View Article Online View Journal

# NJC

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: B. J. López Mayorga, C. Sandoval-Chávez, M. D. P. Carreon-Castro, V. M. Ugalde-Saldívar, F. Cortes-Guzman, J. G. López-Cortés and M. C. Ortega-Alfaro, *New J. Chem.*, 2018, DOI: 10.1039/C8NJ00787J.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the **author guidelines**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the ethical guidelines, outlined in our <u>author and reviewer resource centre</u>, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



## rsc.li/njc

YAL SOCIETY CHEMISTRY

## Journal Name

### ARTICLE

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

# Ferrocene amphiphilic D- $\pi$ -A dyes: Synthesis, redox behavior and determination of Band Gaps.

B. López-Mayorga,<sup>a</sup> C. I. Sandoval-Chávez,<sup>a</sup> P. Carreón- Castro,<sup>a</sup> V. M. Ugalde-Saldívar,<sup>b</sup> F. Cortés-Guzmán,<sup>c</sup> J. G. López-Cortés<sup>c</sup> and M. C. Ortega-Alfaro<sup>\*a</sup>

We report the synthesis of a series of ferrocene amphiphilic donor- $\pi$ -acceptor dyes, with general formula (Fc-CH=CH-HetNC<sub>16</sub>H<sub>33</sub>)<sup>+</sup> X<sup>-</sup> [where: Fc behaves as donor group, a double bond as  $\pi$  bridge, and 2-, 4-pyridinium and 4-quinolinium as potent acceptor groups (**2a-b** and **4**, X= Br<sup>-</sup> or BF<sub>4</sub>-)], in good overall yields. Together with their neutral counterparts (**6a-b** and **7**), the photophysical and electrochemical properties of these compounds are investigated by means of UV-Vis spectroscopy and cyclic voltammetry. The optically and electrochemically band gaps of these dyes are calculated, affording that **4** has the lowest bandgap value. Time-dependent DFT calculations indicate that the lowest energy absorption band displayed for these compounds has mainly metal-to-ligand charge character, being the HOMO-LUMO electronic transition the main contribution.

#### Introduction

Nowadays, dye-like and  $\pi$ -conjugated organic compounds represent attractive targets for diverse application in advanced functional materials.<sup>1</sup> Organic  $\pi$ -systems end-capped with an electron donor (D) and an electron acceptor (A) represent a subclass of these kinds of molecules widely known as push-pull systems. They have predominant applications as chromophores with nonlinear optical (NLO) properties,<sup>2</sup> electro-optic,<sup>3</sup> and piezochromic<sup>4</sup> materials, NLO switches,<sup>5</sup> photochromic,<sup>6</sup> charge-based information storage<sup>7</sup> and solvatochromic probes<sup>8</sup> as well as active layers in DSSCs.<sup>9</sup> When organometallic fragments are included as electron donor, they can enhance the optical behavior of donor- $\pi$ -acceptor (D- $\pi$ -A) systems along with other intrinsic properties.<sup>10</sup>

Among the variety of organometallic compounds that have been generated to achieve this goal, ferrocene-based architectures bearing an unsaturated backbone have been used for wide range of applications, like information storage devices,<sup>11</sup> molecular switches,<sup>12</sup> chemical detection<sup>13</sup> and so on.<sup>14</sup> Likewise, ferrocenyl fragments have been included as component of D- $\pi$ -A systems with NLO properties,<sup>15</sup> as sensors<sup>16</sup> and other related applications.<sup>17</sup> The properties of D- $\pi$ -A systems can be easily changed by varying donor, spacer and acceptor moieties. We have chosen ferrocenyl  $\pi$ -conjugated pyridinium salts as the key building block for the next reasons: i) Literature data reveal that ferrocene is an excellent electron-donating group and exhibits a reversible redox behavior.<sup>18</sup> ii) The ethylene group is a good spacer that allows electronic communication between donor and acceptor in D- $\pi$ -A system<sup>19</sup> and iii) *N*-alkyl heterocyclic cations exhibit higher electro-withdrawing character.<sup>20</sup> These facts should positively contribute to favor a good donor-acceptor interaction in these dyes (Figure 1). Likewise, we have incorporated a long alkyl chain to favor the solubility of these compounds to future optoelectronic applications.

Thus, we describe the synthesis of six ferrocenyl  $\pi$ -conjugated pyridinium salts, incorporating two different heterocycles (pyridine and quinoline) in their cationic and neutral version. The properties of these dyes were investigated by absorption spectroscopy and electrochemical analysis. Using this information, we have also determined their optical and electrochemical band gaps. To analyze the experimental data obtained, time dependent density functional (TD-DFT) calculations were performed using the t-HCTHhyb functional and the 6-311++G(d)/LANL2DZ mixed basis set.

Electronic Supplementary Information (ESI) available: Additional spectroscopic and electrochemical data. See DOI: 10.1039/x0xx00000x



Figure 1. Structural design of ferrocene amphiphilic D- $\pi$ -A dyes

<sup>&</sup>lt;sup>a</sup> Instituto de Ciencias Nucleares, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, Coyoacán, Cd. Mx., 04510, México. carmen.ortega@nucleares.unam.mx.

<sup>&</sup>lt;sup>b.</sup> Facultad de Química, Universidad Nacional Autónoma de México, Av. Universidad 3000, Coyoacán, Cd. Mx., 04510, México.

<sup>&</sup>lt;sup>c</sup> Instituto de Química, Universidad Nacional Autónoma de México, Circuito

Exterior, Cd. Universitaria, Coyoacán, Cd. Mx., 04510, México.



Scheme 1. Synthesis of ferrocene amphiphilic D-π-A dyes [**2a-b** and **4**][X], where X= Br, BF<sub>4</sub> and their neutral counterparts **6a-b** and **7**. Conditions: I) C<sub>16</sub>H<sub>33</sub>Br /110 °C; II) Piperidine, FcC(O)H /MeOH, reflux; III) AgBF<sub>4</sub>, MeCN, RT. IV) n-BuLi /-70 °C/THF, FcC(O)H; V) MsCl, NEt<sub>3</sub>/CH<sub>2</sub>Cl<sub>2</sub>; VI) t-BuOK /THF, FcC(O)H.

#### **Results and discussion**

Published on 28 February 2018. Downloaded by Freie Universitaet Berlin on 03/03/2018 09:48:41

The synthesis of new amphiphilic ferrocene D-π-A dyes was carried out using different modifications of informed methods.  $^{^{21,\ 22}}$  In a first step, the picoline cations (1) were prepared by the reaction of 2- and 4-picoline with the alkyl halide at 110 °C. Then, the corresponding Nhexadecylpicolinium bromide was reacted with ferrocenecarboxaldehyde, in the presence of piperidine as base, affording 2a[Br] and 2b[Br], in excellent global yields (Scheme 1). For 4[Br], a similar reaction between the Nalkylquinolinium bromide and ferrocenecarboxaldehyde gave this compound, in 85 % yield. (Scheme 1). The identities and purities of compounds 2a[Br], 2b[Br] and 4[Br] are confirmed by NMR, IR-ATR, Mass Spectrometry, HRMS and CHN elemental analyses. To evaluate the influence of the counterion included in these compounds, we have also prepared their analogues **2a-b** and **4**, those containing  $BF_4$  in good yields.

The <sup>1</sup>H NMR spectra for **2a**[Br] and **2b**[Br] exhibit the representative signals for a 2- and 4-pyridinium derivatives, respectively. In both cases, we observe a large vicinal coupling constant for the two vinylic protons supporting the (E)configuration for the double bond. The typical signals for a mono substituted ferrocenyl compound appear around 4-5 ppm. Shifted at low fields (~4 ppm), we observed the methylene group bonded to the nitrogen atom. In the <sup>13</sup>C NMR spectra, we observed two signals between 120-125 ppm assigned to the double bond included in these compounds. Likewise, typical signals at 70-80 ppm are consistent with a mono-substituted ferrocene, and shifted to higher fields, we observe the corresponding signals of the aliphatic chain. Similar spectroscopic data are observed for the compounds 2a[BF<sub>4</sub>] and 2b[BF<sub>4</sub>]. To compare the spectroscopic properties of the ionic ferrocenyl compounds 2a-b and 4 and evaluate the effect of the electron-acceptor group, we have synthesized the

neutral analogues 6a-b and 7 (Scheme 1). Compounds 6a-b were obtained by a tandem reaction between 2- or 4-methyl pyridine and ferrocenecarboxaldehyde in basic conditions, affording the corresponding alcohols intermediates 5a-b, which were subsequently dehydrated using MsCl and NEt<sub>3</sub>. 6a**b** were obtained in excellent global yields, and the spectroscopic data are consistent with the literature.<sup>23</sup> The new compound 7 was prepared in one step by a condensation the reaction between 4-methylquinoline and ferrocenecarboxaldehyde in basic conditions, in good yields. As expected, the <sup>1</sup>H NMR spectrum of **7** indicates that only the less-hindered *E* isomer was formed (J = 15.9 Hz).

Analyzing the spectroscopic behavior of these compounds, we observed slight differences of the chemical shift for the vinyl and heterocyclic protons across this series. As expected, the presence of a positive charge on nitrogen atom of compounds 2a[Br], 2b[Br] and 4[Br] resulted in an upfield shift of the vinyl protons  $H_A$  and  $H_B$ (Figure S-25). In the case of 4[Br], the chemical shift of  $H_B$  is very different in comparison with 2a[Br] and 2b[Br]. This reveals the potent electron-withdrawing character of the quinolinium unit that strongly affects  $H_B$ , downfield-shifts this signal in comparison with those for 2a[Br] and 2b[Br], respectively.

Likewise, relative large upfield shifts of protons of heterocyclic moiety for the cationic compounds **2a**[Br], **2b**[Br] and **4**[Br] in comparison with their neutral analogues are observed, revealing that in **2a**[Br], **2b**[Br] and **4**[Br], the electronic delocalization provoked by the polarization across the D- $\pi$ -A system is more effective than **6a**, **6b** and **7**, respectively. Furthermore, the resonances for the protons assigned to ferrocene moiety of **2a**[Br], **2b**[Br] and **4**[Br] are offset upfield compared with **6a**, **6b** and **7** (See, experimental section). This suggests a slight contribution of a fulvene-type resonance structure B as shown in Scheme 2.<sup>18g, 24</sup> A similar behavior was observed for series of BF<sub>4</sub> salts.

#### Journal Name

#### **Optical properties**

The optical properties of the ferrocenyl salts [**2a-b** and **4**][Br] and [**2a-b** and **4**][BF<sub>4</sub>] were studied to determine the suitability of these materials for possible optoelectronic applications and to further understand the effects of the acceptor included in this series of ferrocenyl compounds. Figure 2 shows the electronic absorption spectra for **2a**, **2b** and **4** in CHCl<sub>3</sub> and CH<sub>3</sub>CN.

Compounds **2a-b** display two characteristic absorption bands. For **2a**, the more intense band at higher energy appears at 347 nm (8700 mol<sup>-1</sup>L cm<sup>-1</sup>) in CH<sub>3</sub>CN and at 355 (14100 mol<sup>-1</sup>L cm<sup>-1</sup>) in CH<sub>2</sub>(Tables 1 and S1). According to literature for other ferrocenyl mono-substituted compounds,<sup>25</sup> this band corresponds to a  $\pi$ - $\pi$ \* transition, associated with an intraligand charge transfer (ILCT). However, recent studies involving density functional theory suggests that this band has a largely MLCT character.<sup>26</sup> We also observe a less intense lower energy band at 533 (2000 mol<sup>-1</sup>L cm<sup>-1</sup>) in CH<sub>3</sub>CN and 551 nm (3800 mol<sup>-1</sup>L cm<sup>-1</sup>) for CHCl<sub>3</sub>. This band is due to metal to-ligand charge transfer (MLCT).

Comparing the absorption spectra of **2a-b** salts acquired in CHCl<sub>3</sub> and CH<sub>3</sub>CN, we observe that these compounds show a clear red-shift in both ICT bands, showing higher molar coefficient ( $\epsilon$ ), when CHCl<sub>3</sub> is used as solvent (Table S1, SI). This behavior indicates a negative solvatochromic effect favored by a polar solvent such as acetonitrile, which stabilizes the charged ground state.<sup>27</sup>

We also observe that **2b** salts exhibit a more evident red-shift than **2a** salts, this behavior can be correlated with the relative position of the *N*-pyridinium moiety in the compound **2b**, thus when the yliden-ferrocenyl fragment is bearing at 4-position of



the pyridinium cation, a best  $\pi$ -orbital overlap is favored, which enhances the electronic communication between the ferrocenyl group and the *N*-pyridinium acceptor favoring the mesomeric structure **B** (Scheme 2).

On the other hand, 4 exhibits two well-defined absorption bands around 320 and 409 nm, with  $\varepsilon$  values very similar, assigned to  $\pi$ - $\pi^*$  and n- $\pi^*$  transitions, respectively,<sup>28</sup> and a MLCT absorption at 600 nm in CH<sub>3</sub>CN (Table S1 and Figure 2). We also see that the MLCT absorption band at 600 nm is redshifted regarding compounds 2a-b. This behavior is attributed to the best distribution of positive charge on the additional ring included in the quinolinium unit of 4, which decreases the energy of the MLCT band transition band, thus shifting this absorption at low energy values, which also favors a best contribution of the fulvene-type resonance.<sup>18,24</sup> In general, the presence of BF<sub>4</sub> as counterion does not modify the optical properties of these compounds. Moreover, if we compare the behavior for 6a, 6b and 7 (Table 1 and S1), these compounds display similar absorption spectra in CH<sub>3</sub>CN and CHCl<sub>3</sub>, with similar  $\varepsilon$  values for both absorption bands, revealing a no significant solvatochromic effect, as result of a less polarization effect in these neutral push-pull compounds.

Table 1. Low Energy band displayed for ferrocenyl amphiphilic D- $\pi$ -A dyes and analogues in acetonitrile.

Entry	Compound	$\lambda_{max} \left( nm  ight)^{a}$	ε <sub>max</sub> b
1	<b>2a</b> [Br]	533	2.0
2	<b>2a</b> [BF <sub>4</sub> ]	530	1.9
3	<b>2b</b> [Br]	552	3.6
4	<b>2b</b> [BF <sub>4</sub> ]	551	4.5
5	<b>4</b> [Br]	598	3.3
6	<b>4</b> [BF <sub>4</sub> ]	601	3.3
7	6a	461	1.4
8	6b	465	1.2
9	7	476	1.8
10	8[PF <sub>6</sub> ] <sup>25b</sup>	539	8.1
11	<b>9</b> [1] <sup>29</sup>	478 <sup>c</sup>	40
12	10[I] <sup>29</sup>	543 <sup>c</sup>	46

 $^{a} \lambda_{max}$  (nm),  $^{b} \varepsilon$  (10<sup>3</sup>mol<sup>-1</sup>L cm<sup>-1</sup>),  $^{c}$  Data reported from methanol.



Figure 2. Right: Solid lines for UV/Vis spectra of **2a** [Br] (red), **2b** [Br] (bright green) and **4** [Br] (dark blue) in CH<sub>3</sub>CN. Dash lines for UV/Vis spectra of **2a**[Br] (red), **2b**[Br] (bright green) and **4**[Br] (dark blue) in CH<sub>3</sub>CN. Dash lines for UV/Vis spectra of **2a**[Br] (bright green) and **4**[Br] (dark blue) in CH<sub>3</sub>CN. Dash lines for UV/Vis spectra of **2a**[Br] (bright green), **2b**[BF<sub>4</sub>] (lime) and **4**[BF<sub>4</sub>] (pink) in CH<sub>3</sub>CN. Dash lines for UV/Vis spectra of **2a**[BF<sub>4</sub>] (orange), **2b**[BF<sub>4</sub>] (lime) and **4**[BF<sub>4</sub>] (pink) in CH<sub>3</sub>CN. Dash lines for UV/Vis spectra of **2a**[BF<sub>4</sub>] (orange), **2b**[BF<sub>4</sub>] (lime) and **4**[BF<sub>4</sub>] (pink) in CH<sub>3</sub>CN. Dash lines for UV/Vis spectra of **2a**[BF<sub>4</sub>] (orange), **2b**[BF<sub>4</sub>] (lime) and **4**[BF<sub>4</sub>] (pink) in CH<sub>3</sub>CN. Dash lines for UV/Vis spectra of **2a**[BF<sub>4</sub>] (bright green) (bright green) and **4**[BF<sub>4</sub>] (pink) in CH<sub>3</sub>CN. Dash lines for UV/Vis spectra of **2a**[BF<sub>4</sub>] (bright green) (bright green)

A comparison of the electronic absorption spectra of 2a[BF<sub>4</sub>], 2b[BF<sub>4</sub>] and 4[BF<sub>4</sub>] vs 6a, 6b and 7 in CH<sub>3</sub>CN (Figure 3) indicates that the ferrocenyl cations exhibit a red-shift in both the higher and lower energy bands, displaying a less intense high energy band than compounds 6a-b and 7, likewise, the increasing of acceptor strength in 2a-b and 4 provokes that the lower energy bands (MLCT) gains in relative intensity. These results confirm that the parentage of the higher energy bands is largely  $\pi$  to acceptor and/or  $\pi$ - $\pi^*$ . With regards to the position and relative intensity of the MLTC bands observed in 6a, 6b and 7, this also indicates a weak polar character of these compounds.

Analyzing the electronic absorption spectra for 2b and 4 with the literature data, we observe that the ferrocenyl dye 8 (Table 1, entry 10), displays a blue shifted LE band in comparison to 4, which implies that the incorporation of  $\pi$ -extended system as spacer, possibly diminishes the  $\pi$ -orbital overlap arising from twisting about the ethylene-quinolinium fragment,<sup>25b</sup> which in consequence weakens the electronic communication between the donor-acceptor couple.

Finally, comparing the optical properties of 2b and 4 with the well-known DAS analogues 9[I] and 10[I] (Table 1, entries 11-12),<sup>29</sup> we can see that the presence of ferrocenyl fragment instead dimethylaminophenyl moiety provokes a red shift of the LE band, loosing intensity. This is attributable to the MLCT character of the LE band associated to the ferrocenyl group.



Figure 3. Electronic absorption spectra of ferrocenyl compounds (cations vs neutral): 2a[BF<sub>4</sub>] (orange), 2b[BF<sub>4</sub>] (lime), 4[BF<sub>4</sub>] (pink), 6a (purple), 6b (black), 7 (cyan) in CH<sub>3</sub>CN.



Figure 4. Examples of other D- $\pi$ -A dyads with similar structural features

#### **Optical band gap**

UV-Vis electronic absorption spectroscopy is a well-known technique to evaluate the optical absorption band gap of compounds.<sup>30</sup> The band gap in molecular compounds could be estimated as the energy difference between the HOMO and LUMO orbitals, and can be determined by performing an extrapolation on the absorption spectrum, finding the wavelength at which the material begins to absorb.  $^{\rm 31}\ {\rm The}$ optical band gaps for 2a, 2b and 4 salts were estimated from the first optical absorption edge. Eg is the band gap corresponding to a particular absorption of low photon energy (hv) and express the radiation energy in eV using the following equation (1).

#### Eg (eV)= $hv = hc/\lambda$ .....(1)

Where *h* is Planck constant and *c* is speed of light in vacuum. The optical absorption spectra of all samples were acquired from CH<sub>3</sub>CN solutions, so that they can be directly compared to the results obtained from the CV measurements. Figure 5 shows the absorption spectrum of 2b[BF<sub>4</sub>], where the corresponding wavelength to the band gap energy can be calculated from the cross point of absorption onset and corrected base line.



Figure 5. Absorption spectrum in CH<sub>3</sub>CN and optical onset band gap of 2b[BF<sub>4</sub>].

Table 2. Optical onset band gaps for ferrocenyl salts

Entry	Compound	$\lambda_{max} \left( nm  ight)^{a}$	λ <sub>onset</sub> (nm)	Optical Band gap (eV)
1	<b>2a</b> [Br]	533	662	1.87
2	<b>2a</b> [BF <sub>4</sub> ]	530	657	1.88
3	<b>2b</b> [Br]	552	669	1.85
4	<b>2b</b> [BF <sub>4</sub> ]	551	670	1.85
5	<b>4</b> [Br]	598	761	1.63
6	<b>4</b> [BF <sub>4</sub> ]	601	758	1.63
7	DAST <sup>29b</sup>	478 <sup>b</sup>	534	2.32

The corresponding  $\lambda_{onset}$  for  $\boldsymbol{2b}[\mathsf{BF}_4]$  is 670 nm, which is equivalent to 1.85 eV. The optical band gap estimated from the onset wavelength for salts of 2a-b and 4 are listed in Table 2. As we can see, both salts of 4 display the smaller value of band gap, confirming that the quinolinium group behaves as a potent acceptor, distributes efficiently the electron density in the push-pull system and, shifts the  $\lambda_{onset}$  to lower energy

values in comparison to compounds **2a** and **2b**. Comparing with literature data (Table 2, entry 7), compounds **4** exhibit lower optical band gaps, which denotes their potential as organic semiconductors.

#### Electrochemistry

The electrochemical properties of **2a-b** and **4** salts and compounds **6a-b**, and **7** were studied by cyclic voltammetry – (CV). The CV data give significant information about the oxidation and reduction potentials of materials. The values of the half-wave of all the compounds are summarized in Table 3. Figure 6 shows typical voltammograms for 1 mmol L<sup>-1</sup> CH<sub>3</sub>CN solutions of [**2a-b** and **4**][Br] at 100 mV s<sup>-1</sup>. When the scan potential is initiated in a positive direction in these voltammograms, two oxidation signals ( $I_{ap}$  and  $II_{ap}$ ) are observed for all compounds, for **2a**[Br] ( $E_{ap}$  = 0.19 and 0.31, \_\_\_\_ respectively) for **2b**[Br] ( $E_{ap}$  = 0.19 and 0.35, respectively) and for **4**[Br] ( $E_{ap}$  = 0.19 and 0.33, respectively) all V/Fc<sup>+</sup>-Fc.

When the potential scan was reversed, three or four reduction signals are observed for the three bromide compounds, but only two of them were considered to electrochemical analyses ( $I_{cp}$  and  $III_{cp}$ ) at 0.13 and -1.60 for **2a**[Br], 0.12 and -1.53 to **2b**[Br] and 0.12 and -1.22 for **4**[Br], all in V/Fc+-Fc. Likewise, when switching the scan in  $E_{-2}$  and the potential direction is positive, we observe at less three oxidation signals ( $I_{ap}$ ,  $II_{ap}$  and  $IV_{ap}$ ). The IV<sub>ap</sub> oxidation signal is observed at -0.25 for **2a**[Br], -0.79 for **2b**[Br] and -0.28 V/Fc+-Fc for **4**[Br].

The half-wave potential of the ferrocene/ferrocenium redox couple was identified around 0.1 V and estimated from the following equation:

#### $\boldsymbol{E}_{1/2} = (\boldsymbol{E}_{ap} + \boldsymbol{E}_{cp}) /_2 \dots \dots \dots (2)$

Where,  $E_{ap}$  and  $E_{cp}$  are the anodic and cathodic peak potentials, respectively. For internal reference, the half-wave potential of Fc<sup>+</sup>/Fc was found at 0.62 V relative to the AgCl/Ag reference electrode. In all cases, the reduction signal  $(I_{co})$  was associated with an oxidation signal (I<sub>ap</sub>) and corresponds to Fc<sup>+</sup>-Fc redox couple in this series of bromide salts, with a difference between anodic and cathodic peak potentials of  $E_{ap}$ - $E_{cp} = 0.07 \text{ V}$  (a ferrocene 1.0 mmol L<sup>-1</sup> solution under the same shows a similar value, 0.07 V). These results are consistent with a monoelectronic and reversible process assigned to the ferrocene moiety. The signal II<sub>ap</sub> was assigned to the irreversible oxidation process of bromide anion to bromine. To confirm this assignment, we decided to study the electrochemical behavior of 2a-b and 4 salts, all them containing BF<sub>4</sub> as counter anion (Figures 7 and S-32 to S-34 of SI). The CVs of [2a-b and 4][BF<sub>4</sub>] reveal the absence of oxidation peaks at high potential values associated to the bromide anion. Comparing the CV acquired from a tetrabutylammonium bromide solution (TBAB), we confirmed that the peak II<sub>ap</sub> is correctly assigned to the oxidation of bromide anion (Figure S-35, SI).<sup>32</sup>

We also observe a reduction signal (IIIcp) around of -1.5 V/Fc+-Fc, in accord with literature,  $^{26b, 33}$  at this potential value occurs pyridinium ion reduction. To confirm that, we have also acquired the CVs of precursors **1a**, **1b** and **3**, in cathodic direction. We observe a well-defined reduction signal around - 1.92, -1.97 and -1.42, respectively (Figure 8 and S-36, SI). In the three cases, this signal has its counterpart with the signal  $III_{ap}$ . These results evidence the reduction of the heterocyclic cation in each case.

Table 3. Potential values of ferrocene moiety into ferrocenyl D- $\pi$ -A dyes.

Entry	Compound	$E_{ap}$ (V/Fc <sup>+</sup> -Fc)	$E_{cp}(V/Fc^{+}-Fc)$	<i>E</i> <sup>*</sup> (V/Fc <sup>+</sup> -Fc) <sup>[a]</sup>
1	<b>2a</b> [Br]	0.19	0.13	0.16
2	2a[BF <sub>4</sub> ]	0.18	0.12	0.15
3	6a	0.07	0.00	0.03
4	<b>2b</b> [Br]	0.19	0.12	0.15
5	<b>2b</b> [BF <sub>4</sub> ]	0.18	0.12	0.15
6	6b	0.07	0.00	0.03
7	<b>4</b> [Br]	0.19	0.12	0.16
8	<b>4</b> [BF <sub>4</sub> ]	0.19	0.13	0.16
9	7	0.07	0.00	0.04

[a]  $E_{1/2} = (Epc + Epa)/2$ 



Figure 6. Cyclic voltammograms obtained in 0.1 mmol L<sup>-1</sup> Bu<sub>4</sub>NPF<sub>6</sub> acetonitrile solutions on glassy carbon electrode at 100 mVs<sup>-1</sup> using 1 mmol L<sup>-1</sup> solutions of **2a**[Br] (red), **2b**[Br] (bright green) and **4**[Br] (dark blue).



Figure 7. Comparative cyclic voltammograms obtained in  $0.1M \text{ Bu}_4\text{NPF}_6$  solutions on glassy carbon electrode at 100 mVs<sup>-1</sup>using 1 mmol L<sup>-1</sup> solutions of **2a [Br]** (red), **2a [BF**\_4] (orange).

New Journal of Chemistry Accepted Manuscrip

DOI: 10.1039/C8NJ00787J



Figure 8. Comparative cyclic voltammograms obtained in 0.1 mmol  $L^{-1}$  Bu<sub>4</sub>NPF<sub>6</sub> solutions on glassy carbon electrode at 100 mVs<sup>-1</sup> (negative direction), using 1 mmol  $L^{-1}$  solutions of **3** (black) and **4** [Br] (blue).

#### Electrochemical band gap

Cyclic voltammetry has been recognized as an important technique for measuring electrochemical band gaps, electron affinities and ionization potentials. The oxidations process corresponds to the removal of an electron from the highest occupied molecular orbital (HOMO) energy level, whereas the reduction corresponds to the electron addition into the lowest unoccupied molecular orbital (LUMO).<sup>34</sup> We proceeded to determine the values of band gap from cyclic voltammograms of these compounds and correlate them with the optical onset band gaps previously obtained. It is important to notice that the signal attributed to bromide anion does not affect the determination of the band gap of the first series of bromide salts, since the voltammograms acquired for the series [**2a-b** and **4**][BF<sub>4</sub>] exhibit the same value of  $E_{ap}$  for the system (Fc<sup>+</sup>/Fc) (Figure 7).

Table 4 summarizes the onset oxidation and reduction potential of the **2a**, **2b** and **4**. From the values of  $E_{ox/onset}$  and  $E_{red/onset}$ , we can calculate HOMO and LUMO energy levels. This conventional method has previously used to estimate the HOMO and LUMO energy levels of ferrocenyl compounds<sup>35</sup> including the reference energy level of ferrocene (4.8 eV below the vacuum level)<sup>36</sup> as follows:

 $E_{HOMO} = - [4.8 \text{ eV} + E_{ox/onset}] \dots (3)$  $E_{LUMO} = - [4.8 \text{ eV} + E_{red/onset}] \dots (4)$ 

The onset potentials for the oxidation ( $E_{ox/onset}$ ) and reduction ( $E_{red/onset}$ ) were determined from the intersection of the two tangents drawn at the current rise and background charging current of the CVs as illustrated in Figures S37-S42 (SI). For onset oxidation, CV was acquired when the scan potential is initiated in a positive direction. Onset reduction was calculated from CV initiated in a negative direction. The electrochemical band gap of the all ferrocenyl compounds were deduced by the equation (5):  $E_{Band gap} = LUMO - HOMO.^{37}$ 

As shown in Table 4 and Figure 9a, the onset potential of oxidation for **4**[Br] is shifted to lower values than **2a**[Br] and **2b**[Br]. In all cases, the onset potential of oxidation corresponds to the oxidation process of ferrocene group. Likewise, the onset reduction is assigned to the adding of an electron to the LUMO, which will be based on the pyridinium unit. Analyzing the values of reduction onset potential of [**2a** and **2b**][Br] (Figure 9b), they display values of -1.49 and -1.43 V, respectively. We can also see a significant difference for the compound **4**, which has a value of -1.13 V. Accordingly, the quinolinium cation is a best electron-withdrawing group than pyridinium cation modifying the value of LUMO energy level. The lower energy gap values of **4** salts compared with **2a** and **2b** may be result of the higher electron delocalization favored in these ferrocenyl compounds.

If we compare the band gaps values obtained from the optical and electrochemical measurement (Table 4), we observe that electrochemical band gaps are smaller than those obtained from optical approximation but remains essentially the same tendency. This discrepancy has also been observed by other groups, in measuring these properties for diverse compounds, finding that the interaction solvent-solute can modify the band gap values, as well as the possible interactions between the analyte and the electrode surface.<sup>31, 38</sup>

Moreover, this discrepancy can be attributed to the incertitude to know the real value of LUMO.<sup>39</sup> A common alternative to estimate the LUMO energy level is to use the information obtained from the optical band gap (Eg) obtained by UV-vis measurements and the experimental HOMO energy calculated from CV technique, which is associated to the ferrocene oxidation process, following the equation (6):

 $E_{[LUMO]} = E_{[HOMO]CV} + Eg$  ......(6)

Table 4. Electrochemical potential and estimated homo-como and band gap of renotenyi b-rea dyes [za-b and 4][b] and [za-b and 4][b] a							
Compound	E <sub>onset ox</sub> <sup>a</sup>	E <sub>onset red</sub> <sup>a</sup>	HOMO (eV) <sub>cv</sub>	LUMO (eV) <sub>cv</sub>	Electrochemical Band gap (eV) <sup>b</sup>	Optical Band gap (eV)	LUMO (eV) <sub>opt</sub> <sup>c</sup>
<b>2a</b> [Br]	0.04	-1.49	-4.84	-3.31	1.52	1.87	-2.97
<b>2a</b> [BF <sub>4</sub> ]	0.04	-1.59	-4.84	-3.21	1.63	1.88	-2.96
<b>2b</b> [Br]	0.04	-1.43	-4.84	-3.37	1.47	1.85	-2.99
<b>2b</b> [BF <sub>4</sub> ]	0.04	-1.48	-4.84	-3.32	1.52	1.85	-2.99
<b>4</b> [Br]	-0.03	-1.11	-4.77	-3.69	1.08	1.63	-3.14
<b>4</b> [BF <sub>4</sub> ]	0.03	-1.07	-4.83	-3.73	1.10	1.63	-3.2

Table 4. Electrochemical potential and estimated HOMO HUMO and hand can of forescend D x 4 dues [2a h and 4][Pr] and [2a h and 4][Pr]

<sup>a</sup> Potential values are reported versus Fc<sup>+</sup>/Fc. <sup>b</sup> Electrochemical Band gap was calculated LUMO - HOMO. <sup>c</sup> Energy of LUMO level calculated from E<sub>[LUMO]opt</sub> = E<sub>[HOMO] CV</sub> + Eg<sub>(opt)</sub>.



Figure 9. (a) Comparison of onset potential of oxidation and (b) onset potential of reduction of ferrocenyl compounds **2a**[Br] (red), **2b**[Br] (bright green) and **4**[Br] (dark blue).

#### **Computational studies**

To gain more insight about the charge transfer properties of the molecules studied in this work, we analyzed the excited states of molecules **2a'**, **2b'** and **4'**, which are model structures. The molecular structure predicted for **2b'** agrees relatively well with that determined by X-ray diffraction analyses.<sup>40</sup> The experimental UV spectra were taken as reference to validate the theoretical calculations. The average difference between experimental and theoretical values is 0.2 eV, which is in average an error of less than 10%.

In the three molecules, the HOMO, HOMO-1, HOMO-2 and HOMO-3 are delocalized mostly in the ferrocene group, whereas the LUMO, LUMO+1 are observed around the heterocyclic cation moiety. Images of the frontier molecular orbitals, their energies and energy gaps are shown in Table 5. The calculated energy values of these orbital agree with those estimated by electrochemical and optical experiments (see Table 4). The difference in the HOMO values is around 0.8 eV and 0.5 eV for LUMO electrochemical estimation. The LUMO values obtained by optical approximation is closer to theoretical values (difference of 0.2 eV). However, the theoretical HOMO–LUMO gaps are larger than experimental one, mostly due to the lower HOMO energies.

Most of the electronic transitions observed within the excited states involve these five molecular orbitals, which allow the electron transfer from the metal complex to the heteroaromatic ring and are related with the UV signals around 600 and 400 nm. The features of each excited state are presented in Table 6.

Table 5. Frontier molecular orbitals of structures 2a', 2b' and 4'. Energies are in hartrees and energy differences in eV.



DOI: 10.1039/C8NJ00787J

Journal Name

Table 0. Features of selected excited states of 2a, 2b and 4	Table 6. Features	of selected	excited	states	of 2a',	2b'	and 4'.
--	-------------------	-------------	---------	--------	---------	-----	---------

Structure	λ <sub>max, exp</sub> <sup>a</sup> (nm)	λ <sub>max, calc</sub> <sup>b</sup> (nm)	Excited State	E <sub>calc</sub> (eV)	$f_{\sf OS}$		Orbital Contributions
						73 -> 77	-0.25597 (13.9%, HOMO-1→LUMO+2)
53 <b>2a'</b>			2 singlet			73 -> 78	-0.10274 (2.2%, HOMO-1→LUMO+3)
	522 <b>3</b> -[D+]	<b>CO</b> 2		2.05.45	0.0071	74 -> 75	0.51127 (55.4%, HOMO→LUMO)
	533 <b>Za</b> [Br]	603		2.0545	0.0871	74 -> 76	0.12288 (3.2%, HOMO→LUMO+1)
						74 -> 77	0.10658 (2.4%, HOMO→LUMO+2)
						74 -> 78	-0.32788 (22.8%, HOMO→LUMO+3)
						72 -> 75	0.65690 (90.4%, HOMO-2→LUMO)
	347 <b>2a</b> [Br]	395	7 singlet	3.1418	0.7735	73 -> 77	0.15351 (4.9%, HOMO-1→LUMO+2)
						74 -> 76	0.14901 (4.7%, HOMO→LUMO+1)
5. <b>2b'</b> 3			2 singlet		0.1089	73 -> 78	-0.24415 (12.8%, HOMO-1→LUMO+3)
	552 <b>2b</b> [Br]	618		2.0005		74 -> 75	0.54490 (63.9%, HOMO→LUMO)
						74 -> 77	0.10816 (23.3%, HOMO→LUMO+2)
		404	7 singlet	3.0696	0.9265	72 -> 75	0.67027 (96.4%, HOMO-2→LUMO)
	362 <b>20</b> [Br]	404				73 -> 78	0.12908 (3.6%, HOMO-1→LUMO+3)
			2 singlet	1 9776	0.1696	86 -> 91	-0.18215 (7.0%, HOMO-1→LUMO+3)
4'		660				87 -> 88	0.60531 (77.4%, HOMO→LUMO)
	596 <b>4</b> [DI]	000		1.8770		87 -> 90	0.17331 (6.3%, HOMO→LUMO+2)
						87 -> 92	0.20896 (9.2%, HOMO→LUMO+4)
						84 -> 88	-0.20464 (8.8%, HOMO-3→LUMO)
	406 <b>4</b> [Dr]	110	Cainalat	2 7695	0 7262	84 -> 92	-0.11356 (2.7%, HOMO-3→LUMO+4)
	400 <b>4</b> [DI]	440	o singlet	2.7085	0.7505	85 -> 88	0.62683 (82.8%, HOMO-2 – LUMO)
						86 -> 91	-0.16457 (5.7%, HOMO-1→LUMO+3)

<sup>a</sup> Data obtained from CH<sub>3</sub>CN. <sup>b</sup> Data obtained from the simulated absorption spectra.



Figure 10. Density difference for  $S_2$  and  $S_6$  electronic excited states of 4' (Red = 0.001 a.u., Blue = -0.001 a.u.).

The calculated LE signal around 600 nm of the **2a**' spectrum is associated to the S<sub>2</sub> excited state, which is due mainly to HOMO–LUMO transition but also HOMO–LUMO+3 importantly contributes to that signal. The S<sub>2</sub> excited state for **2b'** and **4'** is also dominated by the HOMO–LUMO transition with important contribution of HOMO–LUMO+2 and HOMO– LUMO+4, respectively. Compounds **2a'** and **2b'** exhibit a calculated HE band around 400 nm, associated to a S<sub>7</sub> state with a dominant contribution HOMO-2–LUMO, whereas for compound **4'**, the HE band has a S<sub>6</sub> state dominated by a HOMO-2–LUMO transition.

Figure 10 depicts the density difference for  $S_2$  and  $S_6$  electronic excited states of **4'**, displaying the electron density reduction around the metal complex and the increase in the  $\pi$  system of the ligand, supporting the fulvene contribution in these compounds. From the theoretical calculations it is possible to say that the molecules studied in this work behaves as push pull system where there is a direct charge transfer from the metal complex to the acceptor group and both signals of the UV spectrum can be characterized as MLCT bands as previously found by Coe *et al.*<sup>26b</sup> where there is a direct charge transfer from the metal complex to the acceptor group. Details

of the excited states are presented in the supplementary information.

#### Conclusions

We have synthesized a series of ferrocene amphiphilic donor-  $\pi$ -acceptor dyes, including *N*-heterocyclic cations as potent acceptor groups. These compounds display a red-shift for both ICT absorption bands that increase with the  $\pi$ -electronaccepting ability of the heterocyclic cation. The band gaps of [**2a-b** and **4**][Br] and [**2a-b** and **4**][BF<sub>4</sub>] salts determined by cyclic voltammetry and the absorption onset show a similar tendency. In comparison to **2a-b** salts, compounds **4** exhibit both smaller optical and electrochemical band gap. These results evidence the clear contribution of the quinolinium acceptor included in **4** for decreasing the HOMO-LUMO gap value, as result of the high delocalization in this ferrocenyl D- $\pi$ -A dye. Likewise, salts of **4** exhibit a less solvent dependence as revealed the UV-vis spectra, which allows a best control on the inter-molecular arrangement.

From the theoretical calculations, we corroborated that compounds **2a-b** and **4** behave as push-pull system, revealing a

#### Journal Name

direct charge transfer from the metal complex to the acceptor group. In three cases, the LE band is dominated by a HOMO-LUMO transition, which allow us to validate the optical band gap determination.

#### Experimental

#### General

All chemicals were purchased as reagent and used without further purification. The solvents were dried and distilled using standard procedures. Column chromatography was performed on 70-230 mesh silica gel. Yields are based on the pure products isolated. All compounds synthesized were covered of light and stored under nitrogen to avoid their decomposition.

All compounds were characterized by IR spectra recorded on a Perkin-Elmer Spectrum 100 FT-IR equipped with ATR accessory and all data are expressed in wave numbers (cm<sup>-1</sup>). NMR spectra were recorded with a Bruker Avance III, at 300 MHz using CDCl<sub>3</sub> and CD<sub>3</sub>COCD<sub>3</sub> as a solvent. Chemical shifts are in ppm ( $\delta$ ) relative to TMS, J values are given in Hz. The following abbreviations are used: s = singlet, d = doublet, t = triplet and m = multiplet. MS-EI spectra were obtained with a JEOL JMSAX505-HA using 70 ev as the ionization energy and for MS-FAB a JEOL JMS-SX102a using nitrobenzyl alcohol and ethylene glycol as a matrix. Elemental analyses for carbon, hydrogen and nitrogen atoms were performed on a Thermo Scientific elemental analyzer, Flash 2000 using sulfanilamide as standard.

The UV–VIS spectra were obtained on a CaryWin 100 Fast-Scan-Varian spectrophotometer, using fresh solutions of the corresponding ferrocenyl compounds in CHCl<sub>3</sub> and CH<sub>3</sub>CN spectrophotometric grade. The precise value of the molar absorption of each ferrocenyl compound was determined from the corresponding calibration curve. 1.  $0 \times 10^{-3}$  mol L<sup>-1</sup> solution stock of each ferrocenyl compound was prepared and the solutions of lower concentrations ( $9.0 \times 10^{-4}$  to  $1.0 \times 10^{-4}$  mol L<sup>-1</sup>) were prepared by accurate dilution.

Cyclic voltammetry (CV) experiments were carried out with a standard three-electrode configuration. NBu<sub>4</sub>PF<sub>6</sub> (0.1 mol L<sup>-1</sup>) in acetonitrile was used as a supporting electrolyte, a carbon glass disc was used as the working electrode and a platinum wire as the auxiliary electrode at a scan rate of 100 mVs<sup>-1</sup> with an CH Instruments Model 660C Potentiostat-Galvanostat. The half-wave potential of the ferrocenium/ferrocene ion couple (Fc<sup>+</sup>/Fc) under these conditions using a AgCl/Ag reference electrode, was 0.62 V and this system was used as internal reference. The electrochemical determinations were carried out without compensation of ohmic drop.

#### **Computational Methods**

The computational study was performed with the t-HCTHhyb<sup>41</sup> functional and the 6-311++G(d) basis set for C, N and H atoms and Lanl2dz for Fe. The t-HCTH-hyb functional has demonstrated to properly reproduce excited state properties such as absorption and emission energies.<sup>42</sup> Excited states were calculated within the time dependent DFT formalism as

implemented in Gaussian 09.<sup>43</sup> 50 states were obtained with acetonitrile as implicit solvent modeled with SMD method.<sup>44</sup> This methodology is like that followed by Buckley *et al.* to describe Ferrocenyl helquats.<sup>26b</sup>

#### Synthesis of ferrocenyl compounds 2a[Br], 2b[Br] and 4[Br].

(E)-1-hexadecyl-2-(ferrocenylvinyl)-pyridin-1-ium bromide. 2a[Br]: To a round-bottomed flask equipped with a condenser, 2-picoline (0.002 mol) and 1-bromohexadecane (0.0024 mol) were heated in an oil bath at 110 °C for 4 hours. The resulting oil was cooled, 10 mL of methanol, 0.1 mL of piperidine and solution of ferrocenyl carboxaldehyde (0.002 mol) in methanol were added and the mixture was refluxed under argon for 12 h. The solvent was evaporated under vacuum then, the crude was purified by chromatography on silica gel using a mixture of diethyl ether and methanol as eluent, to give a dark solid (0.891 g 75 %). Mp 97 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 9.16 (s, 1H, Py), 8.44 (s, 2H, Py), 7.88 (d, J = 15Hz, 1H, CH=CH), 7.78 (s, 1H, Py), 6.91 (d, 1H, J = 15 Hz, CH=CH), 4.86 (s, 4H, 2 CH, Cp subst CH2-N-alkyl), 4.60 (s, 2H, C-H Cp subst), 4.25 (5H, Cp), 1.93 (s, 2H, CH<sub>2</sub>-alkyl) 1.24 (s, 26H, CH<sub>2</sub>-alkyl), 0.88 (s, 3H, CH<sub>3</sub>-alkyl). <sup>13</sup>C NMR (75MHz, CDCl<sub>3</sub>): 152.2 (C<sub>ipso</sub> Py), 147.5 (C-H Py), 145.1 (C-H Py), 144.1 (CH=CH), 125.2 (C-H Py), 124.1 (C-H Py), 111.8(CH=CH), 79.1 (Cipso Cp), 72.5 (C-H Cp subst), 70.1 (Cipso Cp), 69.5 (C-H, Cp <sub>subst</sub>), 69.5 (Cp), 58.7 (-CH<sub>2</sub>-N<sup>+</sup>), 31.9 (CH<sub>2</sub>-alkyl), 29.4 (-CH<sub>2</sub>)<sub>13</sub>), 22.7 (-CH<sub>2</sub>-), 14.1 (CH<sub>3</sub>). ATR-FTIR v (cm<sup>-1</sup>) 2918, 2849, 1603. MS (FAB<sup>+</sup>) *m/z*: 514 [M<sup>+</sup>-Br]; 395 [M<sup>+</sup>-FeCpBr]; 224  $[C_{14}H_{33}]$ . HR-MS (FAB<sup>+</sup>) m/z for  $C_{33}H_{48}$ NFe: calculated 514.3136, found 514.3135. Elemental analysis (%): calcd for C<sub>33</sub>H<sub>48</sub>BrFeN: C, 66.67; H, 8.14; N, 2.36; found: C, 66.50; H, 7.94; N, 2.41.

(E)-1-hexadecyl-4-(ferrocenylvinyl)-pyridin-1-ium bromide, 2b[Br]: The compound 2b[Br] was obtained by a similar procedure, as a dark solid (0.889 g, 75 %). Mp 93 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 8.89 (br s, 2H, Py), 7.96 (br s, 2H, Py), 7.78(d, 1H, CH=CH, J = 15.3 Hz), 6.72 (d, 1H, CH=CH, J = 15.3), 4.67 (br s, 4H, 2H –CH<sub>2</sub>-N<sup>+</sup>, 2H, C-H, Cp <sub>subst</sub>), 4.58 (br s, 2H, C-H Cp <sub>subst</sub>), 4.22 (br s, 5H, C-H, Cp), 1.97 (br s, CH<sub>2</sub>-alkyl), 1.24 (br s, 25 H, CH<sub>2</sub>-alkyl), 0.88 (br s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (75MHz, CDCl<sub>3</sub>): 153.4 (C<sub>ipso</sub> Py), 145.1.5 (CH=CH), 143.7.1 (C-H-Py), 122.9 (C-H Py), 118.8(CH=CH), 79.4 (C<sub>ipso</sub> Cp), 72.3 (C-H, Cp subst), 70.1 (Cp), 69.1 (C-H, Cp subst), 69.5 (Cp), 58.7 (-CH<sub>2</sub>-N<sup>+</sup>), 31.9 (CH2-alkyl), 29.4 (-CH2)13), 22.3 (-CH2-), 14.1 (CH3). ATR-FTIR v (cm<sup>-1</sup>) 2949, 2915, 2849, 3095, 1643. MS (FAB<sup>+</sup>) m/z, 514  $[M^+-Br]$ , 394  $[M^+-FeCp]$ , 289  $[M^+-C_{16}H_{33}]$ . HR-MS (FAB<sup>+</sup>) m/z for C<sub>33</sub>H<sub>48</sub>NFe, calculated 514.3136 observed 514.3147. Elemental analysis (%): calcd for C<sub>33</sub>H<sub>48</sub>BrFeN: C, 66.67; H, 8.14; N, 2.36; found: C, 66.59; H, 8.03; N, 2.40.

(*E*)-1-hexadecyl-4-(ferrocenylvinyl)-quinolin-1-ium bromide, **4**[Br]: To a round-bottomed flask with condenser 4methylquinoline (0.0019 mol) and 1-bromohexadecane (0.0022 mol) were heated in an oil bath at 110 °C for 4 h. The resulting oil was cooled, 10 mL of methanol, 0.1 mL of piperidine and a solution of ferrocenyl carboxaldehyde (0.0019 mol) in methanol were added. The mixture was refluxed under argon for 12 h. The solvent was evaporated under vacuum then, the crude was purified by chromatography on silica gel using a mixture of diethyl ether and methanol as eluent, to

#### ARTICLE

Published on 28 February 2018. Downloaded by Freie Universitaet Berlin on 03/03/2018 09:48:41

give a green dark solid (1.045 g, 85 %). Mp 158-160 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  10.06 (d, 1H, quinoline, J = 6Hz), 8.54 (d, 1H, J = 6 Hz), 8.26 (d, 1H, quinoline, J = 6 Hz), 8.10 (m, 2H, quinoline), 7.86 (m, 2H, CH=CH and C-H quinoline), 7.38 (d, 1H, CH=CH, J = 15 Hz), 5.03 (t, 2H,  $CH_2-N^+$ ), 4.75 (s, 2H, C-H, Cp subst), 4.62 (s, 2H, C-H Cp subst), 4.21 (s, 5H, Cp), 2.0 (br s, 2H,  $CH_2$ -alkyl), 1.18(m, 25H,  $CH_2$ -alkyl), 0.88 (br s, 3H,  $CH_3$ ). <sup>13</sup>C NMR (75MHz, CDCl<sub>3</sub>): 152.3 (C<sub>ipso</sub> quinoline), 148.9 (C-H quinoline), 147.3 (CH=CH), 138.1(Cipso quinoline), 134.6 (C-H quinoline), 128.6 (C-H quinoline), 126.4 (Cipso quinoline), 126.2 (C-H quinoline), 118.1 (C-H quinoline), 116.0 (C-H quinoline), 114.7 (CH=CH) 80.1 (Cipso Cp), 72.8 (C-H, Cp subst), 70.4 (Cp), 69.4 (C-H, Cp <sub>subst</sub>), 57.3 (-CH<sub>2</sub>-N<sup>+</sup>), 31.9, 30.1, 29.6, 29.3, 29.2, 26.7, 22.6 (-CH<sub>2</sub>-), 14.3 (CH<sub>3</sub>). ATR-FTIR v (cm-1) 2954, 2915, 2848, 1698, MS (FAB<sup>+</sup>) m/z, 564[M<sup>+</sup>-Br], 444[M<sup>+</sup>-FeCp], 339  $[M^+-C_{16}H_{33}]$ . HR-MS (FAB<sup>+</sup>) m/z for  $C_{37}H_{50}NFe$ , calculated 564.3293 observed 564.3306. Elemental analysis (%): calcd for C<sub>37</sub>H<sub>50</sub>BrFeN·H<sub>2</sub>O: C, 67.07; H, 7.91; N, 2.11; found: C, 67.36; H, 8.04; N, 2.16.

#### Synthesis of ferrocenyl compounds 2a[BF<sub>4</sub>], 2b[BF<sub>4</sub>] and 4[BF<sub>4</sub>].

In a round-bottomed flask was dissolved the corresponding bromide salt in 10 mL of  $CH_3CN$  and then 1.1 equivalents of  $AgBF_4$  were added. The mixture was stirred overnight at room temperature, covered of light. The AgBr was separated by filtration over celite and the crude was purified by flash chromatography on neutral alumina using a mixture of AcOEt/ methanol as eluent, to give a dark solid.

(E)-1-hexadecyl-2-(ferrocenylvinyl)-pyridin-1-ium

tetrafluoroborate, **2a**[BF<sub>4</sub>]: NH<sub>4</sub>BF<sub>4</sub> was used instead AgBF<sub>4</sub>. Purple solid, 51 %, Mp 90 °C. <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>COCD<sub>3</sub>),  $\delta$  8.89 (d, 2H, J = 6 Hz, Py), 8.51 (m, 2H, Py), 8.00 (d, 1H, *J* = 15 Hz, CH=CH), 7.91 (t, 1H,Py), 7.29 (d, 1H, 15 Hz, CH=CH), 4.90 (t, 2H, C-H, Cp<sub>subst</sub>), 4.86 (d, 2H, -CH<sub>2</sub>-N<sup>+</sup>), 4.64 (t, 2H, C-H, Cp<sub>subst</sub>), 4.29 (s, 5H, C-H Cp), 1.45 (m, 5H, CH<sub>2</sub>-alkyl), 1.28 (br s, 22 H, CH<sub>2</sub>-alkyl), 0.89 (t, 3H, CH<sub>3</sub>). <sup>19</sup>F NMR (282 MHz, CD<sub>3</sub>COCD<sub>3</sub>): 151.6 ppm (B–F). Elemental analysis (%): calcd for C<sub>33</sub>H<sub>48</sub>BF<sub>4</sub>FeN: C, 65.91; H, 8.04; N, 2.33; found: C, 65.83; H, 7.98; N, 2.29.

(E)-1-hexadecyl-4-(ferrocenylvinyl)-pyridin-1-ium

tetrafluoroborate, **2b**[BF<sub>4</sub>]: Purple solid, 87 %. Mp 68 °C. <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>COCD<sub>3</sub>):  $\delta$  9.01 (d, 2H, *J* = 6.3 Hz, Py), 8.18 (d, 2H, *J* = 6.0 Hz Py), 8.03 (d, 1H, CH=CH, *J* = 15.9 Hz), 7.08 (d, 1H, CH=CH, *J* = 15.9 Hz), 4.80 (br s, 2H, C-H Cp <sub>subst</sub>), 4.71 (br s, 2H, -CH<sub>2</sub>-N<sup>+</sup>), 4.60 (br s, 2H, C-H Cp <sub>subst</sub>), 4.25 (br s, 5H, C-H, Cp), 2.07 (br s, 2H, CH<sub>2</sub>-alkyl), 1.41 (br s, 2H, CH<sub>2</sub>-alkyl), 1.29 (br s, 25 H, CH<sub>2</sub>-alkyl), 0.86 (t, 3H, CH<sub>3</sub>). <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>) -151.4 (B-F). Elemental analysis (%): calcd for C<sub>33</sub>H<sub>48</sub>BF<sub>4</sub>FeN: C, 65.91; H, 8.04; N, 2.33; found: C, 65.76; H, 7.89; N, 2.27. (*E*)-1-hexadecyl-4-(ferrocenylvinyl)-quinolin-1-ium

tetrafluoroborate, **4**[BF<sub>4</sub>]: Purple solid, 88 %. Mp 138 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 9.13 (d, 1H, quinoline, J = 9Hz), 8.51 (d, 1H, quinoline), J = 9Hz), 8.21 (m, 1H, quinoline), 8.08 (br s, 2H, quinoline), 7.93-8.88(m, 1H, quinoline), 7.92 (d, 1H, J = 15 Hz), 7.37 (d, 1H, J = 15 Hz), 4.79 (br s, 2H,  $-CH_2-N^{+}$ , and 2H, C-H, Cp subst), 4.71(br s, 2H, CH Cp subst), 4.29 (s, 5H, Cp), 2.02 (br s, 2H, CH<sub>2</sub>-alkyl), 1.25(br s, 25H, CH<sub>2</sub>-alkyl), 0.87 (br s, 3H CH<sub>3</sub>). <sup>19</sup>F

NMR (282 MHz, CDCl<sub>3</sub>): -152.1 (B-F). Elemental analysis (%): calcd for  $C_{37}H_{50}BF_4FeN$ : C, 68.22; H, 7.74; N, 2.15; found: C, 68.17; H, 7.78; N, 2.20.

#### Synthesis of ferrocenyl compounds 6a, 6b and 7.

The compounds **6a** and **6b** were prepared by a modification of the procedure reported in the literature.<sup>23</sup>

To a cooled solution of 2-picoline in 5 mL of anhydrous THF under Argon at -70 °C was added n-BuLi (1.2 mL of 2.5 mol L<sup>-1</sup> in THF), and the resulting solution was reacted for 5 minutes at -70 °C, then the temperature left to reach 0 °C and the mixture was stirred for 1 h at 0 °C. A solution of ferrocene carboxaldehyde in THF (10 mL) was then added dropwise, and the mixture was stirred for 3 hours, before quenching with water and HCl 10%. The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 15 mL), and then washed with brine. The combined organic layer was separated, dried with anhydrous  $Na_2SO_4$  and evaporated to dryness in vacuum. The resulted product was used without further purification. The alcohol I or II was solved in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and cooled at 0 °C, methanesulfonyl chloride was added dropwise and the mixture was stirred for 1 h at 0 °C. Then, the reaction was quenched by adding 30 mL of water. The organic layer was washed with water and then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated to dryness in vacuo. Purification by flash column chromatography using alumina and hexane-CH<sub>2</sub>Cl<sub>2</sub> (9:1) afforded 6a as bright red solid in 75 % yield. 6b was also obtained as bright red solid in 85% yield.

(*E*)-2-ferrocenylvinylpyridine (**6a**): Red bright solid (75%). Mp 114-115 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  8.55 (br s, 1H, Py), 7.62 (br s, 1H, Py), 7.40 (d, 1H, CH=CH, *J* = 15Hz), 7.29 (s, 1H, Py) 7.10 (s, 1H, Py) 6.76 (d, 1H, CH=CH, *J* = 15 Hz), 4.52 (br s, 2H Cp <sub>subst</sub>), 4.32 (br s, 2H Cp <sub>subst</sub>), 4.15 (br s, 5H Cp). <sup>13</sup>C NMR (75MHz, CDCl<sub>3</sub>): 156 (C<sub>ipso</sub> Py), 149.4 (C-H Py), 136.7 (C-H Py), 132.2 (C-H Py), 125.2 (CH=CH), 121.3 (C-H Py) 121.2 (CH=CH), 82.0 (C<sub>ipso</sub> Cp), 69.6 (CH, Cp <sub>subst</sub>), 69.4 (Cp), 67.5 (CH, Cp <sub>subst</sub>) ATR-FTIR v (cm<sup>-1</sup>) 2956, 2927, 2858, 1594, 1547. MS (DART<sup>+</sup>) *m/z* 290 [M<sup>+</sup>+1]. Elemental analysis (%): calcd for C<sub>17</sub>H<sub>15</sub>FeN: C, 70.61; H, 5.23; N, 4.84; found: C, 70.65; H, 5.26; N, 4.82.

(*E*)-4-ferrocenylvinylpyridine (**6b**): Red bright solid. 85 %. Mp: 142 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta_{H}$  8.52 (br s, 2H, Py), 7.28, (br s, 2H, Py), 7.12 (d, 1H, *J* = 15 Hz), 6.60 (d, 1H, *J* = 15 Hz), 4.49, (s, 2H, Cp <sub>subst</sub>), 4.35, (s, 2H, Cp <sub>Subst</sub>), 4.15 (s, 5H, Cp). <sup>13</sup>C NMR (75MHz, CDCl<sub>3</sub>). 150.1 (C-H Py), 145.1 ( $C_{ipso}$  Py), 132.5 (CH=CH), 123.0 (C-H Py) 120.2 (CH=CH), 81.6 ( $C_{ipso}$  Cp), 69.9 (C-H, Cp <sub>subst</sub>), 69.4 (Cp), 67.5. (CH, Cp <sub>subst</sub>). MS (DART<sup>+</sup>) *m/z* 290 [M<sup>+</sup>+1]. ATR-FTIR v (cm<sup>-1</sup>) 3095, 2956, 2927, 1628, 1594. Elemental analysis (%): calcd for C<sub>17</sub>H<sub>15</sub>FeN: C, 70.61; H, 5.23; N, 4.84; found: C, 70.54; H, 5.19; N, 4.80.

(*E*)-4-ferrocenylvinylquinoline (**7**): In a 100 mL two-neck roundbottom flask fitted equipped with a magnetic stirrer and reflux condenser, 4.54 mL (0.0045 mol, potassium *t*-butoxide (1 mol  $L^{-1}$  in THF) was placed in 15 mL of anhydrous THF under argon. After that, 0.0038 mol of 4-methylquinoline was added and the mixture was refluxed. Then, a solution of 0.0038 mol of ferrocenecarboxaldehyde in 10 mL of anhydrous THF was slowly added. The reaction mixture was refluxed overnight.

#### Journal Name

Finally, 15 mL of brine was added, and the product was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 x 30 mL). The combined organic layers were dried with anhydrous Na2SO4, and the solvent was removed in vacuo. Purification by column chromatography on silica-gel with hexane-ethyl acetate (70:30, v/v) afforded 7 as bright red solid, 86 % yield. Mp 108-109 °C, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 8.85 (br s, 1H,), 8.16 (d, 1H J = 9 Hz), 8.10 (d, 1H, J = 9 Hz), 7.70 (t, 1H, J = 6 Hz), 7.60-7.54 (m, 2H), 7.39 (d, 1H, J = 15 Hz), 7.17 (d, 1H, J = 15 Hz), 4.58 (s, 2H), 4.39 (s, 2H), 4.18 (s, 5H).  $^{13}$ C NMR (75MHz, CDCl<sub>3</sub>): 150.2 (C<sub>ipso</sub> quinoline), 148.8 (Cipso quinoline), 143.3 (C-H quinoline), 134.4 (C-H quinoline), 130.0 (CH=CH), 129.3 (C-H quinoline), 126.3 (C-H quinoline), 126.1 (C-H quinoline), 123.4 (C-H quinoline), 119.5 (CH=CH), 116.2 (C-H quinoline), 82.1 (Cipso Cp), 70.0 (C-H, Cp subst), 69.4 (Cp), 67.6 (C-H, Cp <sub>subst</sub>). ATR-FTIR v (cm<sup>-1</sup>) 2925, 2237,1575, 1559, 1504. DART-MS<sup>+</sup> m/z, 339 [M+]. HR-MS [M<sup>+</sup>+1] m/z for C21H18FeN, calculated 340.0788 observed 340.0789. Elemental analysis (%): calcd for C<sub>21</sub>H<sub>17</sub>FeN: C, 74.36; H, 5.05; N, 4.13; found: C, 74.13; H, 5.00; N, 4.07.

#### **Conflicts of interest**

There are no conflicts to declare.

#### Acknowledgements

The authors would like to acknowledge the technical assistance provided by Martin Cruz Villafañe, Luis Velasco, Javier Pérez, Héctor Rios and Ma. Paz Orta Pérez. We thank to DGAPA IN208117 and PAIP 5000-9053 projects and CONACYT for the Ph.D. grant extended to B. J. López-Mayorga. C. I. Sandoval-Chavez also thanks to DGAPA-ICN for the granted post-doctoral fellowship. The authors acknowledge to DGTIC-UNAM (SC17-1-IG-55-MZ0) for supercomputer time.

#### References

- (a) P. Bamfield and M. G. Hutchings, Chromic Phenomena: Technological Applications of Colour Chemistry, The Royal Society of Chemistry, Cambridge, 2nd edn, 2010; (b) F. Bureš, *RSC Adv.*, 2014, 4, 58826–58851; (c) H. Xu, R.-F. Chen, Q. Sun, W.-Y. Lai, Q.-Q. Su, W. Huang and X.-G. Liu, *Chem. Soc. Rev.*, 2014, 43, 3259–3302; (d) R. M. Metzger, *Chem. Rev.*, 2015, 115, 5056–5115.
- 2 (a) Special issue on "Optical nonlinearities in chemistry", ed. D. Burland, *Chem. Rev.*, 1994, 94, 1; (b) G. S. He, L.-S. Tan, Q. Zheng and P. N. Prasad, *Chem. Rev.*, 2008, 108, 1245-1330; (c) Y. Kawabe, H. Ikeda, T. Sakai and K. Kawasaki, *J. Mater. Chem.*, 1992, 2, 1025-1031; (d) S. R. Marder and J. W. Perry, *Adv. Mater.*, 1993, 5, 804-815.
- 3 (a) P. A. Sullivan and L. R. Dalton, *Acc. Chem. Res.*, 2010, 43, 10-18; (b) M. Stähelin, B. Zysset, M. Ahlheim, S. R. Marder, P. V. Bedworth, C. Runser, M. Barzoukas and A. Fort, *J. Opt. Soc. Am. B*, 1996, 13, 2401-2407. (c) Z. Guo, W. Zhu and H. Tian, *Chem. Commun.*, 2012, 48, 6073–6084.
- 4 (a) F. Chen, J. Zhang and X. Wan, *Chem. Eur. J.*, 2012, 18, 4558-4567. (b) Z. Liu, G. Zhang and D. Zhang, *Chem. Eur. J.*, 2016, 22, 462 471.

- 5 (a) B. J. Coe, Chem. Eur. J., 1999, 5, 2464-2471; (b) I.
   Asselberghs, K. Clays, A. Persoons, M. D. Ward and J.
   McCleverty, J. Mater. Chem., 2004, 14, 2831-2839.
- 6 F. M. Raymo and M. Tomasulo, *Chem. Eur. J.*, 2006, **12**, 3186-3193.
- 7 J.S. Lindsey and D.F. Bocian, Acc. Chem. Res., 2011, 44, 638-650.
- 8 (a) C. Reichardt, Solvents and solvent effects in organic chemistry, Wiley-VCH, Weinheim, 2004; (b) F. Bureš, O. Pytela, M. Kivala and F. Diederich, *J. Phys. Org. Chem.*, 2011, 24, 274-281; (c) F. Bureš, O. Pytela and F. Diederich, *J. Phys. Org. Chem.*, 2009, 22, 155-162.
- 9 (a) Y. Wu and W. Zhu, *Chem. Soc. Rev.*, 2013, 42, 2039-2058;
  (b) J. N. Clifford, E. Martínez-Ferrero, A. Viterisi and E. Palomares, *Chem. Soc. Rev.*, 2011, 40, 1635-1646; (c) C. Duan, K. Zhang, C. Zhong, F. Huang and Y. Cao, *Chem. Soc. Rev.*, 2013, 42, 9071-9104; (d) M. Liang and J. Chen, *Chem. Soc. Rev.*, 2013, 42, 3453-3488. (e) A. Mishra, M.K.R. Fischer and P. Bäuerle, *Angew Chem. Int. Ed.*, 2009, 48, 2474 2499.
  (f) D.D. Babu, S.R. Gachumale, S. Anandan and A.V. Adhikari, *Dyes Pigm.*, 2015, 112, 183-191.
- Selected references: (a) S. Di Bella, C. Dragonetti, M. Pizzotti, D. Roberto, F. Tessore and R. Ugo, *Top. Organomet. Chem.*, 2010, **28**, 1–55; (b) O. Maury and H. Le Bozec, in Molecular Materials, ed. D. W. Bruce, D. O'Hare and R. I. Walton, Wiley, Chichester, 2010, pp. 1–59; (c) B. J. Coe, *Coord. Chem. Rev.*, 2013, **257**, 1438–1458; (d) P. G. Lacroix, I. Malfant, J.-A. Real and V. Rodriguez, *Eur. J. Inorg. Chem.*, 2013, 615–627; (e) M. G. Humphrey, T. Schwich, P. J. West, M. P. Cifuentes and M. Samoc, in Comprehensive Inorganic Chemistry II: From Elements to Applications, ed. J. Reedijk and K. R. Poeppelmeier, Elsevier, Oxford, 2013, vol. 8, pp. 781–835; (f) G. Grelaud, M. P. Cifuentes, F. Paul and M. G. Humphrey, *J. Organomet. Chem.*, 2014, **751**, 181–200; (g) P. G. Lacroix, I. Malfant and C. Lepetit, *Coord. Chem. Rev.*, 2016, **308**, 381– 394.
- (a) D. T. Gryko, F. Zhao, A. A. Yasseri, K. M. Roth and D. F. Bocian, J. Org. Chem., 2000, 65, 7356–7362. (b) K. Namiki, A. Sakamoto, M. Murata, S. Kume and H. Nishihara, Chem. Commun., 2007, 2007, 4650–4652. (c) Y.V. Zatsikha, C.D. Holstrom, K. Chanawanno, A.J. Osinski, C.J. Ziegler and V.N. Nemykin, Inorg. Chem., 2017, 56, 991-1000.
- 12 (a) M. Li, Z. Guo, W. Zhu, F. Marken and T.D. James, Chem. Commun., 2015, **51**, 1293-1296.
- 13 J.Y. Lim, M.J. Cunningham, J.J. Davis and P.D. Beer, *Chem. Commun.*, 2015, **51**, 14640–14643.
- 14 (a) X. Xia, H. Yu, L. Wang and Z. Ul-Abdin, *RSC Adv.*, 2016, 6, 105296-105316. (b) P. Debroy and S. Roy, *Coord Chem. Rev.*, 2007, **251**, 203-221. (c) E. Hillard, A. Vessieres, L. Thouin, G. Jaouen and C. Amatore, *Angew Chem. Int. Ed.*, 2006, **45**, 285-290. (d) G.L. Xu, R.J. Crutchley, M.C. DeRosa, Q.J. Pan, H.X. Zhang, X. Wang, and T. Ren, *J. Am. Chem. Soc.*, 2005, **127**,13354-13363.
- 15 Recent examples: (a) S. Kaur, N. Van Steerteghem, P. Kaur, K. Clays and K. Singh, J. Mater. Chem. C, 2016, 4, 9717-9726. (b) Senthilkumar, K. Thirumoorthy, C. Dragonetti, D. Κ. Marinotto, S. Righetto, A. Colombo, M. Haukka and N. Palanisami Dalton Trans., 2016, 45, 11939-11943. (c) S. Kaur, S. Dhoun, G. Depotter, P. Kaur, K. Clays and K. Singh, RSC Adv., 2015, 5, 84643-84656. (d) B. J. Coe, S. P. Foxon, R. A. Pilkington, S. Sánchez, D. Whittaker, K. Clays, G. Depotter and B. S. Brunschwig, Organometallics, 2015, 34, 1701-1715. (e) M. Zaarour, A. Singh, C. Latouche, J. A. G. Williams, I. Ledoux-Rak, J. Zyss, A. Boucekkine, H. Le Bozec, V. Guerchais, C. Dragonetti, A. Colombo, D. Roberto and A. Valore, Inorg. Chem., 2013, 52, 7987-7994. (f) B. J. Coe, S. P. Foxon, M. Helliwell, D. Rusanova, B. S. Brunschwig, K. Clays, G. Depotter, M. Nyk, M. Samoc, D. Wawrzynczyk, J. Garín and J.

DOI: 10.1039/C8NJ00787J

Journal Name

Published on 28 February 2018. Downloaded by Freie Universitaet Berlin on 03/03/2018 09:48:41

Orduna, Chem. Eur. J., 2013, **19**, 6613– 6629. (g) S. Salman, J.-L. Brédas, S. R. Marder, V. Coropceanu and S. Barlow, Organometallics, 2013, **32**, 6061–6068. (h) P. Kaur, M. Kaur, G. Depotter, S. Van Cleuvenbergen, I. Asselberghs, K. Clays and K. Singh, J. Mater. Chem., 2012, **22**, 10597–10608. (i) B. J. Coe, J. Fielden, S. P. Foxon, I. Asselberghs, K. Clays, S. Van Cleuvenbergen and B. S. Brunschwig, Organometallics, 2011, **30**, 5731–5743.

- 16 (a) P. Molina, A. Tárraga and A. Caballero, *Eur. J. Inorg. Chem.*, 2008, 3401–3417. (b) X.-t. Zhai, H.-j. Yu, L. Wang, Z. Deng and Z.-U. Abdin, *J. Zhejiang Univ. Sci. A*, 2015, **17**, 144– 154. (c) A.R. Pike, L.C. Ryder, B.R. Horrocks, W. Clegg, B.A. Connolly and A. Houlton, *Chem. Eur. J.*, 2005, **11**, 344-353.
- (a) A. Vecchi, P. Galloni, B. Floris, S.V. Dudkin and V.N. Nemykin, *Coord. Chem. Rev.* 2015, **291**, 95-171. (b) R. Misra, R. Maragani, T. Jadhav and S.M. Mobin, *New J. Chem.*, 2014, **38**, 1446-1475. (c) J. Kulhánek, F. Bureš, J. Opršal, W. Kuznik, T. Mikysek and A. Růžička, *Asian J. Org. Chem.*, 2013, **2**, 422.
- (a) D. Astruc *Eur. J. Inorg. Chem.*, 2017, 6-29. (b) A. Iordache, M. Oltean, A. Milet, F. Thomas, B. Baptiste, E. Saint-Aman and C. Bucher, *J. Am. Chem. Soc.*, 2012, **134**, 2653-2671. (c) S.Ø. Scottwell and J.D. Crowley, *Chem. Commun.*, 2016, **52**, 2451-2464. (d) R.C.J. Atkinson, V.C. Gibson and N.J. Long, *Chem. Soc. Rev.*, 2004, **33**, 313-328. (e) A. Hildebrandt and H. Lang, *Organometallics*, 2013, **32**, 5640-5653. (f) O.S. Wenger *Chem. Soc. Rev.*, 2012, **41**, 3772-3779. (g) T. Mochida and S. Yamazaki, *J. Chem. Soc. Dalton Trans.*, 2002, 3559-3564.
- 19 (a) H. Meier, J. Gerold, H. Kolshorn and B. Mühling, *Chem. Eur. J.*, 2004, **10**, 360-370. (b) M.U. Winters, E. Dahlstedt, H.E. Blades, C.J. Wilson, M.J. Frampton, H.L. Anderson and B. Albinsson *J. Am. Chem. Soc.*, 2007, **129**, 4291-4297. (c) T.L. Kinnibrugh, S. Salman, Y.A. Getmanenko, V. Cropceanu, W.W. Porter III, T.V. Timofeeva, A. Matzger, J.L. Brédas, S.R. Marder and S. Barlow, *Organometallics*, 2009, **28**, 1350-1357. (d) Q.Y. Cao, X. Lu, Z.H. Li, L. Zhou, Z.Y. Yang and J.H. Liu, *J. Organomet. Chem.*, 2010, **695**, 1323-1327. (e) M.I. Bruce, A. Burgun, C.R. Parker and B.W. Skelton, *J. Organomet. Chem.*, 2010, **695**, 619-625.
- 20 D.R. Kanis, M.A. Ratner and T.J. Marks, J. Am. Chem. Soc., 1992, 114, 10338-10357.
- 21 (a) D.A. Davies, J. Silver, G. Cross and P. Thomas, J. Organomet. Chem., 2001, 631, 59-66. (b) A.P. Philips J. Org. Chem., 1947, 12, 333-341.
- 22 S.R. Marder, J.W. Perry and B.G. Tiemann, *Chem. Mater.*, 1990, **2**, 685-690.
- (a) J. Mata, S. Uriel, E. Peris, R. Llusar, S. Houbrechts and A. Persoons, J. Organomet. Chem., 1998, 562, 197-202. (b)
  M.M. Bhadbhabe, A. Das, J.C. Jeffery, J.A. McCleverty, J.A. Navas Badiola and M.D. Ward, J. Chem. Soc. Dalton Trans., 1995, 2769-2777. (c) Y.F. Yang, Y. Chen, T. Xie and Y.M. Liang, Synth. Commun., 2002, 32, 2627-2631.
- 24 (a) C. Engtrakul and L.R. Sita, *Organometallics*, 2008, 27, 927-937. (b) T. Shoji, A. Maruyama, C. Yaku, N. Kamata, S. Ito, T. Okujima and K. Toyota, *Chem. Eur. J.*, 2015, 21, 402-409.
- 25 (a) E. Peris, Coord. Chem. Rev., 2004, 248, 279-297. (b) B.J. Coe, R.J. Docherty, S.P. Foxon, E.C. Harper, M. Helliwell, J. Raftery, K. Clays, E. Franz and B.S. Brunschwig, Organometallics, 2009, 28, 6880-6892, and references cited here.
- 26 (a) S. Salman, J.L. Brédast, S.R. Marder, V. Voropceanu and S. Barlow, Organometallics, 2013, **32**,6061-6068. (b) L.E.R. Buckley, B.J. Coe, D. Rusanova, S. Sánchez, M. Jirásek, V.D. Joshi, J. Vávra, D. Khobragade, L. Pospíšil, Š. Ramešova, I. Císařová, D. Šsaman, R. Pohl, K. Clays, N. Van Steerteghem, B.S. Brunschwig and F. Teplý, Dalton Trans., 2017, **46**,1052-1064.

- (a) U.M. Rabie, Spectrochim. Acta A, 2009, 74, 746-752. (b)
   A.M. Asiri, Appl. Organomet. Chem., 2001, 15, 907-915.
- 28 N.V. Pilipchuk, G.O. Kachkovsky, L. Slominskii Yu and O.D. Kachkovsky, *Dyes Pigm.*, 2006, **71**, 1-9.
- (a) S. R. Marder, J. W. Perry and C. P. Yakymyshyn, *Chem. Mater.* 1994, **6**, 1137-1147. (b) C. Karthikeyan, A. S. H. Hameed, J. S. A. Nisha and G. Ravi, *Spectrochim. Acta Part A*, 2013, **115**, 667–674. (c) A. Teshome, M. D. H. Bhuiyan, G. J. Gainsford, M. Ashraf, I. Asselberghs, G. V. M. Williams, A. J. Kay and K. Clays *Opt. Mater.*, 2011, **33**, 336–345
- 30 (a) J. C.S. Costa, R. J. S. Taveira, C. F.R.A.C. Lima, A. Mendes and L. M.N.B.F. Santos, *Opt. Mater.*, 2016, **58**, 51-60. (b) T. Michinobu, C. Boudon, J.P. Gisselbrecht, P. Seiler, B. Frank, N.N.P. Moonen, M. Gross and F. Diederich, *Chem. Eur. J.*, 2006, **12**, 1889-1905.
- 31 R. Schlaf, P.G. Schroeder, M.W. Nelson, B.A. Parkinson, C.D. Merrit, L.A. Crisafulli, H. Murata and Z.H. Kafafi, *Surf. Sci.*, 2000, **450**, 142-152.
- 32 (a) N. Ortega-Villar, V.M. Ugalde-Saldívar, M.C. Muñoz, L.A. Ortiz-Frade, J.G. Alvarado-Rodríguez, J.A. Real and R. Moreno-Esparza, *Inorg. Chem.*, 2007, **46**, 7285-7293. (b) L. Yu, X. Jin and G.Z. Chen, *J. Electroanal. Chem.*, 2013, **688**, 371-378.
- 33 Y.H. Gong, P. Audebert, F. Yang, F. Miomandre, X.C. Lian and J. Tang, J. Electroanal. Chem., 2007, **606**, 8–16.
- 34 M. Al-Ibrahim, H.K. Roth, M. Schroedner, A. Konkin, U. Zhokhavets, G. Gobsch, P. Scharff and S. Sensfuss, Org. Electron., 2005, 6, 65-77.
- 35 (a) R. Teimuri-Mofrad, K. Rahimpour and R. Ghadari, J. Organomet. Chem., 2016, 811, 14-19. (b) A. Telleria, J. Pérez-Miqueo, A. Altube, E. García-Lecina, A. de Cózar and Z. Freixa, Organometallics, 2015, 34, 5513-5529. (c) T. Shoji, S. Ito, T, Okujima and N. Morita Chem. Eur. J., 2013, 19, 5721-5730.
- 36 J. Pommerehene, H. Vestweber, W. Guss, R.F. Mahrt, H. Bassler, M. Prorsch and J. Daub, Adv. Mater., 1995, 7, 551-554.
- 37 Q. Zhao, C.Y. Jiang, M. Shi, F.Y. Li, T. Yi, Y. Cao and C.H. Huang, Organometallics, 2006, 25, 3631–3638.
- 38 T. Johanson, W. Mammo, M. Svensson, M.R. Andersson and O. Inganäs, *J. Mater. Chem.*, 2003, **13**, 1316-1323.
- 39 P. I. Djurovich, E. I. Mayo, S. R. Forrest and M. E. Thompson, Org. Electron., 2009, 10, 515-520.
- 40 K. Roque, F. Barangé, G. G. A. Balavoine, J.-C. Daran, P. G. Lacroix, E. Manoury, *J. Organomet. Chem.*, 2001, **637-639**, 531-537.
- 41 A.D. Boese and N.C. Handy, J. Chem. Phys., 2002, 116, 9559– 956.
- 42 D. Jacquemin, E.A. Perpète, I. Ciofini and C. Adamo, J. Chem. Theory Comput., 2010, 6, 1532–1537.
- Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. 43 Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

Journal Name

44 M. Cossi, N. Rega, G. Scalmani, and V. Barone, J. Comp. Chem., 2003, 24, 669-681.

# Ferrocene amphiphilic D- $\pi$ -A dyes: Synthesis, redox behavior and determination of Band Gaps.

Byron López-Mayorga,<sup>1</sup> César I. Sandoval-Chávez<sup>1</sup>, Pilar Carreón- Castro<sup>1</sup>, Víctor M. Ugalde-Saldívar<sup>2</sup>, F. Cortés-Guzman,<sup>3</sup> José G. López-Cortes<sup>3</sup>, M. Carmen Ortega-Alfaro<sup>\*,1</sup>

<sup>1</sup>Instituto de Ciencias Nucleares, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, Coyoacán, Cd. de México, 04510, México.

<sup>2</sup> Facultad de Química, Universidad Nacional Autónoma de México, Edificio B. Av. Universidad 3000, Coyoacán, Cd. de México, 04510, México.

<sup>3</sup>Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior, Cd. Universitaria, Coyoacán, Cd. de México, 04510, México



"For table of contents"

The synthesis of six ferrocenyl  $\pi$ -conjugated pyridinium salts, incorporating two different heterocycles (pyridine and quinoline) in their cationic and neutral version is informed. The properties of these dyes were investigated by absorption spectroscopy and electrochemical analysis. We have also determined the optically and electrochemically band gaps of these dyes. Time-dependent DFT calculations indicate that the lowest energy absorption band displayed for these compounds has mainly metal-to-ligand charge character, being the HOMO-LUMO electronic transition the main contribution.