

Electrochemical and Spectroscopical Characterization of Ferrocenyl Chalcones

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We report on the electrochemical and spectroscopical characterization of 10 ferrocenyl chalcones. These compounds were synthesized via the Claisen–Schmith condensation from acetylferrocene and the corresponding benzaldehyde or pyridine carboxal-dehyde. The compounds were obtained in good yields (>60%) and purified by recrystallization. All compounds exhibit a quasi-reversible electrochemical behavior and chemical reversibility, as evidenced by ΔE_p of 72–90 mV and I_{pa}/I_{pc} values equal to 1.0–1.17. The redox formal potential ($E^{0'}$) for these compounds range between 665 and 774 mV. The heterogeneous electron-transfer rate constants calculated from the Nicholson method are in the range of (2.0–4.4) × 10⁻² cm/s. Their diffusion coefficients are on the order of (1.65–3.7) × 10⁻⁵ cm²/s, and the number of electrons transferred equals 1. 1-ferrocenyl-3-(p-N,N-dimethylaminophenyl)prop-2-en-1-one shows a behavior similar to dimethylaniline and undergoes electrophymerization, producing cationic oligomers and dimeric species. The UV/visible spectra show the characteristic bands for aromatic systems in the UV region (200 and 280 nm) and bands in the visible (400 and 500 nm). The molar absorbance coefficient (ε) values are in the ranges (2.1–7.5) × 10⁴ L/(mol cm) for λ_{max} of 200–300 nm and (1.8–17.6) × 10² L/(mol cm) for λ_{max} of 300–500 nm.

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Ferrocene derivatives have been extensively studied for many reasons. First, they exhibit the well-defined one-electron redox process that is characteristic of ferrocene. The redox process is electrochemically reversible or quasi-reversible, and the formal redox potential ($E^{o'}$) depends on the nature of the substituents attached to the cyclopentadienyl rings.^{1,2} Through a variety of synthetic routes, derivatives can be made with tunable redox and spectroscopical properties.^{2,3} They have found applications in different fields such as biosensors,³⁻⁵ drug delivery systems,⁶ electrocatalyts,^{7,8} and optoelectronics,⁹ among others.

A family of ferrocene derivatives that have drawn considerable attention from scientists in recent years is that of the ferrocenyl chalcones (FCs).¹⁰⁻¹² These compounds not only possess the redox activity of ferrocene, but they also show intense colors.¹² An FC is a compound where ferrocene is linked to an aromatic group through an enone moiety. Several derivatives of FCs have been synthesized and characterized structurally.¹⁰⁻¹³ More recently, studies on FCs have focused on their biological properties, in particular their potential antiplasmodial and anticancer activity.¹¹

In our case, we are interested in exploiting these compounds for applications in biosensing and electrocatalysis. For that purpose, we conducted a study of the electrochemical and UV/visible (UV/vis) behavior of several FCs (Fig. 1). To the best of our knowledge, few studies have been published using FCs for these applications.

Experimental

Chemicals.-- Ferrocene (98%), acetylferrocene (95%). (99%), 3-nitrobenzaldehyde (98%), 4-nitrobenzaldehvde 4-methoxybenzaldehyde (98%), 4-chlorobenzaldehyde (98%). 4-(dimethylamino) benzaldehyde (≥99%), 2-fluorobenzaldehyde (97%), 3-fluorobenzaldehyde (97%), 2-pyridinecarboxaldehyde (99%), 3-pyridinecarboxaldehyde (98%), 4-pyridinecarboxaldehyde (97%), tetrabutylammonium perchlorate (TBAP), acetonitrile (ACN)-d₃ (99.6% D), chloroform-d (99.8% D), acetone, and ethanol (American Chemical Society grade) were obtained from Aldrich. ACN (Burdick and Jackson) was dried over 4 Å molecular sieves. Diamond paste (no. 40-6244) and metadi fluid (no. 40-6032) were

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from Buehler Co. Nanopure water (17 M Ω cm, Barnstead) was used in all experiments. Thin-layer chromatography (TLC) was done with 250 μ m Al₂O₃ plates (Whatman).

Synthesis and characterization of the compounds.— FCs were synthesized in Dr. I. Montes' laboratory following the Claisen–Schmidt reaction, as previously published.^{11,14,15} ¹H and ¹³C NMR spectra were taken in a 500 MHz Bruker-AV spectrometer, while the UV/vis spectra were done in a Perkin-Elmer (Lambda 35) spectro-photometer.

Synthesis of FCs.— 1 mmol of acetylferrocene was added to a 50 mL erlenmeyer flask and dissolved in a 1:1 ethanol/water solution with 10 mmol of NaOH at room temperature. In another flask, 1 mmol of the desired aromatic derivative was mixed with 3-5 mL of ethanol. The acetylferrocene solution was added slowly to the solution of the substituted benzaldehyde or pyridine carboxaldehyde under continuous stirring. The reaction progress was followed by TLC until completion. The resultant precipitate was collected by vacuum filtration and recrystallized. Compounds 2a and 2e were recrystallized from acetone, 2d from ethanol, and 2j from 1:1 ethanol/water. Mixtures of 1:1 acetone/water were used to recrystallize compounds 2b, 2f, 2g, 2h, 2i, and 2k, while a 2:1 mixture was used for compound 2c.

Methylation of DMAPP.— In a round flask, 1 mmol of 1-ferrocenyl-3-(p-N,N-dimethylaminophenyl) prop-2-en-1-one (DMAPP) and 8 mmol of sodium bicarbonate were dissolved in 2-methyl tetrahydrofuran. The mixture was stirred under N₂, while 16 mmol of dimethylsulfate was added dropwise. After 1 h stirring at room temperature, the temperature was raised to 60°C for 2 h. The resulting precipitate was collected and dried. The purification was done by recrystallization from 1:1 acetone/water mixture.

Electrochemistry.— All electrochemical experiments were done in a BAS 100 B/W. A three-electrode electrochemical cell was used with Pt (area = 0.0197 cm²) or glassy carbon (area = 0.080 cm²), Ag/AgCl (NaCl 3 M), and nichrome as the working, reference, and counter electrodes, respectively. The Pt electrode surface was polished with diamond paste/metadi fluid in a microcloth and rinsed with water. Subsequently, the electrode was cycled in 1 M H₂SO₄ solution from -200 to 1200 mV at 100 mV/s for 50 cycles, rinsed with water and air dried.

For each compound, a 10 mL of $\sim 1 \times 10^{-3}$ M solution was prepared in 0.1 M TBAP/ACN. Cyclic voltammetry (CV) was run for each compound at scan rates of 20, 50, 100, 200, 500, 1000, and

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Figure 1. Synthesis of FCs.

2000 mV/s. 1 and 10 cycles were done for each scan rate, and the electrode was cleaned between scan rates. Each experiment was run three times, every time with a fresh solution. The background was recorded for each compound under the same experimental conditions of the sample. The cell was degasified with N₂ for 10–15 min before each measurement. To determine the number of electrons transferred, a 10 mL TBAP 0.1 M/ACN solution containing ~1 \times 10⁻³ M of both ferrocene and the FC was prepared. A CV of the solution was recorded at 100 mV/s between 0 and 1200 mV. Chronocoulometry (CC) was done in a similar solution but without the ferrocene to determine the diffusion coefficient of the compounds. The applied potential pulse was from 200 to 1200 mV for 250 ms.

UV/vis spectroscopy.— The molar extinction coefficients of the most prominent UV/vis bands of the compounds were calculated from calibration curves following Beer's law. A 1×10^{-3} M stock solution of each compound was prepared in ACN followed by dilutions with concentrations in the (2–1000) $\times 10^{-6}$ M range. Absorption spectra of all compounds were taken from 190–820 nm. The cell path was 1.00 cm.

Results and Discussion

Synthesis and chemical characterization.- The FCs differ in the aromatic derivative attached to the double bond. The o- and m-fluorophenyl derivatives (2f, 2g) have not been reported until now. All the compounds were obtained in good yields (>60%) and were characterized by ¹H and ¹³C NMR after purification. Figure 2 shows the ¹H and ¹³C NMR spectra of DMAPP (2c). The ¹H NMR shows three characteristic regions: the ferrocene [δ (ppm) = 4.894 (s, 2H), 4.555 (s, 2H), 4.184 (s, 5H)], the p-N,N-dimethylaminephenyl [δ (ppm) = 7.612 (d, J = 9 Hz, 2H), 6.758 (d, J = 8.5 Hz, 2H), 3.003 (s, 6H)], and the double bond [δ (ppm) = 7.600 (d, J = 13.5 Hz, 1H), 7.082 (d, J = 15.5 Hz, 1H].¹³C NMR spectra show the expected number of signals according to the number of carbon atoms with chemical shifts as follows: ferſδ (ppm) = 82.59,73.19, rocene 70.78, 70.36]. *p-N,N*-dimethylaminephenyl [δ (ppm) = 153.07, 131.02, 112.90, 40.38], the carbonyl [δ (ppm) = 193.13], and double bond [δ (ppm) = 141.72, 123.62]. All FC compounds showed signals corresponding to these three distinct regions. The ¹H chemical shifts corresponding to the ferrocene and double-bond regions were basically unaltered by the aromatic derivatives. As expected, the ¹H chemical shifts of the aromatic derivative changed depending on the substituents on the phenyl or the position of the nitrogen atom in the pyridine. Similar results were observed for the ¹³C NMR where the ferrocene, carbonyl, and double-bond signals did not change significantly. The ¹³C NMR for the aromatic derivative followed the expected pattern depending on the compound molecular structure. Our results compare favorably with previously published values by Sol-



Figure 2. ¹H and ¹³C NMR of DMAPP (2c) in CD₃CN.

caniova and co-workers.¹⁶ See tables in the supporting information section¹⁷ for a summary of the spectral analysis of the studied compounds.

Electrochemical characterization.— The redox activity of the FCs was studied using CV and CC. Figure 3A-C shows the CVs, I_{pa} vs the square root of the sweep rate curve (insert log I_{pa} vs log v), and the Anson plot of DMAPP (2j) (insert: Q vs time, ms). The same electrochemical measurements were done for all FCs. Table I summarizes the electrochemical parameters of all the compounds.

The number of electrons transferred was determined by comparing the cathodic peak currents for ferrocene and each individual FC from a cyclic voltammmogram of a solution containing both compounds at the same concentration and correcting by differences in their diffusion coefficients. Using this approach, from the Randles and Sevcik equation,¹⁸ assuming a comparable rate of heterogeneous electron transfer (k_s), the *n* values ranged from 0.87 to 1.47. Based on these data, we conclude that all FC compounds exhibit the expected 1e⁻ redox process centered on the ferrocene moiety.

The formal redox potential $(E^{\circ'})$ of the FCs varies from +665 mV for DMAPP (2c) to +773 mV for the 2-pyridinyl derivative (2h). Compared to ferrocene $(E^{\circ'})$, the $E^{\circ'}$ values are higher by at least +206 mV (DMAPP) to +314 mV (2-pyr). These $E^{\circ'}$ changes can be explained by electronic effects. As reported by Wu and collaborators,¹¹ the carbonyl group on FCs is highly polarized, and as such it withdraws electron density from the ferrocene moiety, making its oxidation more difficult, a fact that is reflected on higher $E^{\circ'}$ values. Simultaneously, but to a lesser extent, the substituents also exert an electronic influence by modulating the electron with-drawing capacity of the carbonyl group; this explains the small but



Figure 3. Cyclic voltammograms of a solution of 2j 1.00 mM in 0.101 M TBAP/ACN at a platinum working electrode: (A) voltammogram at various scan rates, (B) I_{pa} vs $v^{1/2}$ (insert: log I_{pa} vs log v), and (C) Anson plot (insert: Q vs time).

still significant $E^{\circ\prime}$ differences among the various derivatives. This is consistent with our observation that the nitro derivatives (Hammet values of $\sigma_p = 0.81$ and $\sigma_m = 0.71$) exhibit higher $E^{\circ\prime}$ (as expected for electron withdrawing groups), while an electron donating substituent such as *N*,*N*-dimethylamino (Hammet value of $\sigma_p = -0.63$) shows a lower $E^{\circ\prime}$. In general, the log $E^{\circ\prime}$ correlates satisfactorily (*r* = 0.935) with the corresponding Hammet values^{12,19,20} or the various substituents (see Fig. 4).

The $I_{\rm pc}/I_{\rm pa}$ ratio, with the exception of the DMAPP (vide infra), is close to 1, showing that the redox process of the FCs is chemically reversible. The $\Delta E_{\rm p}$ values range between 72 and 90 mV, which is higher than the expected Nernstian value of 59 mV per electron, indicating that the redox process is electrochemically quasi-reversible.¹⁸ The plots of $I_{\rm pc}$ (or $I_{\rm pa}$) vs the square root of the sweep rate shows a linear dependence, and the slopes of the plots of log $I_{\rm pc}$ (or $I_{\rm pa}$) vs log sweep rate are close to 0.5, evidencing that the redox process is diffusion controlled. The diffusion coefficients ($D_{\rm ox}$) are between 1.65 and 3.7×10^{-5} cm²/s, which closely agrees with the $D_{\rm ox}$ of ferrocene, 2.4×10^{-5} cm²/s.²¹

Electropolymerization of DMAPP.— Figure 5A shows the CV of 1 mM DMAPP derivative in 0.1 M ACN/TBAP. We observe three well-defined oxidations with (a) $E_{pa} = +694$ mV, (b) +974 mV, and (c) +1521 mV and a cathodic process with (e) $E_{pc} = +632$ mV. On top of the cathodic wave, there is a barely discernible shoulder around (d) +760 mV. Figure 5B shows that on reversing the potential at +850 mV, there is only one reversible wave with $E^{o'} = +665$ mV. We assigned this wave to the oxidation and reduction of the ferrocene nucleus in the DMAPP in analogy with other FCs. The (b) second and (c) third oxidations, which are chemically irreversible are assigned to the successive loss of the nitrogen electrons in the *p*-*N*,*N*-dimethylamino group. The shoulder at (d) +760 mV corresponds to the reduction of this group.

Figure 5C shows that on continuous cycling (50 cycles), the original waves [(a)-(e)] started to decrease with the peak at (c) +1521 mV, decreasing faster than the others. Concurrently, we observe a small anodic wave growing between (f) 1070 and 1400 mV with a cathodic counterpart between (g) 900 and 1300 mV. The background current close to (h) 0 mV increases toward the negative potentials. We attribute these changes to the electropolymerization of DMAPP similar to what happens in the electrochemically induced polymerization of N,N-dimethylaminoaniline (DMA). Oyama and co-workers²² reported the electrochemical oxidation of DMA, a compound that is structurally similar to the R group in DMAPP. DMA oxidizes electrochemically at +800 and +1000 mV vs saturated sodium chloride calomel electrode in 0.5 M Na₂SO₄. The first oxidation generates a radical cation (DMA+*) that oxidizes further into a dication (DMA²⁺). On continuous cycling, DMA^{+•} electropolymerizes forming an electroinactive cationic polymeric film at the electrode surface.

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Compound	$\frac{E^{\circ\prime}}{(mV/s)}$	n	$D_{ m ox} (imes 10^{-5}) \ (m cm^2/s)$	$I_{\rm pc}/I_{\rm pa}$	${\Delta E_{ m p}} { m (mV)}$	Slope $\log I_{\rm pa}$ vs $\log v$
2a	723.667 ± 0.001	0.93 ± 0.01	2.17 ± 0.01	1.01 ± 0.01	72.000 ± 0.0001	0.453
2b	722.69 ± 0.02	0.88 ± 0.01	3.33 ± 0.01	1.1 ± 0.4	90.00 ± 0.02	0.487
2c	664.50 ± 0.02	_	_	2.0 ± 0.5	47.67 ± 0.03	0.433
2d	680.833 ± 0.002	0.87 ± 0.02	3.7 ± 0.8	1.1 ± 0.1	86.333 ± 0.002	0.478
2e	691.50 ± 0.01	0.90 ± 0.02	3.4 ± 0.1	1.17 ± 0.04	75.67 ± 0.01	0.487
2f	699.00 ± 0.01	1.44 ± 0.13	1.65 ± 0.2	1.1 ± 0.2	79.67 ± 0.02	0.471
2g	693.00 ± 0.01	1.47 ± 0.10	1.73 ± 0.08	1.1 ± 0.1	79.333 ± 0.004	0.467
2h	773.17 ± 0.02	0.90 ± 0.01	3.17 ± 0.01	1.0 ± 0.2	72.000 ± 0.004	0.400
2i	733.667 ± 0.004	1.25 ± 0.01	2.80 ± 0.01	1.11 ± 0.04	83.33 ± 0.01	0.473
2j	760.000 ± 0.004	0.91 ± 0.01	3.12 ± 0.01	1.0 ± 0.2	82.67 ± 0.01	0.467
2k	692.66 ± 0.02	_	_	1.0 ± 0.7	74.00 ± 0.01	0.455

Table I. Electrochemical parameters of the FCs.



Figure 4. Hammett plot for ferrocene derivatives [log of $E^{\circ\prime}$ as a function of Hammett values (σ)].

Figure 5. CV at a platinum electrode of 1.00×10^{-3} M compounds (2c) and (2k) in 0.101 M TBAP/ACN: For (2c), (A) 1 cycle at 20, 100, 500, 2000 mV/s, (B) 200 mV/s in the window potential of ferrocene oxidation, (C) 50 cycles at 200 mV/s 0–1600 mV/s scan window, (D) 50 cycles at 200 mV/s on-1200 mV/s scan window, (E) 50 cycles at 200 mV/s in supporting electrolyte only after cycling in (D), and (F) voltammogram of (2k) at 200 mV/s.





In analogy to Oyama's results, we propose that the small wave that grows between +900 and +1400 mV (g, h) corresponds to the oxidation and the reduction of a dimeric species produced by the chemical reaction of two radical monocations generated after the first oxidation of the *N*,*N*-dimethylamino group. The increment in background signal at 0 mV could result from the reduction of protons produced during the electropolymerization. The production of an electroactive polymeric film might be the reason for the voltammetric waves fading away eventually.

An experiment where the potential was cycled 50 times between +0 and +1200 mV showed that the wave corresponding to the ferrocene nucleus decrease slightly while the one due to the first DMAPP redox process decreased steadily (Fig. 5D). When this electrode was removed from the solution, dried in air, and put in an ACN solution with supporting electrolyte only, a voltammetric wave with $E^{o'} = +696$ mV was observed (Fig. 5E). As before (Fig. 5C), this wave decreases continuously until it disappears completely. In this experiment, the observation of the ferrocene wave confirms that the reason for losing the ferrocene signal is the formation of low molecular weight cationic species.

As has been reported for DMA,²² we propose that DMAPP undergoes electrochemical polymerization after its first oxidation. The electropolymerization results in the formation of a film at the glassy carbon electrode. Contrary to the DMA case, DMAPP electropolymerization does not produce a high molecular weight polymer because the *p* position is not available. The formation of the oligomers occurs through the chains growth at the meta positions These positions are sterically hindered thus decreasing the probability of the formation of a high MW polymer (Fig. 6A-C). This is consonant with what has been observed for DMA and aniline.^{22,23} In both cases, the polymerization preferably occurs through a head to tail attack initiated by the cation radical. Although the polymerization also occurs at the ortho positions relative to the amino and dimethylamino groups, the polymer grows mainly at the para position. In our case, the para position is sterically hindered because of the presence of the ferrocenyl moiety.

When the DMAPP is quaternized with dimethylsulfate (Fig. 5F), only one voltammetric wave is observed with a $E^{o'}$ = +693 mV. Likewise, the quaternization of the DMAPP prevents its electrochemical polymerization.

Electron-transfer heterogeneous rate constant (k_s) .— To determine the heterogeneous electron-transfer rate constant (k_s) , we treated the CV data according to Nicholson.²⁴ We constructed a working curve of $\Delta E p^* n$ $(n = 1e^-)$ as a function of log Ψ using the values for $\Delta E_p^* n$ (V) and Ψ published by Nicholson. The equation for this curve is $\Delta E_p^* n = -0.02\Psi^3 + 0.0536\Psi^2 - 0.0545\Psi + 0.083$. By taking the product of the *n* and ΔE_p values of each compound and substituting in the cubic equation, we obtained the Ψ values. The k_s was calculated from the following equation

$$k_{\rm s} = \Psi [D_{\rm o} \pi (F/{\rm RT})\nu]^{1/2} / [(D_{\rm o}/D_{\rm R})^{\alpha/2}]^{1/2}$$

where Ψ is the value obtained from the cubic equation, D_0 is the diffusion coefficient (cm²/s), *F* is the Faraday constant (96,500 C/mol), *R* is 8.314472 J/mol K, *T* is 298 K, and $\alpha = 0.5$. D_0/D_r is assumed to be equal to 1. Table II summarizes the values of k_s for all

Table II. Heterogeneous electron-transfer rate constants (k_s) for the FCs.

Compound	k _s (cm/s)			
2a	(0.027 ± 0.003)			
2b	(0.042 ± 0.004)			
2c	—			
2d	(0.024 ± 0.003)			
2e	(0.037 ± 0.002)			
2f	(0.023 ± 0.005)			
2g	(0.024 ± 0.002)			
2h	(0.020 ± 0.009)			
2i	(0.027 ± 0.004)			
2j	(0.044 ± 0.007)			

the compounds. The k_s are between 0.020 to 0.044 cm/s. When compared to the k_s reported for ferrocene of 0.035–0.076 cm/s,²⁴ the values for the FCs are comparable and in accordance with previous papers.

UV/vis spectra and absorption coefficients.— Figure 7A-D shows the UV/vis spectra of the compounds grouped by the nature of the aromatic derivative. Table III summarizes the absorption coefficients for the most prominent bands in the spectra. With few exceptions,

all FCs showed three bands in the UV region and one in the visible region. The absorption coefficients ranges from 1.8×10^2 to $7.5\times10^4~M^{-1}~cm^{-1}.$

It can also be observed in the spectra that the region between 275–328 nm is variable for all FCs. This region corresponds to the $n - \pi^*$ electronic transition attributed to the carbonyl. As pointed out in the electrochemical section, these differences demonstrate the effect that the electrodonating and electrowithdrawing substituents exert on the carbonyl polarization.¹²

Different from ferrocene which is yellow-orange solid, all FC solids exhibit a strong purple reddish color. The color of the ACN solution was the same as the solid. Some of the FCs exhibit solvatochromism. The solutions were stable for 24 h without protecting them from the room light.

Conclusion

In this study, we demonstrated the synthesis and characterization of 10 FCs. Our results show that all compounds are chemically reversible $I_{\rm pa}/I_{\rm pc} = 1.0-1.17$ for all compounds except DMAP and are electrochemically quasi-reversible, $\Delta E_{\rm p} = 72-90$ mV. The *n* and $D_{\rm ox}$ values reported agree with the values published for ferrocene (1e⁻, $D_{\rm ox} = 2.4 \times 10^{-5}$ cm²/s).²¹ The $k_{\rm s}$ values ranges 0.020–0.044 cm/s compared to 0.035–0.076 cm/s values for ferrocene.

The DMAPP electrochemical parameters were difficult to obtain because the proximity of the ferrocene and first DMAPP redox process and the complication introduced by its electropolymerization.



Figure 7. UV/vis spectra of 2.0 \times 10⁻⁵ M compounds (2a-2j) in ACN for: (A) 2a and 2b, (B) 2c, (C) 2d-2g, and (D) 2h-2j.

Table III. Absorption coefficients of FCs.

Compound	$\begin{array}{c} \lambda_{max} \\ (nm) \end{array}$	$arepsilon(imes 10^4)$ (L/mol cm)	$\begin{array}{c} \lambda_{max} \\ (nm) \end{array}$	$\epsilon(\times 10^4)$ (L/mol cm)	$\begin{array}{c} \lambda_{max} \\ (nm) \end{array}$	$\varepsilon(\times 10^2)$ (L/mol cm)	$\begin{array}{c} \lambda_{max} \\ (nm) \end{array}$	$\epsilon(\times 10^2)$ (L/mol cm)
2a	198.82	5.2 ± 0.3	_		315.46	290 ± 1	517.55	20.3 ± 0.5
2b	204.24	5.7 ± 0.5	280.87	3.7 ± 0.3	390.05	15.6 ± 0.8	503.30	16.8 ± 0.8
2c	200.17	7.5 ± 0.2	252.39	2.44 ± 0.05	393.44	421 ± 9	_	
2d	199.17	5.7 ± 0.3		_	328.33	280 ± 2	488.06	16.1 ± 0.3
2e	199.17	3.8 ± 0.2	303.11	2.1 ± 0.2	384.89	17.6 ± 0.6	497.23	15.8 ± 0.5
2f	199.94	5.6 ± 0.1	295.47	2.2 ± 0.3	386.42	16.5 ± 0.1	498.00	15.4 ± 0.1
2g	201.46	3.4 ± 0.2	297.00	2.0 ± 0.1	387.94	16.1 ± 0.7	497.23	15.5 ± 0.6
2h	201.53	6.2 ± 0.9	301.22	2.9 ± 0.1	390.73	15.6 ± 0.2	500.59	16.1 ± 0.1
2i	201.53	6.5 ± 0.3	296.47	3.29 ± 0.04	391.41	1.8 ± 0.3	493.81	1.8 ± 0.3
2j	199.49	4.7 ± 0.6	275.45	3.1 ± 0.2	394.80	14.4 ± 0.3	506.70	16.5 ± 0.3

The electropolymerization of DMAPP results in cationic oligomers that are soluble and not suitable for further polymerization and the formation of polymeric films at electrode surface.

We report that the substituent in the aromatic ring influences the $E^{0'}$ of the FCs by modulating to a certain extent the polarization of the carbonyl group. This result is consistent with the UV/vis variations in the $n - \pi^*$ region that corresponds to the carbonyl absorption.

In summary, FCs with tunable redox and spectroscopical properties can be produced by the reaction of acetylferrocene and appropriate derivatives of aromatic aldehydes. These compounds could be used as electrochemical and optical labels in sensor arrays. We are currently exploring ways to immobilize these compounds at electrode surfaces and studying their applications in biosensing and electrocatalysis.

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