Internship report MASTER 2

2018

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lumomat
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Recherche, Formation & Innovation en Pays de la Loire

Subject:

Study of the intramolecular electron transfer in amino-ferrocene pi-conjugated systems

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UNION EUROPÉENNE
Région PAYS de la LOIRE
CE PROJET EST COFINANCÉ PAR
LE FONDS EUROPÉEN DE DÉVELOPPEMENT RÉGIONAL

Acknowledgments

Sincere thanks to the laboratory MOLTECH-Anjou and his director Marc SALLE for giving me the opportunity to do this internship.

Thanks to Charles Cougnon for his help all along this internship, for his humour sometimes borderline and for his memorable “raclette”. I want to thanks also Frederic Gohier for his advices in organic chemistry and for the Easter eggs with their surprises which I keep always on my desk.

All my gratitude to Eric Levillain for accepting me in ERDySS group. I want also to give my gratitude to all the ERDySS group. In particular, Christelle Gautier for her wonderful laugh which can be heard in all the laboratory, Dr Adam for tolerating me in the office (Sorry for being rude with you all the time), Isidoro for asking me to do his coffee all the time (I am not your intern Isidoro!), Marius for joining me sometimes in the organic chemistry lab to make me feel less lonely with my syntheses and Ismael for our conversations on football.

I want to give my sincere thanks to Ewen Touzé for helping me in organic chemistry, electrochemistry, oral presentation, report writing, NMR… It will never be enough to say every time he helped me even while he was writing his thesis.

I want to thank also all the interns, who were with me and helped me during this internship. Specially, Laure Pichereau who supported me even while I had moments of madness, Marine le Cléach for our coffee breaks and our time at the gym and Steven Vertueux for our nights watching football games.

Abbreviations

ACN: Acetonitrile

CE: Counter Electrode

Collidine: 2,4,6-Trimethylpyridine

C.V.: Cyclic Voltammetry

DABCO: 1,4-Diazabicyclo[2.2.2]octane

DMF: Dimethylformamide

DMSO: Dimethylsulfoxide

Et_3N: Triethylamine

E: Potential

Epa: Anodic potential

ESR: Electron Spin Resonance

F: Farad

GCE: Glassy Carbon Electrode

mL: Millilitre

$Pd(OAc)_2$: Palladium (II) Acetate

$Pd(PPh_3)_4$: Tetrakis(triphenylphosphine)palladium

PPF: Pyrolyzed Photoresist Film

PPh_3: Triphenylphosphine

THF: Tetrahydrofuran

V / SCE: Volts / Saturated Calomel Electrode

WE: Working Electrode

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Introduction

Amines are present in numerous biomolecules. This is why these entities have been studied for grafting since the publication from J. Pinson and B. Barbier in 1990.[1] Frequently, the amine function is converted to a diazonium salt which is easier to graft on a surface because of the low reduction potential of aryl diazonium compounds.[2] However, several drawbacks have been observed in the electrografting of diazonium salts over the last two decades. Beyond their poor stability, surface coverages are most often consistent with multilayers, due to the high reactivity of the aryl radicals. Consequently, the electrografting by direct oxidation of amines has been studied to overcome these limitations. This approach offers the benefit of a rapid covalent coupling reaction between an amine group and the untreated carbon surface without the need to prepare the reactive diazonium ion intermediate. In this procedure, amines produce a radical cation upon oxidation and after deprotonation, favoured by the presence of a base in solution, the radical aminyl obtained can react with carbon or metallic surfaces to be covalently attached.[3]

Unfortunately, due to the poor delocalization of the charge in the amino cation-radical, the oxidation of aliphatic amines occurs most often beyond 1 V / SCE.[4] Because of a better delocalization of the charge in the cation radical of arylamines, the oxidation of aromatic primary amines becomes easier and grafting is possible in aqueous media.[5] Recently, a conjugated amino-ferrocifen complex could even be grafted at very low potential, by oxidizing the ferrocene (0.4 V / SCE) through an intramolecular electron transfer from the amine to the ferrocenium moiety acting as a redox shuttle.[6,7]

The main objective of this work is to study the electrochemical behaviour of amino-ferrocene complexes having unsaturated bridges, in order to demonstrate the impact of the conjugation on the grafting efficiency. Electrochemical techniques and electron spin resonance (ESR) were applied to gain insight into the behaviour of molecules following the one-electron oxidation of the ferrocene moiety, while electrodes modified at different potential values were investigated by X-ray photoelectron spectroscopy (XPS).

I. Electrografting of an amine system

Electrografting refers to the electrochemically induced attachment of an organic layer on a carbon or metallic electrode.[3] To address this issue, amine is a key surface attachment functionality to prepare modified surfaces for sensor applications due to its presence in a wide variety of biomolecules. Two pathways are used nowadays for the grafting of an organic molecule containing an amine function, depending on whether the amine is directly oxidized or converted previously into the corresponding diazonium salt before being reduced. In this part, the formation and the reduction of the diazonium salt will be discussed with all the advantages/drawbacks linked to this technique. The oxidation of the amine will be also discussed with the mechanism of grafting on a surface. Advantages and drawbacks of this method will also be detailed.

I. 1. Electrografting by reduction of a diazonium salt

I. 1. a. Formation of the diazonium salt

Diazonium salts have been known for centuries in organic synthesis (discovered in 1858 by Peter Griess [8]) because of the numerous reactions (Sandmeyer[9], Gomberg-Bachmann[10], Meerwein[11] reactions…) which can be used on this moiety due to its strong electronwithdrawing effect. More recently, the diazonium chemistry has been widely studied for grafting since the publication of Pinson's group in 1992.[12]

A diazonium salt can be formed in aqueous or organic media.[13] The mechanism in both media are similar since an acid and a precursor of the nitrosonium ion are necessary. This mechanism is detailed below (**Figure 1**) with the formation of the nitrosonium ion and its reaction on an aniline derivative.

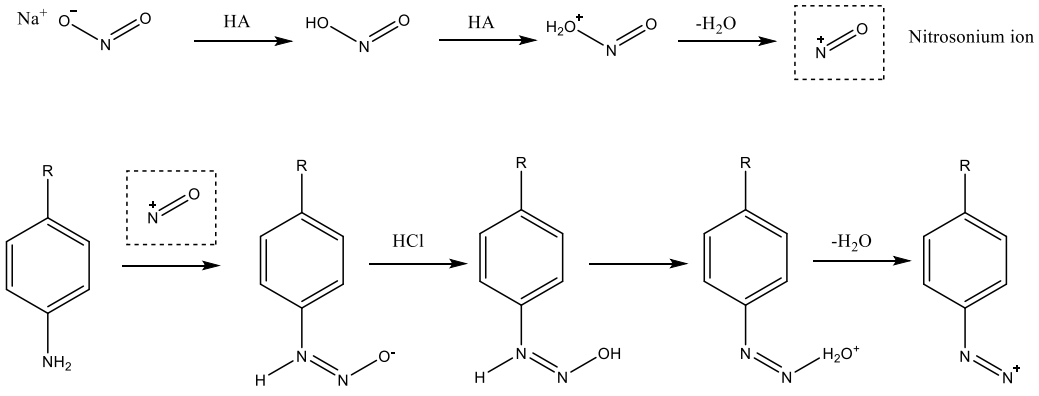


Figure 1. Mechanism of formation of a diazonium salt.[14]

I. 1. b. Mechanism of the electrografting of diazonium salts

Several pathways have been found through years to carry out the dediazotation. Both acidic and reducing agent such as H_3PO_2[15] was used to promote the spontaneous reduction of diazonium salts. Nevertheless, the electrochemistry is the most popular procedure to reduce a diazonium salt.

Even if the product formed after dediazotation can be difficult to determine (Heterolytic or Homolytic dediazotation [16,17], concerted or stepwise aryl radicals generation [18]) the electrografting is often described from the radical aryl formed after the homolytic reaction. [2,19,20] The mechanism of diazonium salts grafting was first described in 1997 [2] by the reaction of the radical directly on the surface (**Figure 2**).

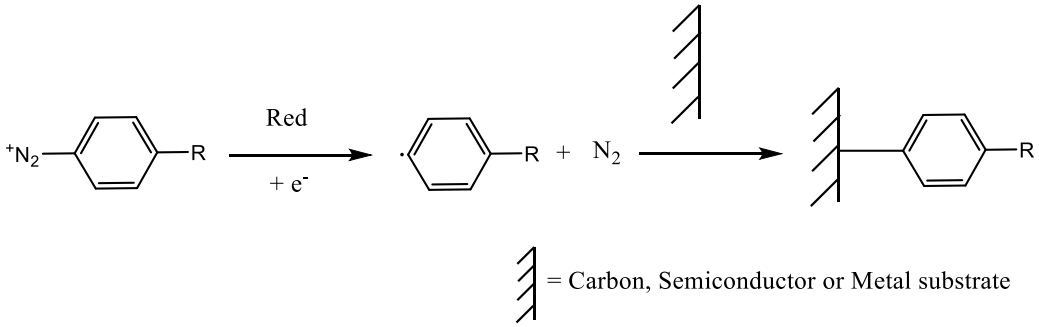


Figure 2. Mechanism of aryl diazoniums grafting.

The grafting of an aryl diazonium can be characterised by Cyclic Voltammetry (CV). Indeed, diazonium salts reduction is defined by a broad irreversible wave at low reduction potential. The disappearing of this reduction peak at the second cycle indicates a blocked surface. The example of the 4 - nitrobenzene diazonium tetrafluoroborate is given by Jean Pinson and Fetah Podvorica (Figure 3).[20]

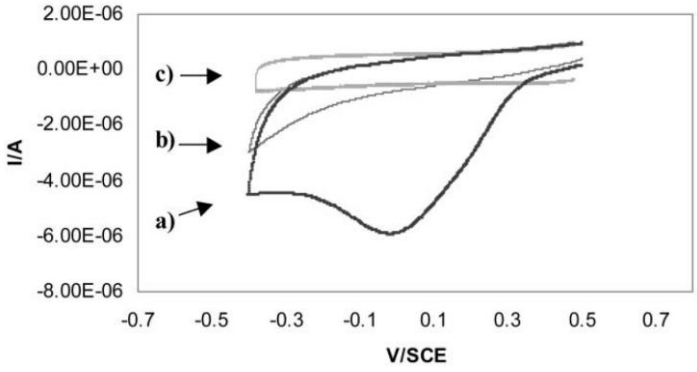


Figure 3. (Extracted to the reference 19)**.** Glassy carbon disk electrode (d = 3 mm) in ACN + 2 mM $N_2C_6H_4NO_2$ BF_4 + 0.1 M NBu_4BF_4 a) first and b) second scan and c) the same electrode in ACN + 0.1 M NBu_4BF_4.

I. 1. c. Advantages / Drawbacks of diazonium salts

The main advantage of grafting via diazonium chemistry is its low reduction potential. This characteristic is very interesting for industrial applications because of the low energy consumption necessary to functionalise a surface.[2,20] Typically, the low reduction potential of most aryl diazonium compounds allows a spontaneous functionalisation by simple immersion of the surface in a diazonium solution.[3,20] A wide variety of derivatives are also possible with diazonium salts.[19,20] For all these reasons, diazonium salts are very popular for surface modification. Nevertheless, aryl diazonium has a wide potential window according to substituents (between -0.3 V and 0.5 V / SCE?).[2,18,21] These substituents are also decisive in the layer morphology.[22]

Finally, the main drawback of diazonium salts is related to the condition of its grafting on surface. A surface which is sensitive to reduction or acidic conditions will not be adapted to diazonium compounds. [3,19,20]

I. 2. Electrografting by the oxidation of the amine function

I. 2. a. Mechanism of Electrografting of the amine

Since the publication of Jean Pinson's group in 1990 [1], the interest of amine for grafting has grown. The grafting of amines is characterised by an irreversible peak in oxidation which decreased progressively over time (passivation of the electrode). An oxidation and a deprotonation are necessary for this grafting since it is the aminyl radical which interacts on the substrate (**Figure 4**).

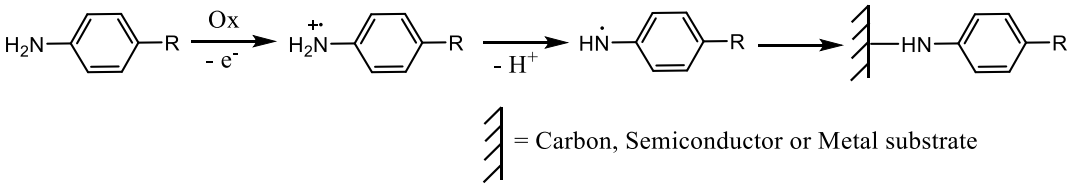


Figure 4. Mechanism of grafting.

The main problem with grafting by oxidation of amines is their high oxidation potential. An aliphatic amine has an oxidation potential beyond 1 V / SCE, while an aromatic amine has a potential below 1 V / SCE.[4] The mechanism described on **Figure 4** can be applied only to primary and secondary amines. Tertiary amines cannot be grafted due to the steric hindrance around the nitrogen atom and because no loss of proton is possible.[3]

I. 2. b. Advantages / Drawbacks of amines grafting

Amine grafting is a direct process (contrary to diazonium salts which necessitates one preparation step from amine). However, as it has been mentioned above, the high oxidation potential of amines is the main problematic for the direct grafting of this moiety. Several solutions have been developed to lower this potential, in particular the oxidation via an intramolecular electron transfer.[6,7] Moreover, the deprotonation necessary for the grafting can be assisted by a base which could be an issue for some substrates. Finally, the substrate needs to be non-oxidizable because of the high oxidation potential of certain amines.[3,19]

I. 3. Spontaneous grafting

I. 3. a. Diazonium salts

Spontaneous grafting with diazonium salts is possible since their cathodic potential are closed to 0 V / SCE. Mechanism is similar to that previously presented in the Figure 2, excluding the generation of the aryl radical which is generated spontaneously (**Figure 5**). The high reactivity of the aryl radical induces a multilayer film since the aryl radical reacts on a moiety already grafted on the surface.[17,23]

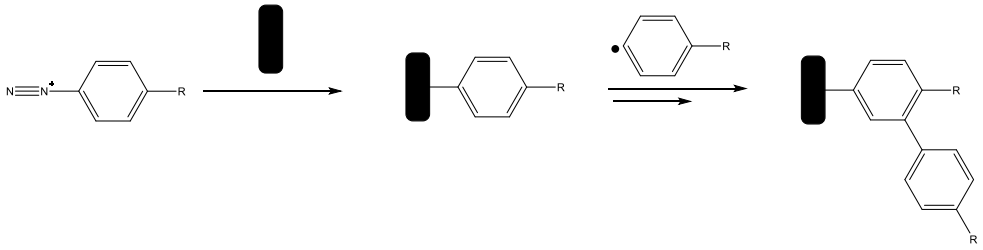


Figure 5. Mechanism of diazonium spontaneous grafting.

For the grafting, the surface needs to be immersed in the diazonium solution without any polarisation of the substrate (carbon, metals or semiconductors). Therefore, the interaction between the diazonium salt and the substrate is important since the reduction of the diazonium salt may only take place at the open-circuit voltage of the substrate.[24]

I. 3. b. Amines

Spontaneous grafting of amines has been found by Daniel A. Buttry *et al.* in 1999.[25] The mechanism is not an electrochemical reaction since it is based on the Michael reaction. The alkyl amine is added to the carbon surface thanks to an electron withdrawing group (aldehyde for instance) giving a carbon poor in electron. A nucleophilic attack is carried out by the amine, then the amine loses a proton which is retrieved by the carbon surface (**Figure 6.** Mechanism of amine spontaneous grafting.). [23]

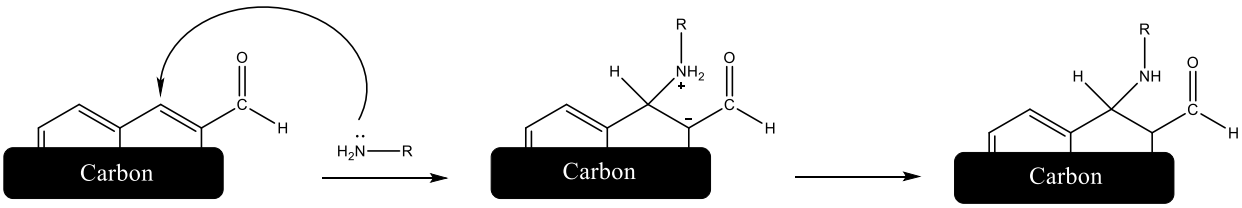


Figure 6. Mechanism of amine spontaneous grafting.[23]

To be grafted on surface, the carbon substrate needs only to be immersed in a highly concentrated solution. However, the surface needs to be immersed at least 15 hours (and up to 5 days) in a solution at high temperature, because such reaction is under thermodynamic control.[23,25]

Softer conditions have been found by Illuminada Gallardo *et al.* since the grafting is carried out at room temperature for alkyl amines.[26]

II. Electrochemical study of amino-ferrocene systems

II. 1. Project Overview

Despite the good properties related to aryl diazonium and the wide variety of compounds which can be converted into a diazonium salt, grafting via an oxidation of the amine offers several advantages. This is why amines are thoroughly studied for grafting, in particular to lower the oxidation potential of this group. In 2008, Amatore *et al.* reported an aminoferrocifen moiety which can be grafted just by oxidizing the ferrocene instead of direct oxidation of the amino group. In this aminoferrocene complex, the indirect oxidation of the amine occurs through an intramolecular electron transfer from the amine to the ferrocenium group acting as a redox shuttle. Moreover, the slow intramolecular electron transfer process can be helped by addition of a base, such as collidine, which favours the deprotonation of the amino cation-radical, yielding easier the radical aminyl. [6]

Following these researches, another amino-ferrocene system separated by an ethynylbenzene bridge has been synthesised and studied by Ewen Touzé, *et al.* (**Figure 7**). In this previous work, two amino-ferrocene complexes have been studied (with saturated and unsaturated bridges) to differentiate the grafting efficiency with or without a pi-conjugated system. Results showed an easier grafting of the molecule with the unsaturated bridge (**ET18**), while the saturated bridge did not graft by oxidising the ferrocene group. Moreover, the ethynyl linker of **ET18** avoids the use of a base by increasing the acidity of the protons in the amino group, due to its electron withdrawing effect. For this reason, the conjugated amino-ferrocene complex can be grafted without the help of a base.[27]

My contribution to this work was to study in detail the impact of a base in the intramolecular electron transfer in such conjugated aminoferrocene complexes. In a first part, the extension of the conjugation in the system has been studied, and in a second part, the effect of an organic base such as the collidine was investigated to optimise the electrografting of such compounds on carbon surface.

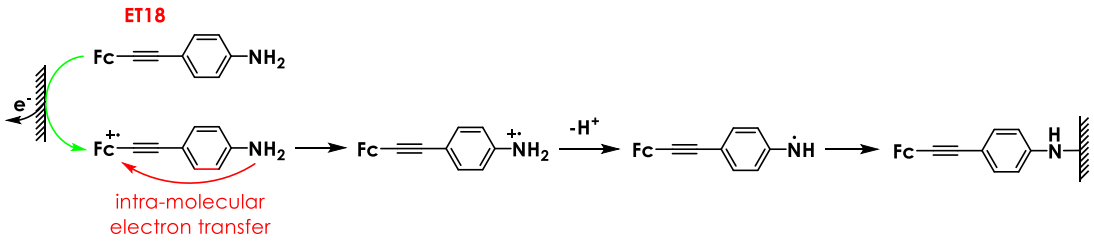


Figure 7. Mechanism of amine oxidation and grafting via an intramolecular electron transfer.

II. 2. Effect of the conjugation

II. 2. a. Synthesis

Following the previous studies performed on **ET18**, we became interested in similar molecules with an increased conjugation. Several conditions have been tried to synthesise the compound **CAN-06** (**Figure 8**). A Sonogashira coupling between 4-ethynylaniline and 1-bromo-4-iodobenzene has been performed and lead to **CAN-01** in 71 % yield. However, the coupling of the bromine derivatives generated (**CAN-01**) with ethynylferrocene did not afford **CAN-06** whatever the solvent or the catalysts used.

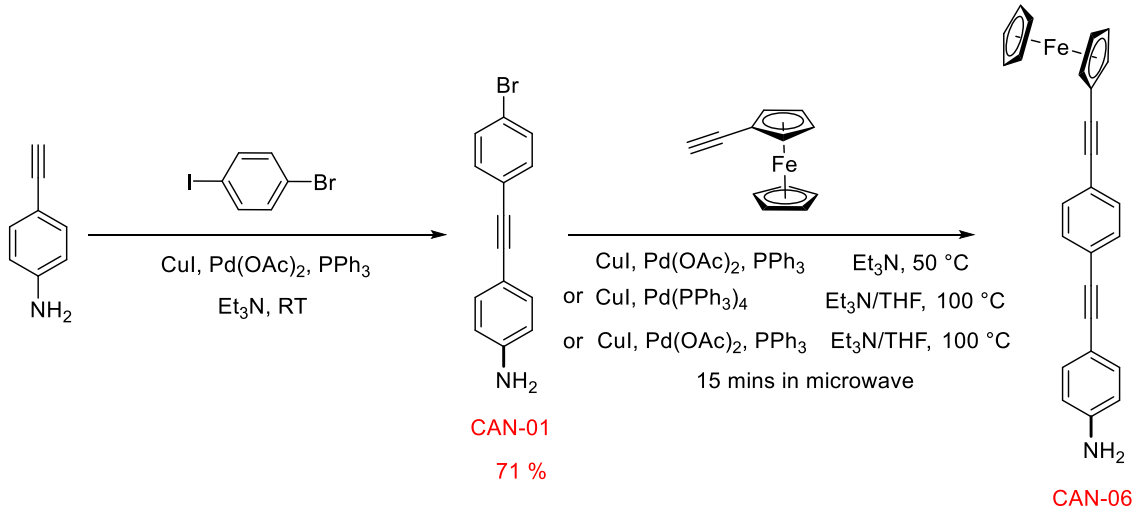


Figure 8. Scheme of synthesis of **CAN-06** through a 4-((4-bromophenyl)ethynyl)aniline (**CAN-01**) intermediate .

After these various attempts with 4-((4-bromophenyl)ethynyl)aniline (**CAN-01**), another pathway has been tried (Figure 9). First coupling was performed with 1,4-diidobenzene. Then, 4-((4-iodophenyl)ethynyl)aniline (**CAN-05**) was coupled with ethynyl ferrocene to obtain **CAN-06**.

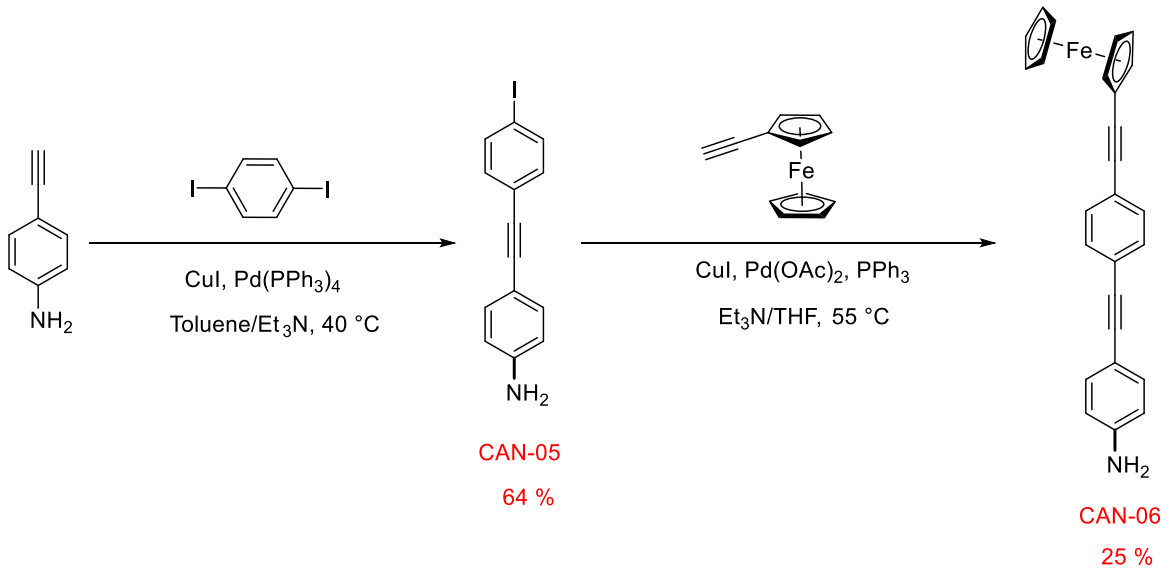


Figure 9. Synthesis of **CAN-06** through an 4-((4-iodophenyl)ethynyl)aniline (**CAN-05**) intermediate.

Conclusive results have been obtained with **CAN-06** (detailed later on). Therefore, a novel molecule has been synthesised to observe the tendency observed between **CAN-06** and **ET18**. Same pathway as **CAN-06** has been used for the synthesis of **CAN-08 (Figure 10)**. A Sonogashira coupling was performed between 1,4-Diiodobenzene and 4-((4-ethynylphenyl)ethynyl)aniline previously synthesised. The resulting compound (**CAN-07**) was coupled with ethynylferrocene via another Sonogashira coupling. **CAN-08** was obtained with a yield of 64 %.

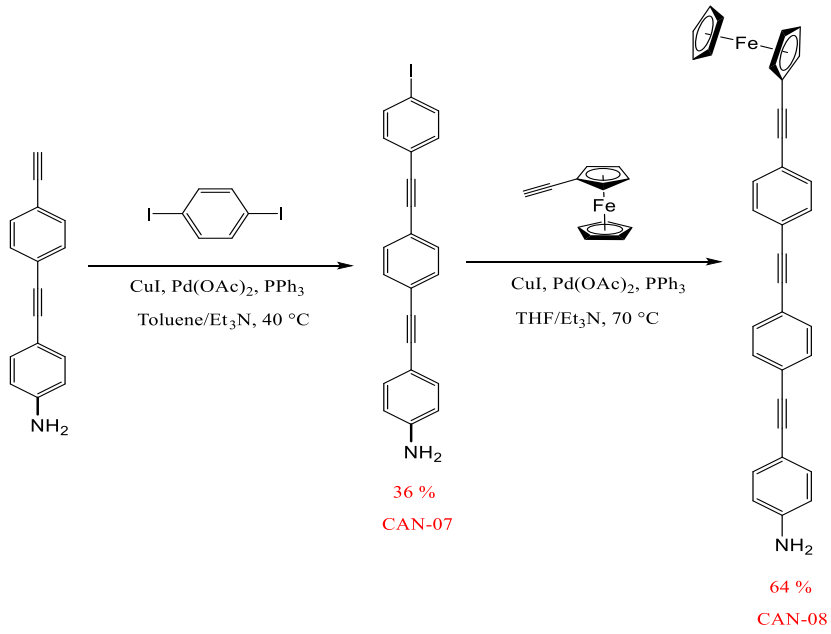


Figure 10. Scheme of synthesis of **CAN-08**.

II. 2. b. Cyclic voltammetry in solution of amino-ferrocene systems

All these new amino-ferrocene systems have been studied by cyclic voltammetry (CV) to understand how the conjugation impact the electric communication between the ferrocene and the amino group (**Figure 11**)

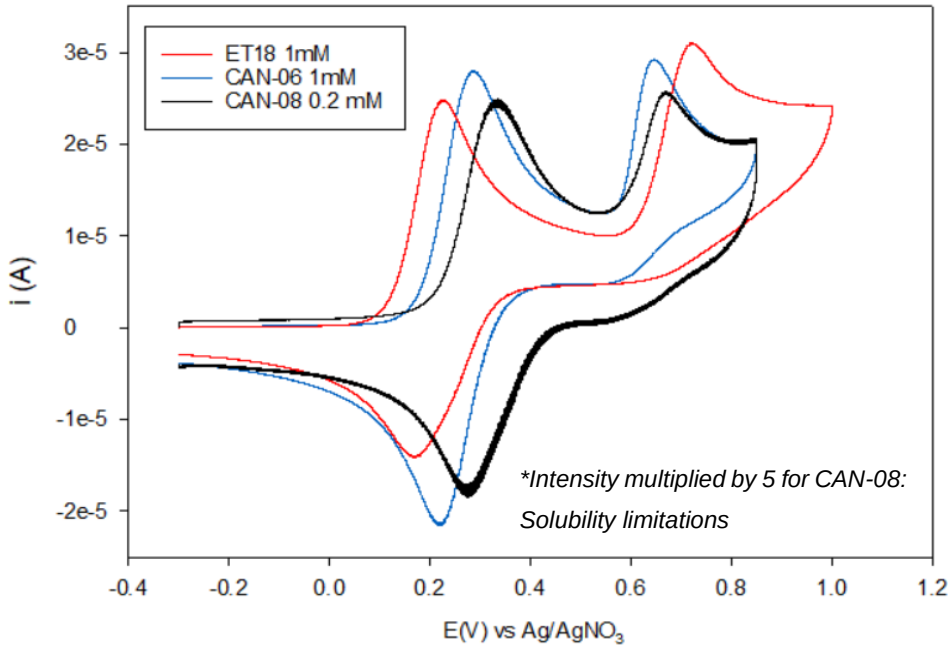
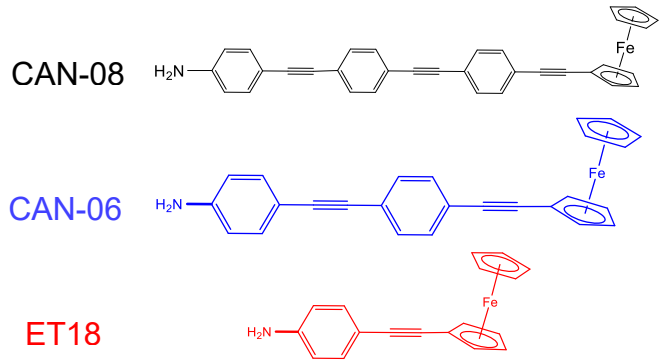


Figure 11. Cyclic Voltammetry of: 0.2 mM CAN-08*(-0.3 to 0.85 V); 1 mM CAN-06 (-0.3 to 0.85 V); 1 mM ET18 (-0.3 V to 1 V). (ACN + 0.1 M Bu_4NPF_6, 100 mV/s, n = 1st cycle)

Table 1. Potential separation between the two oxidations peaks of amine and ferrocene in **ET18**, **CAN-06** and **CAN-08**.



Compound	ET18	CAN-06	CAN-08
Oxidation peaks gap	506 mV	364 mV	334 mV

As we can see on **Figure 11**, various anodic potentials are obtained for **ET18**, **CAN-06** and **CAN-08**. The first oxidation peak around 0.3 V / SCE corresponds to the reversible oxidation of ferrocene. According to the CVs of each compound, when the conjugation is increased ferrocene becomes more difficult to oxidise (E = 0.22 V / SCE for **ET18**, E = 0.29 V / SCE for **CAN-06** and E = 0.33 V / SCE for **CAN-08**). This effect can be explained by the presence of carbon-carbon triple bonds in the carbon bridge between the ferrocene and the amine which is an electron withdrawing group (Hammet coefficient = 0.23).[28]

The second oxidation peak corresponds to the primary amine. In this case, the evolution is completely different. An increased conjugation induces a primary amine easier to oxidise (E = 0.72 V / SCE for **ET18**, E = 0.65 V / SCE

for **CAN-06** and E = 0.67 V / SCE for **CAN-08**) due to a better stabilization of the amino cation radical. However, this tendency is not confirmed between **CAN-06** and **CAN-08** since their oxidation potentials are quite close.

II.3. Electrografting with the help of a base

II. 3. a. Choice of the base (collidine, DBU and DABCO)

The choice of a base is quite important for electrochemical studies because several restrictions are induced by electrochemical experiments. For instance, the base needs to be non-electroactive in the potential window of the compound studied. This is why before any experiment the electroactivity of each base needs to be verified.

At the beginning of the project, three bases had been chosen because of their structure and their pKa. 2,4,6-collidine was chosen firstly since several publications reported a good interaction between collidine and amino-ferrocene species.[7,27] Then, DABCO (1,4-Diazabicyclo[2.2.2]octane) and DBU (1,8-Diazabicyclo[5.4.0]undec-7-ene) were chosen because they are organic bases containing amines as collidine (**Figure 12**) while their pKas are significantly different (pKa_{DABCO} = 8.82 ; pKa_{DBU} = 12; $pKa_{Collidine}$ = 7.43).

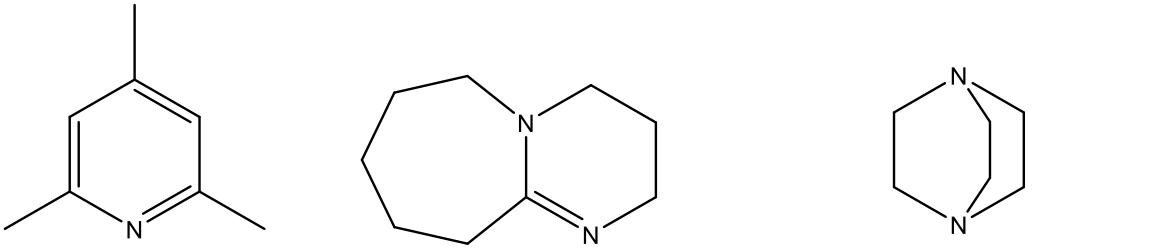


Figure 12. Schemes of collidine, DBU and DABCO bases.

Among these various bases, collidine is the only one to have no oxidation peak in the potential window of **ET18** (-0.5 V to 1.2 V). DBU and DABCO have oxidation peaks at 0.88 V / SCE and 0.43 V / SCE respectively. DABCO oxidation lies between the two oxidation peaks of **ET18** and DBU oxidation is slightly more positive than the amine oxidation of **ET18** (**Figure 13**). Therefore, DABCO and DBU are not suitable for the following studies.

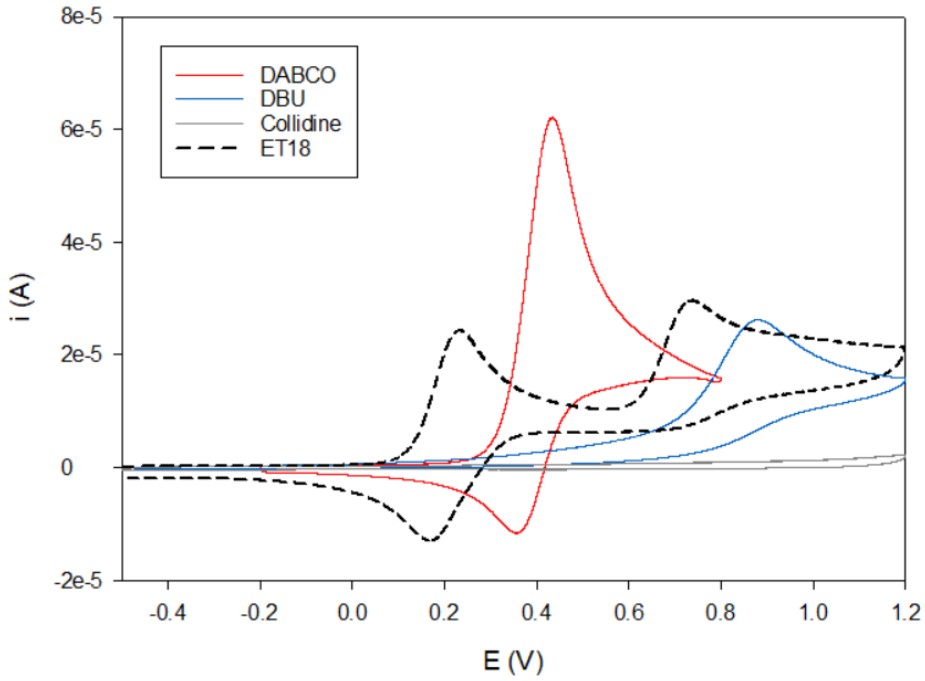


Figure 13. Electroactivities of DABCO (2 mM), DBU (1 mM), collidine (2 mM) and **ET18** (1 mM). ACN + 0.1 M Bu_4NPF_6, 100 mV.s-1, n = 1st cycle

II. 3. c. Electrografting with different amounts of base

The first experiment performed on **ET18** was to add an increasing amount of base (collidine in the project) to observe the effect on **ET18** properties (oxidation of amine and ferrocene, grafting on surface…).

As it was demonstrated before, **ET18** or more generally amino-ferrocene systems can be grafted at the oxidation potential of the ferrocene via an intramolecular electron transfer.[6,7,27] Collidine is also described as a promotor to increase the surface grafting on substrates by favouring the deprotonation of the amino cation radical. Therefore, one aim of the project was to determine the amounts of collidine needed to optimise this grafting. For this purpose, chronoamperometric experiments were performed on a 1 mM **ET18** acetonitrile solution. Hence the glassy carbon (GC) electrode was polarized at the peak potential of the oxidation of ferrocene for 5 mins, then the GC electrode was studied in a solution of ACN + 0.1 M Bu_4NPF_6 after sonication in acetonitrile for 5 mins (**Figure 14**). This procedure was performed with a solution of 1 mM of **ET18** and different equivalents of collidine.

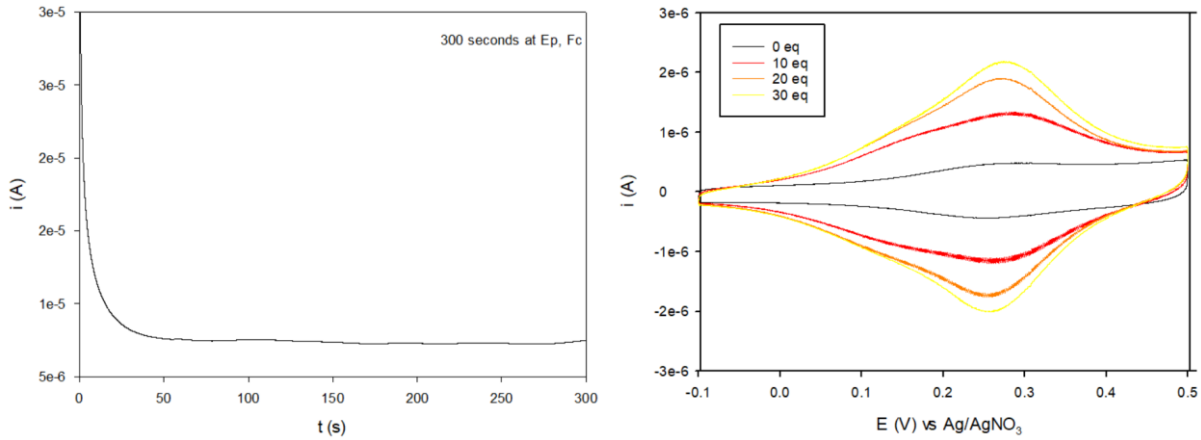


Figure 14. chronoamperometric i-t curve for 300 s at $Epa_{,Fc}$.(left) and electrochemical surface coverage of **ET18** in ACN + 0.1 M Bu_4NPF_6 for carbon electrodes modified in presence of different equivalents of collidine (right).

From the CVs showed in the **Figure 14**, the electrochemical surface coverage is calculated. Calculations were made from the software SAM_CV_Analysis to have precise measurements. Baseline is adjusted and surface coverage is calculated from the integration of the area under the peak (yielding the charge Q) according to this equation:[13]

$$\Gamma = \frac{Q}{nFS}$$

Γ = surface coverage mol/cm²; Q = charge (peak area); n = number of electrons exchanged during the electrochemical process; F = Faraday constant; S = Surface of the WE.

In this case, the number of electrons exchanged is equal to 1 (one electron from the grafted ferrocene). Faraday constant and the surface of the electrode are equal to 96485 C/mol and 0.07 cm² (3 mm of diameter) respectively.

Therefore, a surface coverage for all the electrodes modified was obtained (each electrode was modified at the same potential but with different equivalents of collidine). Afterwards, a trend curve can be traced from the amounts of collidine and the corresponding surface coverage (**Figure 15**). These experiments were repeated with CAN-06 and the results for the two different amino-ferrocene compounds are depicted in **Figure 15**. However, for **CAN-08** the experiment was not possible since the compound precipitated after collidine addition (even with 0.1 equivalents).

As demonstrated in **Figure 15**, a plateau is obtained from 10 to 30 equivalents for **CAN-06** and from 25 to 40 equivalents for **ET18**. The intramolecular electron transfer is likely faster with **CAN-06** compared to **ET18**. A maximum surface coverage is reached for both molecules: around 4×10^{-10} mol/cm² for **CAN-06** and around 3.5×10^{-10} mol/cm² for **ET18**. Those values are close to an ideal monolayer covering according to the electrochemical surface coverage ($\Gamma_{theo} = 2.3 \times 10^{-10}$ mol/cm², calculated from A.Downard *et al.*).[29] However, previous publications have already demonstrated that a multilayer was formed.[7,27]

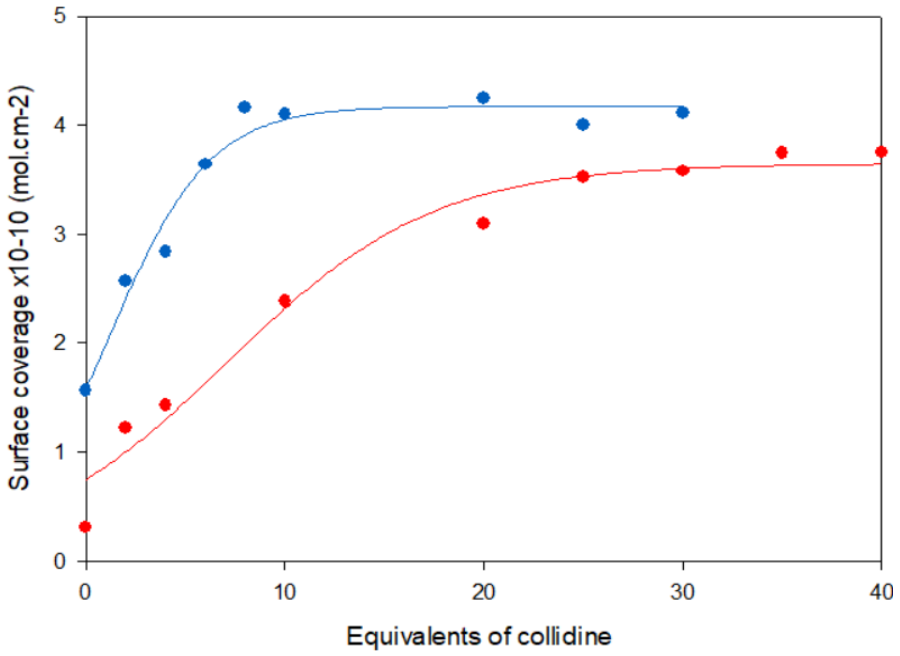


Figure 15. Electrochemical surface coverage of 1 mM of **ET18** and **CAN-06** in ACN + 0.1 M Bu_4NPF_6 on GC according to equivalents of collidine.

According to the literature, collidine is helpful for the formation of the aminyl radical. Indeed, amine grafting requires a loss of one electron but also a loss of a proton. Therefore, after the loss of one electron by oxidation of ferrocene and intramolecular electron transfer from the amine, collidine deprotonates the oxidised amine (**Figure 16**).[6]

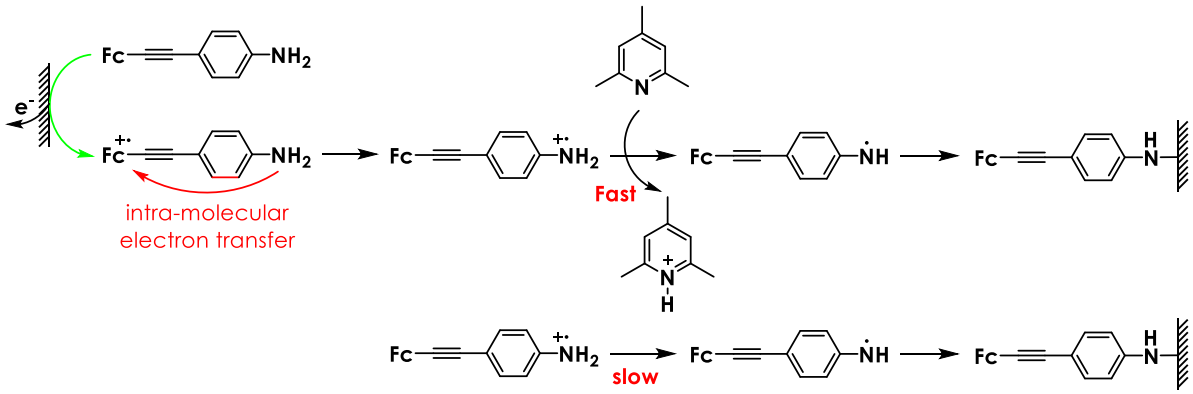


Figure 16. Mechanism of **ET18** grafting with the help of collidine.

II. 4. Electrochemical study of the intramolecular electron transfer

II. 4. a. Electrolysis at oxidation potential of ferrocene

Next step in the project was to determine if the amino group can completely be oxidized at ferrocene potential.To address this point, a complete electrolysis of a 1 mM **ET18** acetonitrile solution was achieved with a GC plate at the potential of the oxidation of ferrocene (0.23 V vs. $Ag/AgNO_3$). On **Figure 17**, CVs at different time of the electrolysis are presented to observe the evolution of the current peak intensity of the oxidation of amine.

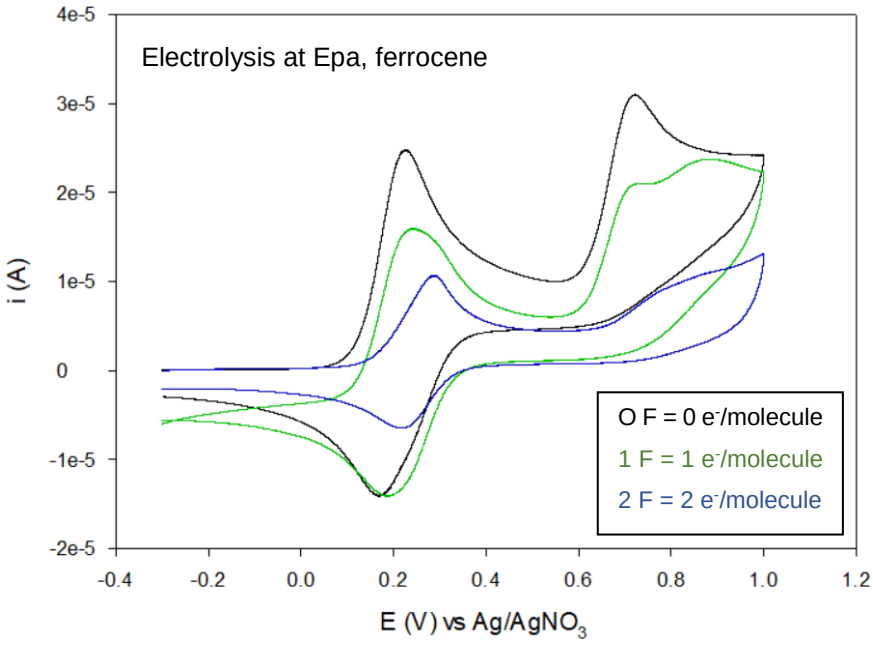


Figure 17. CV of 1 mM **ET18** in ACN + 0.1 M Bu_4NPF_6 during an electrolysis at 0.228 V (100 mV/s; n = 1)

This electrolysis has been stopped at several points to observe the evolution of current intensity of the amine oxidation peak after having consume different charge at the potential of the ferrocene (0 Farad, 1 Farad and 2 Farad). The charge consumed to reach 1 Farad (F) was calculated following this equation:

$$Q = n \times F$$

Q: Charge; n: number of moles; F: Faraday constant

1 Farad is equal to 0.48 Coulomb (C) for a 5 mL solution of 1 mM (1 F correspond to 1 e^- removed from each molecule in solution). Then, after 1 F was reached, the electrolysis was stopped to perform a CV in the study solution (1 mM of **ET18** in ACN + 0.1 M Bu_4NPF_6). The same procedure was carried out after 2 Farad was consumed. Importantly, when 2 electrons are removed from each molecule (2 F), amine peak has disappeared, meaning that the amino group in **ET18** has been completely oxidised at the ferrocene potential. This result strongly suggests that an intramolecular electron transfer occurs in **ET18** between the amine and the ferrocenium moieties.

However, more than 10 hours were necessary to reach 2 F. Therefore, this intramolecular transfer has a very slow kinetics.

II. 4. b. Regeneration of ferrocene moiety

The electrolysis until 2 Farad afforded promising results. This is why another study with an electrolysis has been performed. The objective of this study was to evidence the various species formed during the electrolysis. Analyses (ESR measurement) at different time of the electrolysis have been carried out (**Figure 18**).

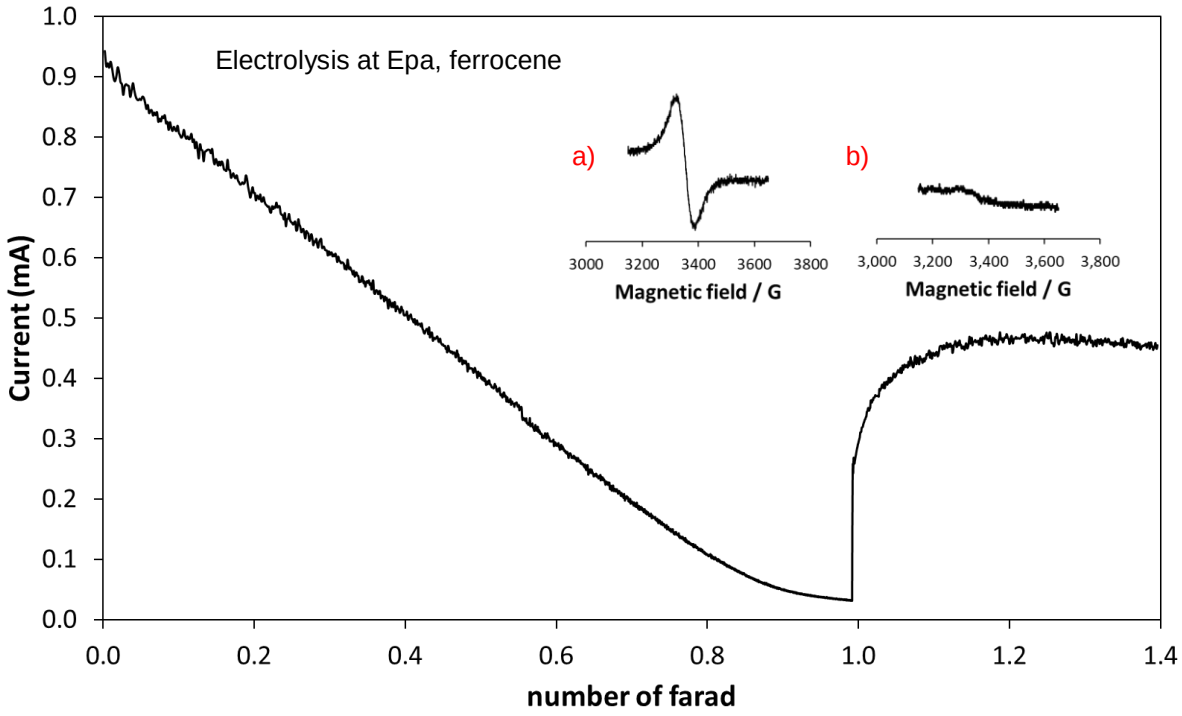


Figure 18. Electrolysis at ferrocene potential with regeneration of the ferrocene by addition of collidine after 1 F and ESR measurement before and after addition of collidine. 1 mM **ET18** in ACN + 0.1 M Bu_4NPF_6

After having consumed 1 F at the potential of the ferrocene, we supposed that only the paramagnetic cation of the ferrocene (ferrocenium) is obtained, which was confirmed by ESR (Electron Spin Resonance) measurement (**Figure 18**.a). After the addition of 40 equiv. of collidine while maintaining the GC plate polarized at the potential of the ferrocene, the regeneration of ferrocene can be clearly seen by the rapid increase in the current intensity. Therefore, the radical cation of ferrocene moiety was no longer in solution, as it was confirmed by another ESR measurement (**Figure 18**.b). The aminyl radical is most likely formed in solution according to the mechanism (**Figure 19**). However, this aminyl radical was not seen with ESR (**Figure 18**.b) due to the instability of this specie.

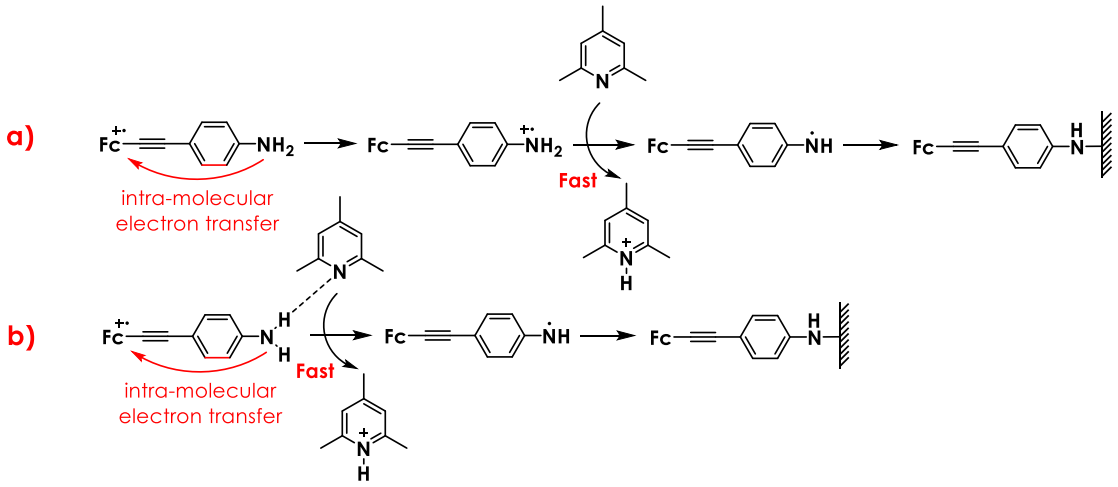


Figure 19. Mechanism previously described (a) [6] and the novel mechanism supposed (b).

This experiment is not consistent with the mechanism proposed by Amatore *et al.*[6] In this publication, the collidine is assumed to deprotonate the amino cation radical. Nevertheless, according to the electrolysis and ESR measurement (**Figure 18**), at 1 Farad only ferrocenium is in solution. The addition of collidine to the oxidised solution of**ET18**, regenerates the ferrocene moiety producing the aminyl radical. In that case, we can tentatively suggest that the collidine interacts with the amino group through the formation of a hydrogen-bonded complex, as it will be evidenced later on the report.

II. 4. c. Spontaneous grafting

After 1 F was consumed and collidine was added, evidences have been given of the possible formation of the radical aminyl with **ET18**, but this radical species was not detected by ESR. During the electrolysis another experiment has been carried out to confirm this formation. Indeed, several GC electrodes has been immersed without polarisation in a 1 mM solution of **ET18** at different time of the electrolysis in an attempt to capture the aminyl radical on the carbon surface (**Figure 20**). The aim of this experiment was to demonstrate that the regeneration of ferrocene obtained with collidine is simultaneous to the formation of the aminyl radical.

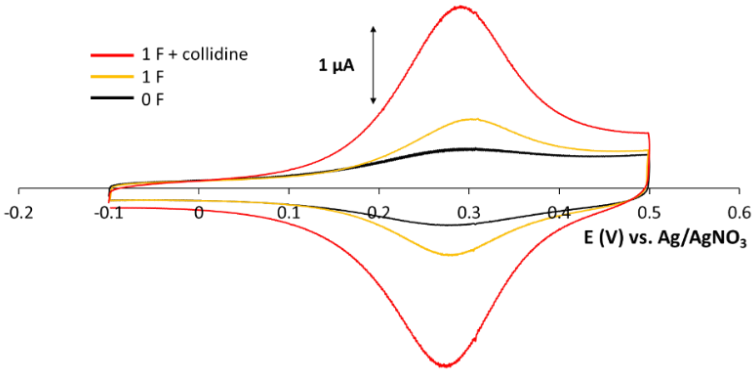


Figure 20. Spontaneous grafting (5 mins) on GCE dipped in 1mM **ET18** solution at different stages of the electrolysis.

Results obtained were quite encouraging since a good surface coverage has been obtained for the GCE immersed at 1 F + collidine, whereas without collidine, only a few amount of **ET 18** was grafted. Therefore, if grafting is occurring on GCE after addition of collidine, another evidence of radical aminyl formation is given. XPS measurements on glassy carbon sheets have confirmed that **ET18** was grafted on our substrates (**Figure 21**).

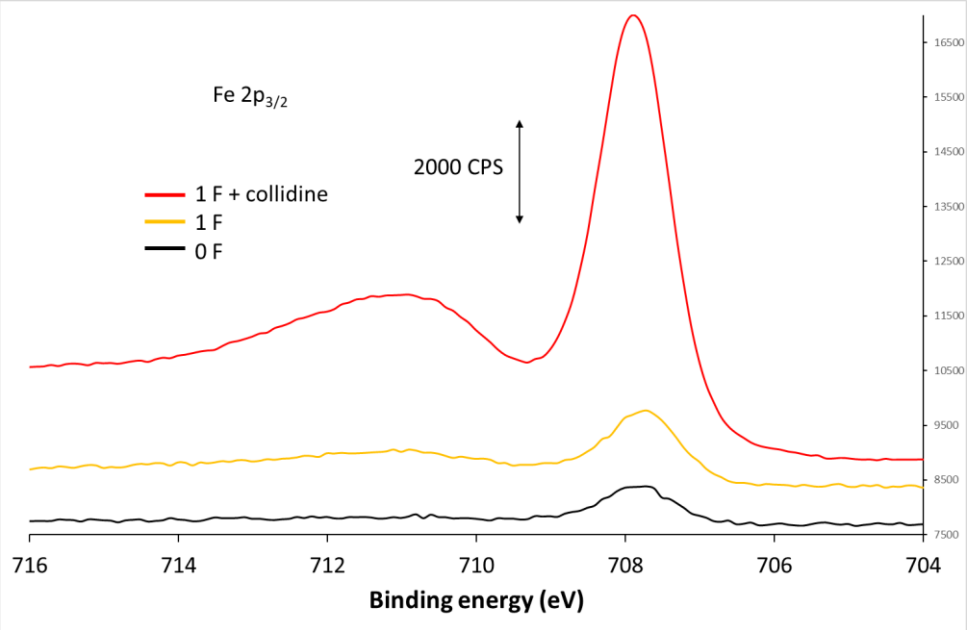


Figure 21. Fe 2p XPS spectra of a GC sheet modified with ET18.

In conclusion, spontaneous grafting of an amine moiety has been successfully achieved. The spontaneous grafting of an amine moiety is not easy due to its high anodic potential. This grafting is an evidence of the spontaneous generation of the aminyl radical. Following these results, the interaction between the base and the amino group has been studied in detail with different equivalents of base, various bases, solvents and para substituents to address this point. That was the subject of the following part.

III Role of the base

III. 1. Overview of recent results and mechanism described

The literature describes the collidine as acting as a base in the grafting of the amine function (**Figure 22.**a).[6,7] The recent results obtained points out a different role of the collidine on amino-ferrocene systems (see Erreur ! Source du renvoi introuvable.). Electrolysis performed at anodic potential of ferrocene revealed that the base interacts with the non-oxidised amine. This is why we propose a concerted mechanism involving a hydrogen interaction between the collidine and the amino-ferrocene system. We think that the formation of a hydrogen bonded complex between the aniline group and the collidine would cause an increase in the electron density on the aniline nitrogen, thus lowering the energy barrier for oxidation (**Figure 22**.b). The amine function would be more electron rich thanks to the hydrogen interaction and it could be thus more easily oxidised by the ferrocenium centre.

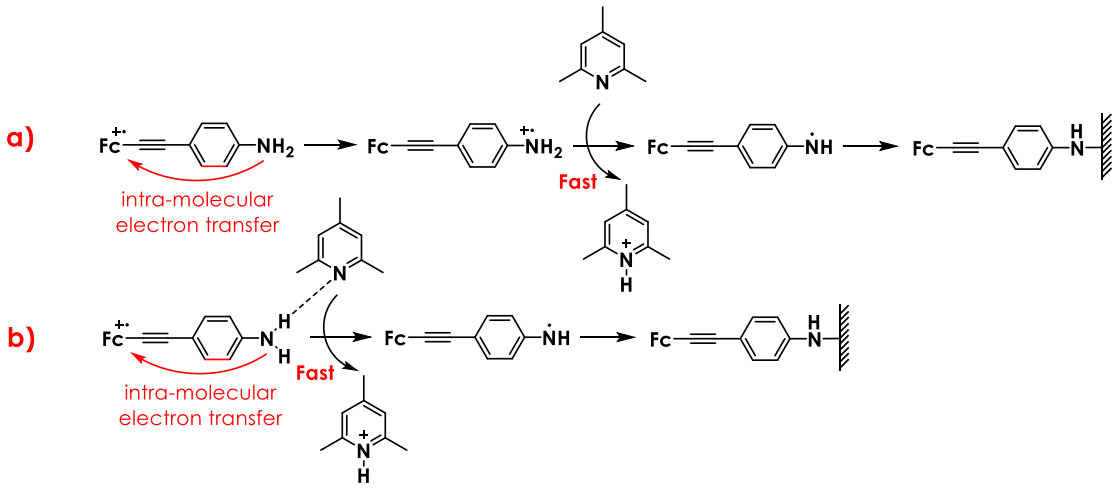


Figure 22. Mechanism previously described (a)[6] and the novel mechanism supposed (b).

Evidences of the mechanism will be given by studying the effect of bases on various aniline derivatives in different solvents.

III. 2. Various studies of the base

III. 2. a. Effect of a progressive addition of base

The first experiment which has been performed to demonstrate the mechanism was a progressive addition of a base. The objective was to observe the evolution of the oxidation peak of the amine (**Figure 23**). 4-bromoaniline was chosen as the studied compound due to its Hammet coefficient (equal to 0.23)[28].

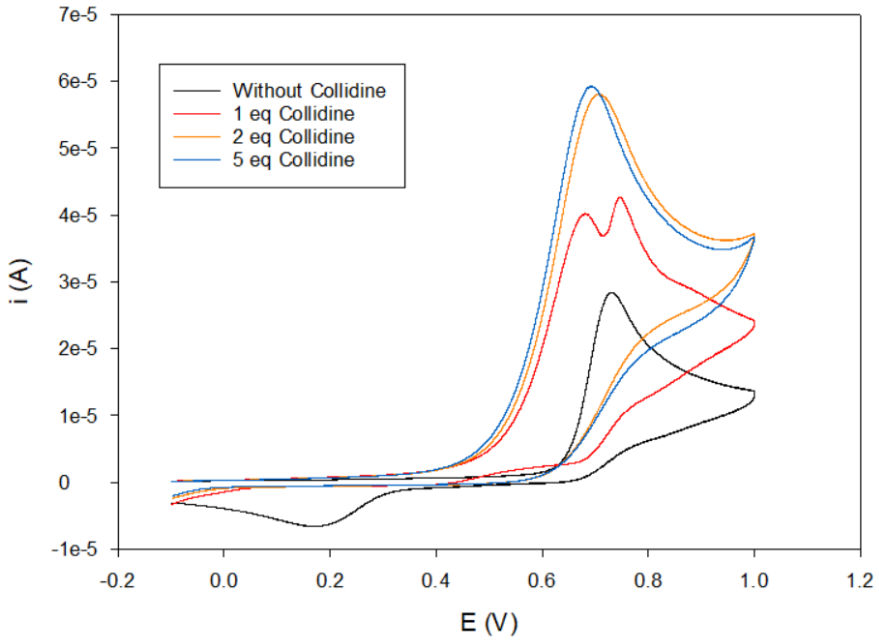


Figure 23. CV of 1 mM of 4-bromoaniline in ACN + 0.1 M Bu_4NPF_6 with a progressive addition of collidine. (100 mv/s; n = 1st cycle)

On **Figure 23**, after addition of 1 equivalent of collidine, another peak can be clearly seen before the original anodic peak of 4-bromoaniline. This second oxidation was caused by the probable interaction between collidine and 4-bromoaniline (one oxidation peak for the complex amine-base and one oxidation for the amine not complexed). The hydrogen interaction induces an aniline richer in electron which becomes easier to oxidise. When 2 equivalents were reached, the 2 peaks cannot be distinguished. However, the intensity between 1 equivalent and 2 equivalents had still increased. At 2 equivalents of collidine, 4-bromoaniline is fully complexed and as a consequence only one anodic peak is visible. Therefore, CVs did not change after addition of further equivalents of collidine (see **Figure 23**, 5 equivalents collidine).

In conclusion, after addition of a base, the oxidation peak of the amine does not change, but another peak linked to the base-amine interaction has appeared. Moreover, 2 equivalents of the base are sufficient to shift totally the anodic peak of the system. In next studies, 5 equivalents of the base will be used to assure the maximum shift of the amine anodic peak.

III. 2. b. Effect of bases

Next studies were devoted to the shift in potential which occurs after addition of base. The potential shift obtained after addition of 5 equivalents of collidine has been studied. Then, different bases have been used to diminish the potential of the anodic peak of 4-bromoaniline and observe the shift according to the pKa of each base (**Figure 24**).

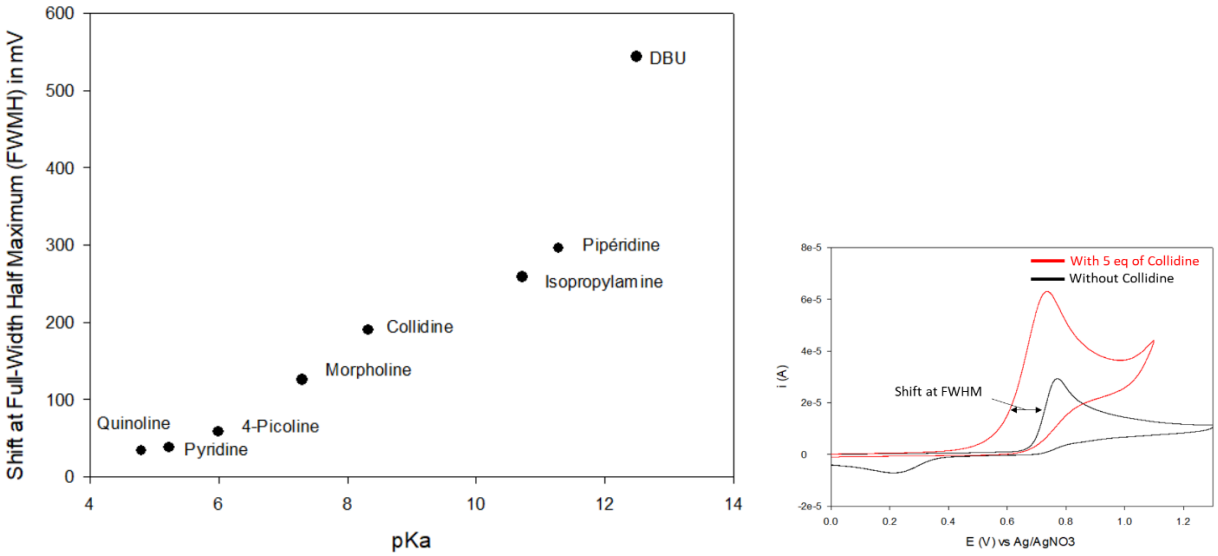


Figure 24. Shift at FWMH of 1 mM 4-bromoaniline according to the pKa of various bases in ACN + 0.1 M Bu_4NPF_6 (100 mV/s; n = 1st cycle) (left) and how the shift is calculated (right).

Organic bases having a nitrogen atom have been chosen to compare results obtained with collidine.[30] Various pKa were studied to obtain a tendency of the shift in potential according to the pKa. DBU produces the largest shift on the oxidation of 4-bromoaniline (550 mV). This trend is confirmed on **Figure 24** , the higher the pKa is, the higher is the shift. Therefore, hydrogen interaction between the base and aniline derivative is stronger when the base has a higher pKa. This effect can be explained by the strength of the hydrogen bond. The stronger is the base, the stronger is the hydrogen bonding (**Figure 25**).

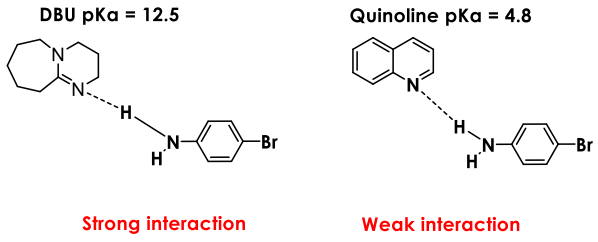


Figure 25. Differences between Quinoline and DBU hydrogen bonding.

III. 2. c. Effect of solvents

Another parameter which has been modified is the solvent. Solvents play a key role in the hydrogen bonding. Hansen parameter characterises the strength of the competitive hydrogen interaction between the solvent and the solubilised compound. Higher is the Hansen parameter, stronger is the interaction.[31] Shifts were calculated after addition of 5 equivalents of collidine. Various solvents have been chosen to determinate the tendency of the shift according to the Hansen parameter of each solvent (**Figure 26**).

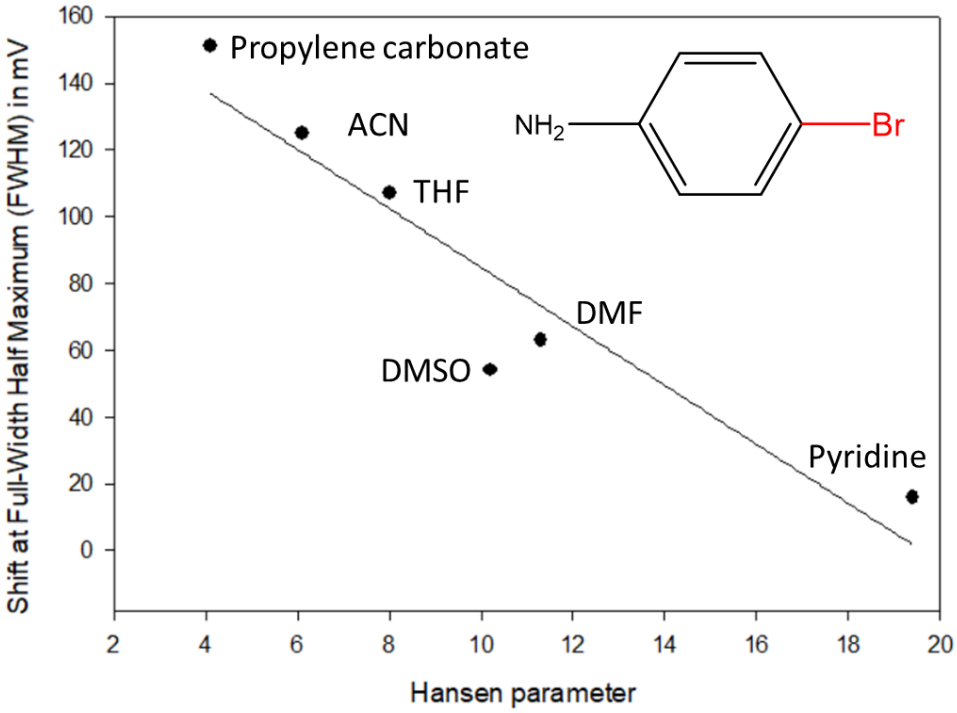


Figure 26. Shift at FWHM of 4-Bromoaniline in 0.1 M Bu_4NPF_6 in different solvents. (100 mV/s; n = 1st cycle)

On **Figure 26**, higher is the Hansen parameter, shorter is the shift after addition of collidine. This can be explained by the competitive interaction between the collidine and the solvent. Solvents with a high Hansen parameter have a strong hydrogen interaction with the 4-bromoaniline, then the addition of collidine has a little effect on the anodic potential of 4-bromoaniline.

III. 2. d. Effect of substituents

Finally, the effect of the para-substituent has been studied. Para-substituent has a key role on where the density of electrons is located. With an electron donating group, the density will be located on the amine, while with an electron withdrawing group the density will be located on the para-substituent. Aniline derivatives were used to perform this study with different Hammet coefficient (**Figure 27**).[28]

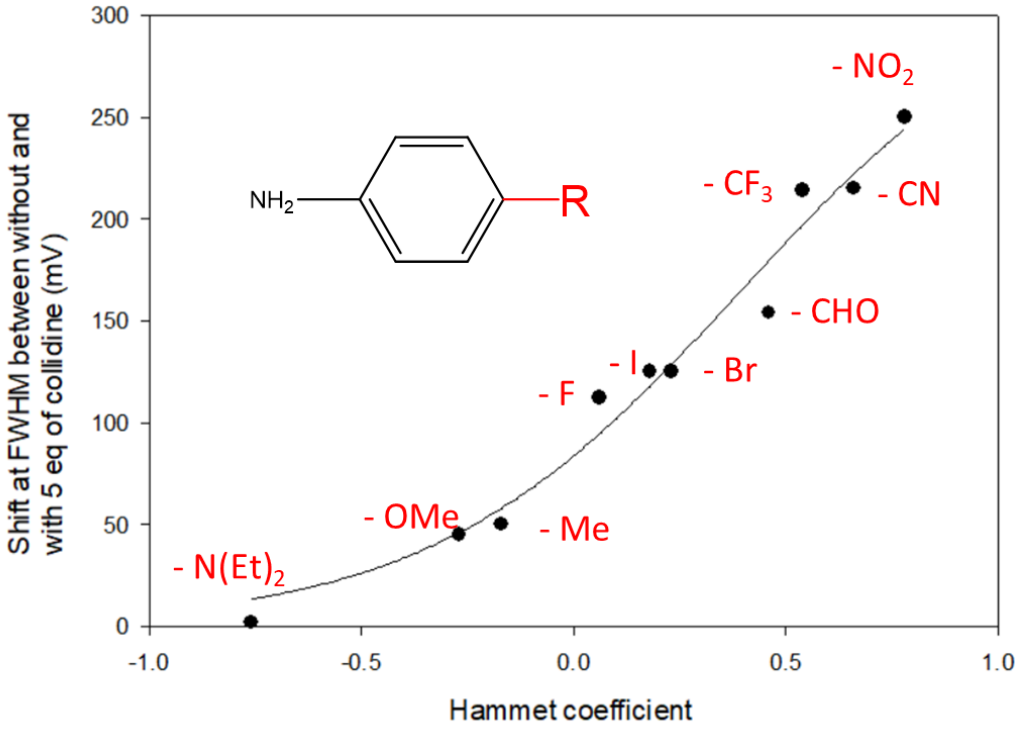


Figure 27. Shift at FWHM with collidine of 1mM aniline with different para-substituent.
ACN + 0.1 M Bu_4NPF_6 (100 $mv.s^{-1}$; n = 1)

The study performed has confirmed the results expected. When the amine is electron-deficient, the addition of collidine has a strong effect on the oxidation of the amine since hydrogen bond is stronger. If an electron donating group is in para position, the electron density is not significantly changed and the addition of collidine has a little effect.

All these experiments have confirmed the hydrogen interaction between the aniline derivative and the base.

Conclusion

Different electrochemical studies performed on amino-ferrocene systems give evidence of a spontaneous grafting of the amine moiety by radical attacks on GCE. This work is the first mention of a spontaneous production of a radical aminyl and its subsequent grafting. This result is promising for lowering the high anodic potential of amine derivatives and facilitating their grafting. These results have also assessed the role of the base in the grafting mechanism. The effect of collidine has been traditionally associated to a simple acid/base reaction with the radical cation of the amine. However, our results support a different mechanism in which the collidine reacts with the non-oxidised amine. These results envisaged a hydrogen interaction between the collidine and aniline derivatives which lead to an amine group easier to oxidise.

Therefore, studies were carried out to determine the nature of this interaction. The different bases, equivalents of base, solvents and aniline derivatives have evidenced the formation of a hydrogen bond. Literature has already described a similar complex between a secondary amine (indoline) and a base.[32,33] However, primary amines and grafting applications have not been discussed. Particular conditions (solvent, base and substituent) need to be determine for a possible spontaneous grafting of amines.

References

[1] B. Barbier, J. Pinson, G. Desarmot, M. Sanchez, *J. Electrochem. Soc.* **1990**, *137*, 1757–1764.
[2] Michel Delamar, Rachid Hitmi, Jean Pinson, Jean Michel Savéant, *J. Am. Chem. Soc.* **1992,** *114*, 5883-5884
[3] D. Bélanger, J. Pinson, *Chem. Soc. Rev.* **2011**, *40*, 3995–4048.
[4] A. Adenier, M. M. Chehimi, I. Gallardo, J. Pinson, N. Vilà, *Langmuir* **2004**, *20*, 8243–8253.
[5] O. D. Benjamin, M. Weissmann, D. Bélanger, *Electrochimica Acta* **2014**, *122*, 210–217.
[6] O. Buriez, E. Labbé, P. Pigeon, G. Jaouen, C. Amatore, *J. Electroanal. Chem.* **2008**, *619–620*, 169–175.
[7] O. Buriez, F. I. Podvorica, A. Galtayries, E. Labbé, S. Top, A. Vessières, G. Jaouen, C. Combellas, C. Amatore, *J. Electroanal. Chem.* **2013**, *699*, 21–27.
[8] R. Wizinger-Aust, *Angew. Chem.* **1958**, *70*, 199–204.
[9] D. chemische G. A. from paper, *Berichte der Deutschen chemischen Gesellschaft zu Berlin*, Berlin, **1884**.
[10] M. Gomberg, W. E. Bachmann, *J. Am. Chem. Soc.* **1924**, *46*, 2339–2343.
[11] H. Meerwein, E. Büchner, K. van Emster, *J. Für Prakt. Chem.* **n.d.**, *152*, 237–266.
[12] M. Delamar, R. Hitmi, J. Pinson, J. M. Saveant, *J. Am. Chem. Soc.* **1992**, *114*, 5883–5884.
[13] S. Baranton, D. Bélanger, *Electrochimica Acta* **2008**, *53*, 6961–6967.
[14] R. G. Gillis, *J. Chem. Educ.* **1954**, *31*, 344.
[15] M. Toupin, D. Bélanger, *Langmuir* **2008**, *24*, 1910–1917.
[16] Thibaud Menanteau, PhD thesis defended at the University of Angers the 19th September 2016
[17] A. Mesnage, X. Lefèvre, P. Jégou, G. Deniau, S. Palacin, *Langmuir* **2012**, *28*, 11767–11778.
[18] C. P. Andrieux, J. Pinson, *J. Am. Chem. Soc.* **2003**, *125*, 14801–14806.
[19] Alison J. Downard, *Electroanalysis*, **2000**, *12*, 1085-1096
[20] J. Pinson, F. Podvorica, *Chem. Soc. Rev.* **2005**, *34*, 429-439
[21] Michael P. Doyle, Judith K. Guy, Kathlynn C. Brown, Surendra N. Mahapatro, Craig M. VanZyl, Jack R. Pladziewicz, *J. Am. Chem. SOC.* **1987,** *109*, 1536-1540
[22] T. Menanteau, M. Dias, E. Levillain, A. J. Downard, T. Breton, *J. Phys. Chem. C* **2016**, *120*, 4423–4429.
[23] F. Barrière, A. J. Downard, *J. Solid State Electrochem.* **2008**, *12*, 1231–1244.
[24] A. Adenier, N. Barré, E. Cabet-Deliry, A. Chaussé, S. Griveau, F. Mercier, J. Pinson, C. Vautrin-Ul, *Surf. Sci.* **2006**, *600*, 4801–4812.
[25] D. A. Buttry, J. C. Peng, J.-B. Donnet, S. Rebouillat, *Carbon* **1999**, *37*, 1929–1940.
[26] I. Gallardo, J. Pinson, N. Vilà, *J. Phys. Chem. B* **2006**, *110*, 19521–19529.
[27] E. Touzé, S. Dabos-Seignon, T. Cauchy, F. Gohier, C. Cougnon, *Electrochem. Commun.* **2017**, *82*, 52–55.
[28] C. Hansch, A. Leo, R. W. Taft, *Chem. Rev.* **1991**, *91*, 165–195.
[29] L. Lee, N. R. Gunby, D. L. Crittenden, A. J. Downard, *Langmuir* **2016**, *32*, 2626–2637.
[30] Masaichiro Masui, Yorie Kaiho, Takahiro Ueshima, Shigeko Osaki, *Chem. Pharm. Bull.*, **1982**, *30*, 3225-3230
[31] S. Park, J. An, I. Jung, R. D. Piner, S. J. An, X. Li, A. Velamakanni, R. S. Ruoff, *Nano Lett.* **2009**, *9*, 1593–1597.
[32] A. J. Peters, M. P. Rainka, L. Krishnan, S. Laramie, M. Dodd, J. A. Reimer, *J. Electroanal. Chem.* **2013**, *691*, 57–65.
[33] M. P. Rainka, A. Peters, G. Soloveichik, *Int. J. Hydrog. Energy* **2013**, *38*, 3773–3777.

[34] P. Srinivas, S. Prabhakar, F. Chevallier, E. Nassar, W. Erb, V. Dorcet, V. Jouikov, P. R. Krishna, F. Mongin, *New J. Chem.* **2016**, *40*, 9441–9447.
[35] M. Liu, L. Wang, J. Deng, Q. Chen, Y. Li, Y. Zhang, H. Li, S. Yao, *Analyst* **2012**, *137*, 4577–4583.
[36] K. Li, Q. Wang, *Chem. Commun.* **2005**, *0*, 4786–4788.

Experimental part

Chemicals

All reagents were commercial reagent grade (SIGMA Aldrich, TCI, Acros-Fischer) and were used without further purification. Solvents were dried and purified using standard techniques. Silica gel chromatography was performed with a SIGMA Aldrich Chemistry SiO2 (pore size 60 Å, 40-63 µm technical grades). Flexible plates ALUGRAM® Xtra SIL G UV254 from MACHEREY-NAGEL were used for TLC. Compounds were detected by UV irradiation (Bioblock Scientific).

Melting Points (MP)

Melting point were determined on a Stuart SMP30 from room temperature to 350 °C with a ramp of 5 °C per minute.

Mass Spectrometry

Matrix Assisted Laser Desorption/Ionization was performed on MALDI-TOF MS BIFLEX III Bruker Daltonics spectrometer using dithranol, DCTB as matrix.

Nuclear Magnetic Resonnance (NMR)

NMR spectra were recorded with a Bruker AVANCE III 300 (^{1}H, 300 MHz and ^{13}C, 75 MHz). Chemical shifts are given in ppm (^{1}H and ^{13}C) and coupling constants J in Hz. Multiplets are given with the following abbreviations: s: singlet, d: doublet, dd: doublet of doublets, dt: doublet of triplets, t: triplet, td: triplet of doublets, q: quartet and br: broad signal. Residual non-deuterated solvent was used as an internal standard.

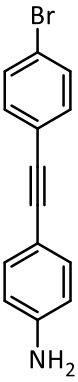
Cyclic Voltammetry (CV)

Cyclic voltammetry studies with glassy carbon (GC) working electrodes was performed using a potentiostat/galvanostat model VSP (from Bio-logic) monitored by ECLab software. Acetonitrile solutions (HPLC grade, Carlo Erba) and tetrabutylammonium hexafluorophosphate (Sigma-Aldrich) were used. Experiments were carried out in a one-compartment cell equipped with GC working electrode from Bioanalytical Systems Inc. (model MF-2012; 3 mm in diameter) and a platinum wire counter electrode. An $Ag/AgNO_3$ (0.01 M in 0.1 Bu_4NPF_6/CH_3CN) electrode was used as reference.

X-ray Photoelectron Spectroscopy (XPS)

XPS measurements were performed with a Kratos Axis Ultra spectrometer using a Al Kα monochromatic beam working at 1486.6 eV. All spectra were recorded in the constant energy mode at a pass energy of 20 eV. Data treatment was performed with CasaXPS software and all spectra were calibrated taking 284.5 eV (graphite like carbon) as a reference binding energy.

4-((4-bromophenyl)ethynyl)aniline (CAN01)



$C_{14}H_{10}BrN$
MW: 272.1450

A mixture of 1-bromo-4-iodobenzene (1.21 g, 4.27 mmol, 1 equiv.), $Pd(OAc)_2$ (19 mg, 0.08 mmol, 0.02 equiv.), CuI (8 mg, 0.04 mmol, 0.01 equiv.), PPh_3 (45 mg, 0.17 mmol, 0.04 equiv.) in 25 mL of triethylamine was stirred under argon. Then, 4-ethynylaniline (500 mg, 4.27 mmol, 1 equiv.) was added dropwise. The mixture was stirred at room temperature during 24 hours. After addition of cyclohexane (20 mL), the catalyst was removed by filtration through a short pad of Celite, and the filtrate was washed with water (3 x 50 mL) and extracted with dichloromethane (20 mL) and finally the organic phase layers were dried with anhydrous $MgSO_4$, concentrated under reduced pressure and purified by chromatography on silica gel using dichloromethane / petroleum ether (4:1) as eluent to obtain 828 mg (71 %) of desired compound as a beige solid.

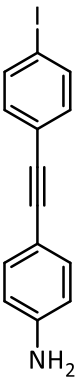
MP: 178 – 179 °C.

^{1}H NMR ($CDCl_3$): 7.45 (d, 2H, *J* = 8.7 Hz), 7.34 (tt, 4H, *J* = 8.7, 4.7, 2.1 Hz), 6.63 (d, 2H, *J* = 8.7 Hz), 3.84 (br. s, 2H).

^{13}C NMR ($CDCl_3$): 147.0, 133.1, 132.9, 131.6, 123.1, 121.8, 114.9, 112.3, 91.5, 86.5.

HRMS (EI) calculated for $C_{14}H_{10}BrN$ $[M]^+$: 270.9997, found: 272.9988.

4-((4-iodophenyl)ethynyl)aniline[34] **(CAN05)**



$C_{14}H_{10}IN$
MW: 319.1455

A mixture of 1,4-diiodobenzene (3.5 g, 10.61 mmol, 3 equiv.), $Pd(PPh_3)_4$ (39 mg, 0.11 mmol, 0.03 equiv.), CuI (40 mg, 0.21 mmol, 0.06 equiv.) in toluene and triethylamine (respectively 25 and 5 mL) was stirred under argon. Then, 4-ethynylaniline (414 mg, 3.54 mmol, 1 equiv.) was added dropwise. The mixture was stirred at 40 °C during 3 hours. After addition of cyclohexane (20 mL), the catalyst was removed by filtration through a short pad of Celite, and the filtrate was washed with water (3 x 50 mL) and extracted with dichloromethane (20 mL) and finally the organic phase layers were dried with anhydrous $MgSO_4$, concentrated under reduced pressure and purified by chromatography on silica gel using dichloromethane / petroleum ether (95:5) as eluent to obtain 720 mg (64 %) of the desired compound as a beige solid.

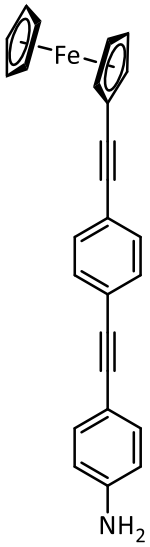
MP: 172 – 173 °C.

^{1}H NMR ($CDCl_3$): 7.65 (d, 2H, *J* = 8.5 Hz), 7.32 (d, 2H, *J* = 8.6 Hz), 7.21 (d, 2H, *J* = 8.5 Hz), 6.63 (d, 2H, *J* = 8.6 Hz), 3.84 (br. s, 2H).

^{13}C NMR ($CDCl_3$): 146.9, 137.4, 133.0, 132.9, 123.6, 114.8, 112.3, 93.2, 91.7, 86.5.

HRMS (FAB+) calculated for $C_{14}H_{10}IN$ $[M]^+$: 318.9858, found: 318.9852.

4-(2-(4-(2-(ferrocenyl)ethynyl)phenyl)ethynyl)aniline[35] **(CAN06)**



$C_{26}H_{19}FeN$
MW: 401.2900

A mixture of 4-((4-iodophenyl)ethynyl)aniline (250 mg, 0.78 mmol, 1 equiv.), $Pd(OAc)_2$ (5.28 mg, 0.02 mmol, 0.03 equiv.), CuI (9 mg, 0.05 mmol, 0.06 equiv.), PPh_3 (25 mg, 0.09 mmol, 0.12 equiv.) in 25 mL of tetrahydrofuran and 5 mL of triethylamine was stirred under argon. Then, ethynylferrocene (520 mg, 4.45 mmol, 1 equiv.) was added dropwise. The mixture was stirred at 40 °C during 24 hours. After addition of cyclohexane (20 mL), the catalyst was removed by filtration through a short pad of Celite, and the filtrate was washed with water (2 x 10 mL) and extracted with dichloromethane (20 mL) and finally the organic phase layers were dried with anhydrous $MgSO_4$, concentrated under reduced pressure and purified by chromatography on silica gel using dichloromethane / petroleum ether (6:4) as eluent to obtain 80 mg (25 %) of desired compound as a red solid.

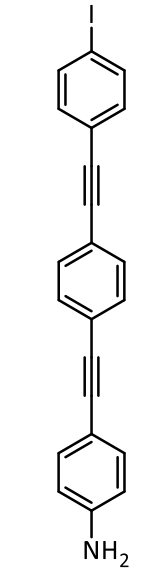
IR (v, cm^{-1}): 3449, 3383, 2922, 2852, 2202, 1619, 1520, 1289, 1104, 832.

^1H NMR ($CDCl_3$): 7.43 (s, 4H), 7.34 (d, 2H, *J* = 8.6 Hz), 7.21 (d, 2H, *J* = 8.5 Hz), 6.64 (d, 2H, *J* = 8.6 Hz), 4.51 (t, 2H, *J* = 1.8 Hz), 4.25 (s, 7H), 3.84 (br. s, 2H).

^{13}C NMR ($CDCl_3$): 146.8, 133.1, 131.3, 123.2, 114.9, 112.6, 91.9, 90.3, 87.5, 85.8, 71.6, 70.1, 69.1, 65.2.

HRMS (FAB+) calculated for $C_{26}H_{19}FeN$ $[M]^+$: 401.0867, found: 401.0865.

4-((4-((4-iodophenyl)ethynyl)phenyl)ethynyl)aniline[36] **(CAN07)**



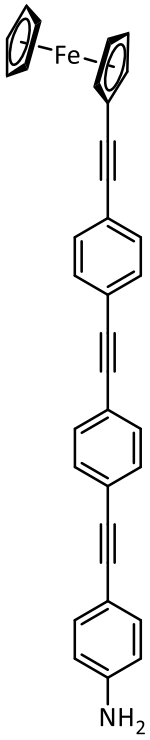
$C_{22}H_{14}IN$
MW: 419.2655

A mixture of 1,4-diiodobenzene (911 mg, 2.76 mmol, 3 equiv.), $Pd(OAc)_2$ (6.20 mg, 0.02 mmol, 0.03 equiv.), CuI (10.5 mg, 0.05 mmol, 0.06 equiv.), PPh_3 (29 mg, 0.11 mmol, 0.12 equiv.) in tetrahydrofuran and triethylamine (respectively 25 and 5 mL) was stirred under argon. Then, 4-(2-(4-ethynylphenyl)ethynyl)aniline (200 mg, 0.9 mmol, 1 equiv.), was added dropwise. The mixture was stirred at 40 °C during 3 hours. After an adding of cyclohexane (20 mL), the catalyst was removed by filtration through a short pad of Celite, and the filtrate was washed with water (3 x 50 mL) and extracted with dichloromethane (20 mL) and finally the organic phase layers were dried with anhydrous $MgSO_4$, concentrated under reduced pressure and purified by chromatography on silica gel using dichloromethane / petroleum ether (95:5) as eluent to obtain 140 mg (36 %) of desired compound as a beige solid.

^1H NMR ($(CD_3)_2SO$): 7.81 (d, 2H, *J* = 8.5 Hz), 7.55 (d, 2H, *J* = 8.6 Hz), 7.48 (d, 2H, *J* = 8.6 Hz), 7.35 (d, 2H, *J* = 8.5 Hz), 7.21 (d, 2H, *J* = 8.6 Hz), 6.56 (d, 2H, *J* = 8.7 Hz), 5.64 (br. s, 2H).

HRMS (FAB+) calculated for $C_{22}H_{14}IN$ $[M]^+$: 419.0171, found: 418.8

4-(2-(4-(2-(4-(2-(ferrocenyl)ethynyl)phenyl)ethynyl)phenyl)ethynyl)aniline (ET58-CAN08)



$C_{34}H_{23}FeN$
MW: 501.4100

A mixture of 4-((4-((4-iodophenyl)ethynyl)phenyl)ethynyl)aniline (110 mg, 0.26 mmol, 1 equiv.), $Pd(OAc)_2$ (1.77 mg, 0.008 mmol, 0.03 equiv.), CuI (3 mg, 0.02 mmol, 0.06 equiv.), PPh_3 (6 mg, 0.02 mmol, 0.09 equiv.) in 25 mL of tetrahydrofuran and 5 mL of triethylamine was stirred under argon. Then, ethynylferrocene (82 mg, 0.39 mmol, 1.5 equiv.) was added dropwise. The mixture was stirred at 40 °C during 24 hours. After an adding of cyclohexane (20 mL), the catalyst was removed by filtration through a short pad of Celite, and the filtrate was washed with water (2 x 10 mL) and extracted with dichloromethane (20 mL) and finally the organic phase layers were dried with anhydrous $MgSO_4$, concentrated under reduced pressure and purified by chromatography on silica gel using dichloromethane / petroleum ether (6:4) as eluent to obtain 85 mg (64 %) of desired compound as a red solid.

^{1}H NMR ($CDCl_3$): 7.47 (d, 8H, *J* =1.9 Hz), 7.34 (d, 2H, *J* = 8.5 Hz), 6.64 (d, 2H, *J* = 8.5 Hz), 4.51 (s, 2H), 4.25 (s, 7H).

HRMS (FAB+) calculated for $C_{34}H_{23}FeN$ $[M]^+$: 501.1180, found: 318.9852.