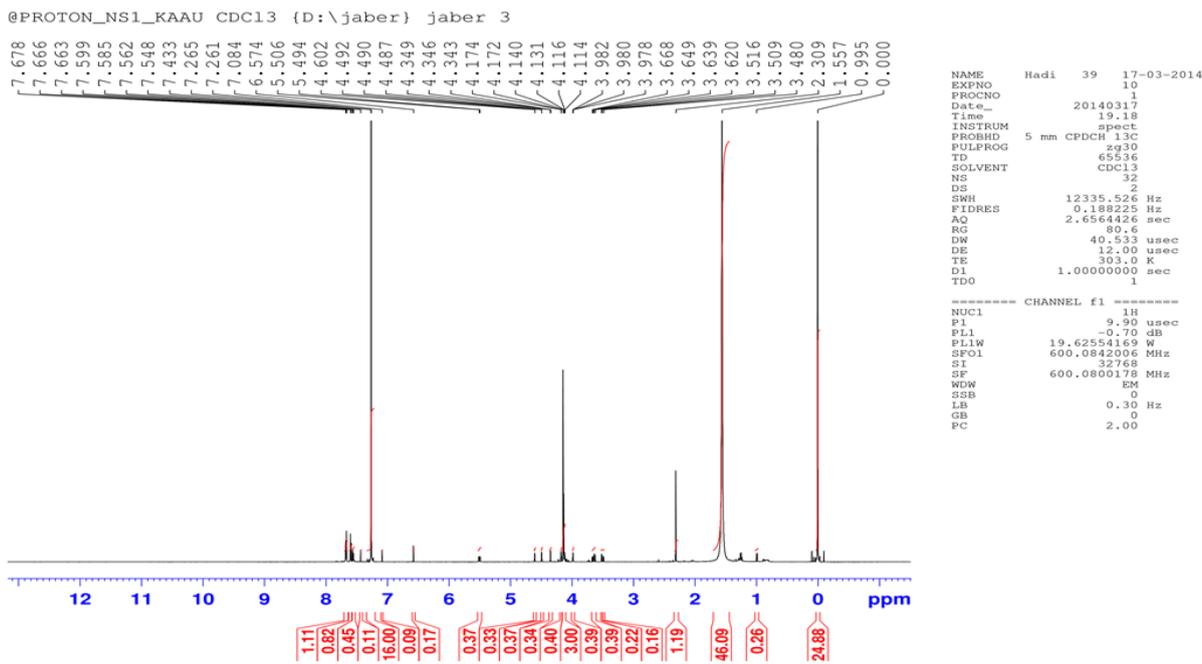


Figure S3: <sup>1</sup>H-NMR of Pyrazoline

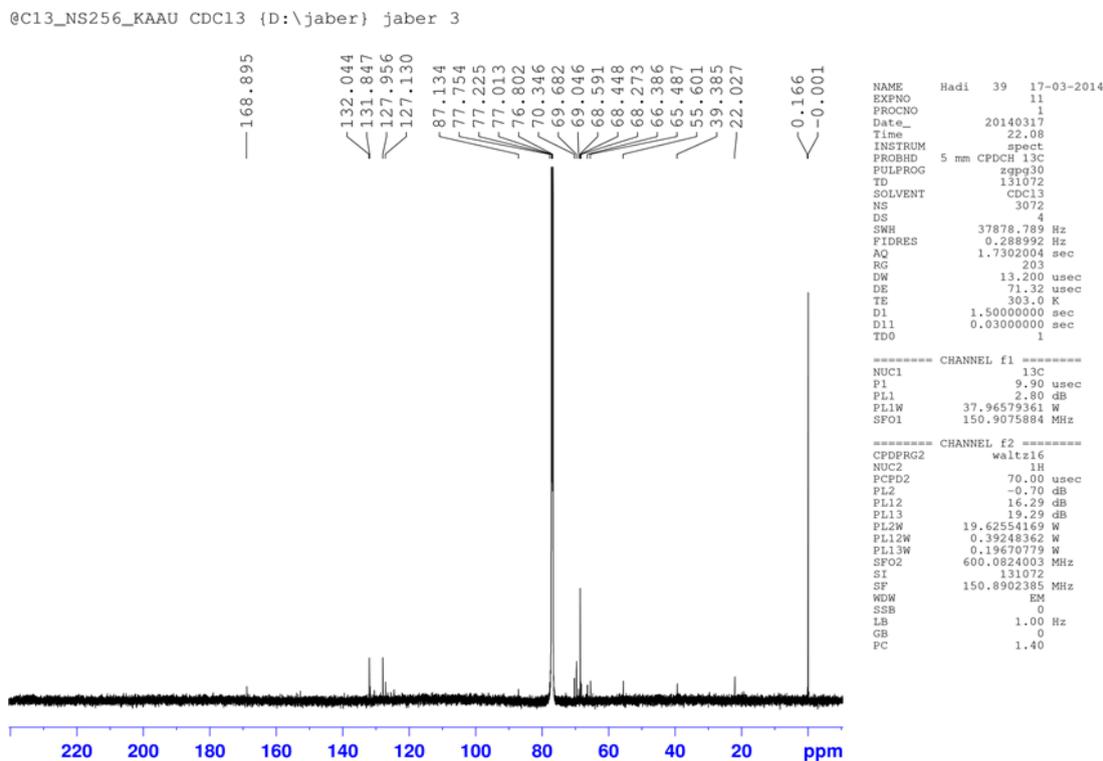


Figure S4: <sup>13</sup>C-NMR of Pyrazoline

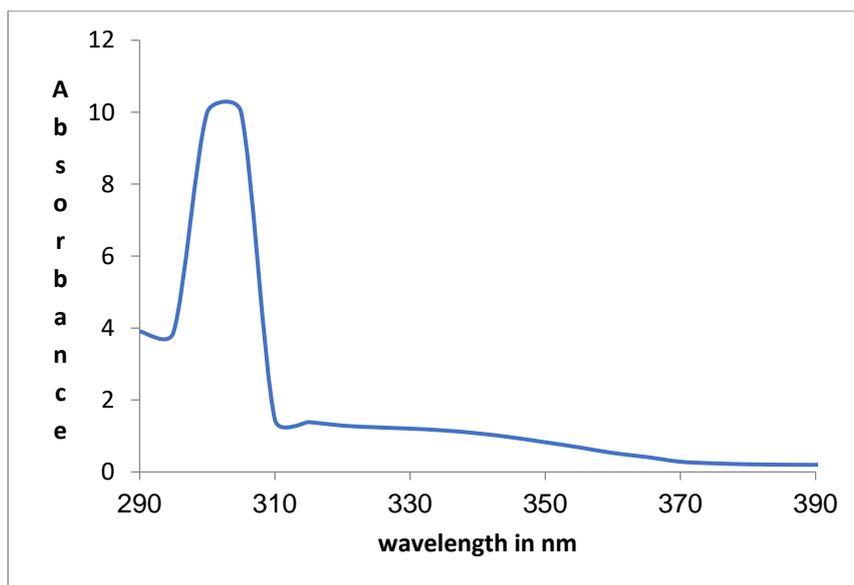


Figure S5: UV spectrum of compound I.

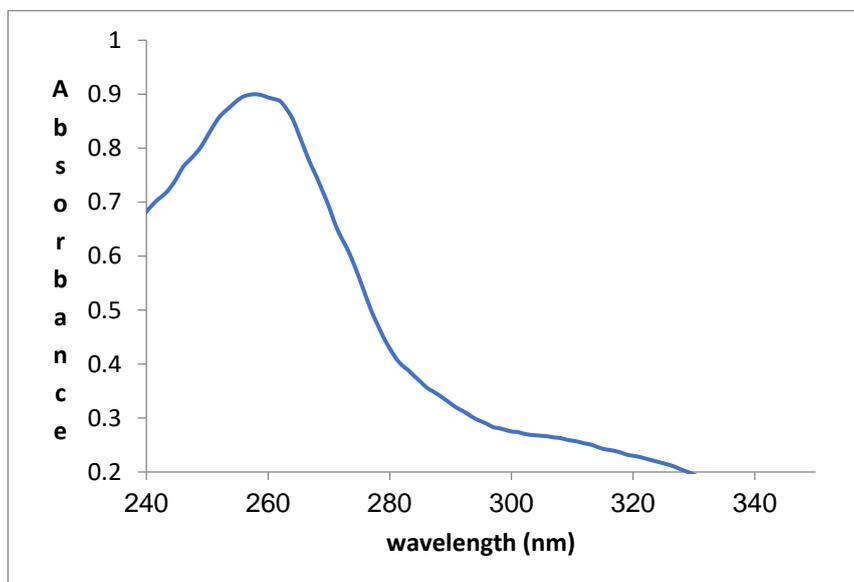
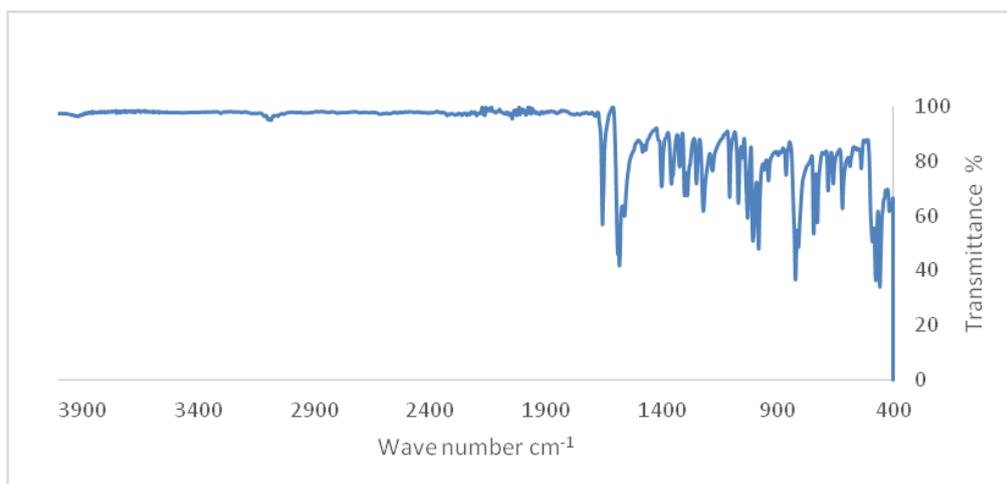
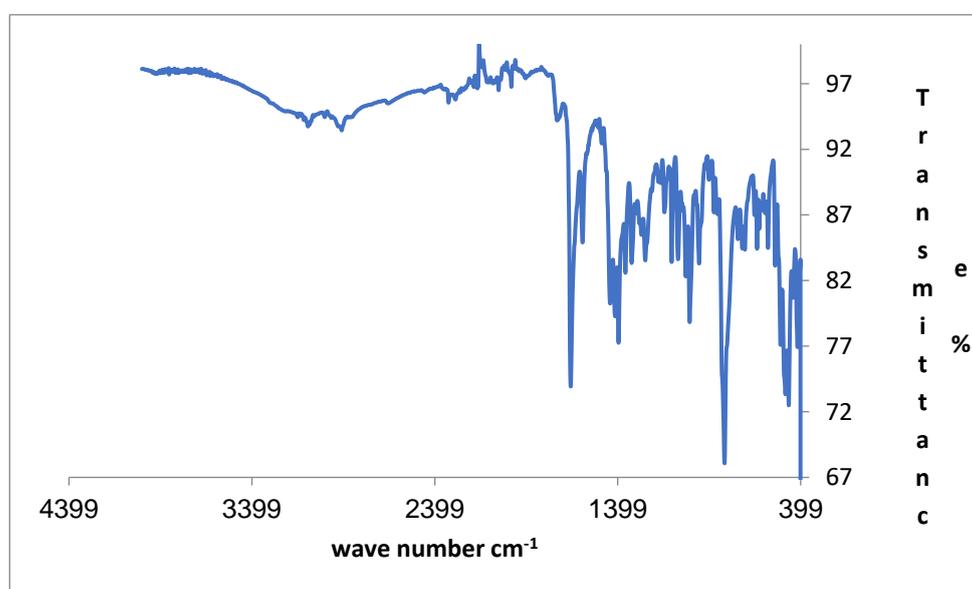


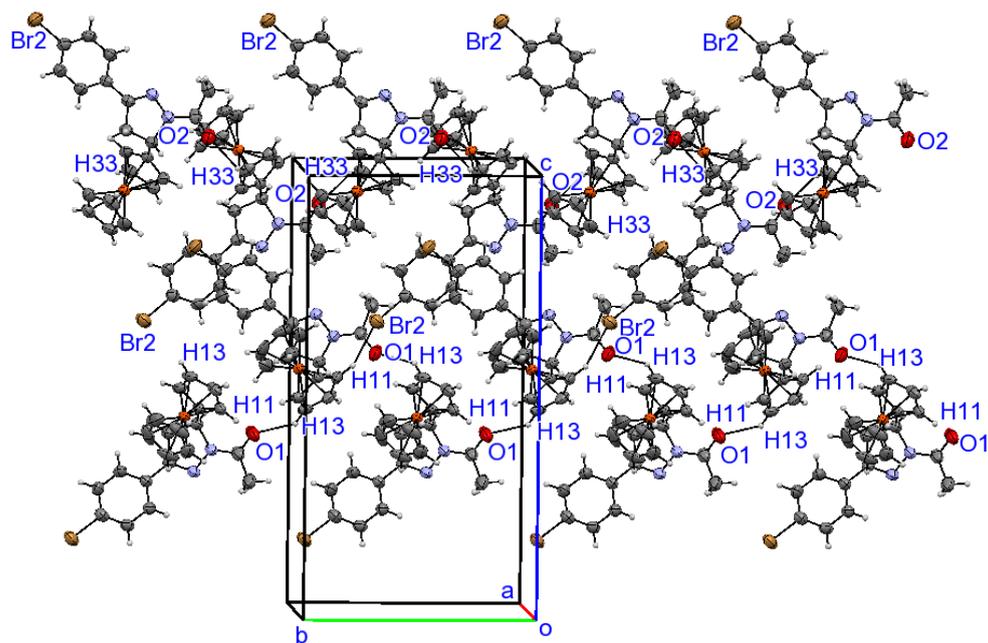
Figure S6: UV spectrum of compound II.



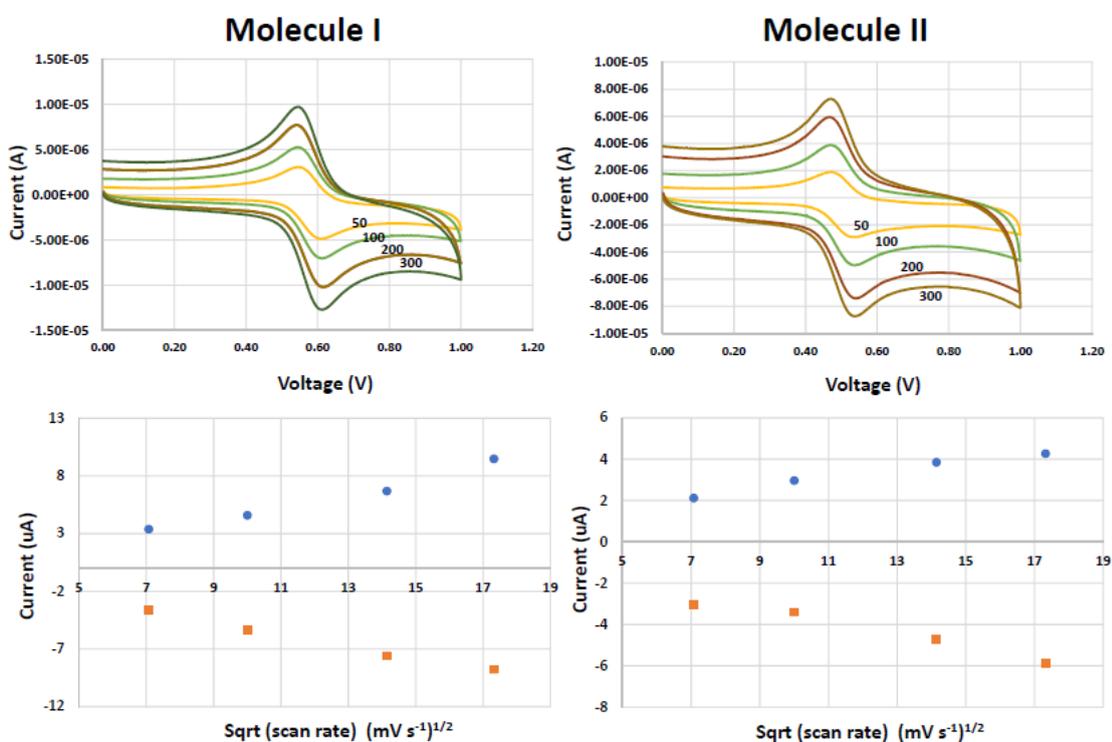
**Figure S7:** IR spectrum of compound I.



**Figure S8:** IR spectrum of compound II.



**Figure S9:** A unit cell view showing the hydrogen bonding interactions among molecules of compound II.



**Figure S10:** Cyclic voltammograms (top, 0.1 M  $\text{Bu}_4\text{N}^+\text{PF}_6^-$ , scan rate from 50 to 300  $\text{mV s}^{-1}$ ) and current-sqrt(rate) plots (bottom) of compounds I and II in acetonitrile vs. vs  $\text{Ag}/\text{AgCl}$ .

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