

Monosubstituted ferrocenyl chalcones: Effect of structural changes upon the ability to detect calcium by absorption spectroscopy

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Abstract

We show how structural changes in the basic framework of ferrocenyl chalcone $[(C_5H_5)Fe(C_5H_4COCH=CHC_6H_4NEt_2)]$ (**1**) induce different capabilities of detecting calcium by UV/vis absorption spectroscopy. In particular, compound **1**, and its derivatives (**2**) and (**3**) incorporating a supplementary ethylenic unit into the conjugated link, allow a specific detection of calcium triflate with regard to calcium perchlorate. Investigations related to the unprecedented behaviour of these chalcone-like derivatives are presented. This study confirms that while the interaction of ligands **1–3** with calcium is centred on the CO group, the interaction of ligand **4** with calcium is aza-centered. The strength of these interactions was examined by processing the UV/vis absorption data with a curve fitting model. Remarkably, in the case of compound **4**, the set of association constants issued from processing the absorption data was successfully used to fit the NMR data. In addition, mass spectrometry experiments provided strong support for the formation of the different species involved in the interaction of compounds **1–4** with calcium. This work underlines the importance of considering the nature of the salt used as well as the experimental conditions in cation detection processes.

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Keywords: Chalcone; Ferrocene; Chemosensors; Ligand–cation interaction; UV/vis absorption properties

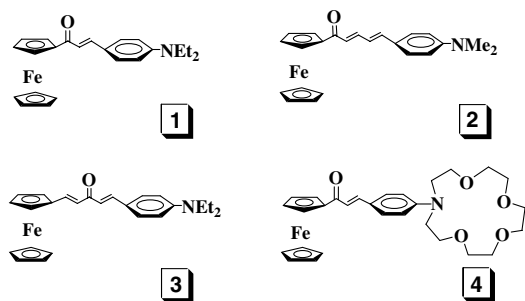
1. Introduction

Since more than 40 years, ferrocenyl chalcones have aroused a constant interest. Their synthesis, characterization, spectroscopic properties, and reactivity have been the subject of many papers [1]. More recently, their potential use in different fields such as non linear optics [2] or pharmaceutical sciences have even been considered [3]. Surprisingly, until the beginning of our work, these compounds had never been examined as ion chemosensors. However, they proved to be multiresponsive ferrocenyl receptors, which could lead to an attractive new generation of chemosensors [4]. Actually, an electroactive receptor

with optical properties may provide thorough information resulting from the different physical responses gathered upon addition of one analyte, and can even be used in different conditions to detect several ions [5]. One exciting advantage of this kind of sensor could be the tuning of the optical properties, via the oxidation state modulation of the redox center [6].

As far as we are concerned, we recently designed a new family of ferrocenyl chalcones to obtain both electroactive and optical sensors for cations [4b,4c,7]. In particular, in previous papers [8], we have established that the monosubstituted compounds (**1–4**) (Scheme 1) lead to peculiar and rather selective electrochemical detection of calcium. Their behaviour in presence of calcium salts has also been examined by NMR spectroscopy. In the present paper, we focus on the capabilities of these compounds to detect calcium by

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Scheme 1. Compounds 1–4.

UV/vis absorption spectroscopy. We have investigated the influence of structural changes brought into the molecular framework of **1** upon this optical cation detection. To do so, we describe first the UV/vis absorption characteristics of compounds **1–4**. Then, the absorption behaviour of compounds **1–3** upon calcium addition was studied, to examine the effect of the insertion of a $-\text{CH}=\text{CH}-$ unit into the conjugated system of **1**. Similarly, the behaviour of compound **4** was also investigated, to see the effect of the substitution of the diethylamino group by an aza-15-crown-5 residue. We show that some of these ligands exhibit different responses for calcium detection depending on the use of calcium triflate or calcium perchlorate, thus evidencing an unprecedented spectroscopic behaviour of chalcone-like derivatives. For the sake of useful comparison, the UV/vis absorption characteristics of the protonated homologues of **1–4** are also presented. Finally, the results of spectroscopic data processing, and mass spectrometry measurements allowed us to study the nature of the possible interactions of our compounds with calcium perchlorate.

2. Results and discussion

2.1. Absorption characteristics of compounds 1–4

For comparison purpose, the absorption properties of these compounds were studied in CH_3CN , as it was the case for their NMR and electrochemical properties [8]. The absorption spectrum of compound **1** (Fig. 1) displays two characteristic bands at 254 and 404 nm. It also shows a shoulder near 330 nm, and a long-wavelength absorption tail. This spectrum shares many common features with that of organic derivative $\text{CH}_3\text{COCH}=\text{CHC}_6\text{H}_4\text{NEt}_2$ (**5**) and related compounds, which have been studied in the literature [9], and the band attribution can be done on this basis. Therefore, the band at 254 nm can be attributed to a $\pi-\pi^*$ transition characteristic of aromatic ketones, while the weak shoulder arises from a $n \rightarrow \pi^*$ transition [10]. The intense long-wavelength band was assigned to charge transfer (CT) occurring between the donor amino group and the acceptor carbonyl group. It can be noted that this CT band was red-shifted by 24 nm with respect to that of compound

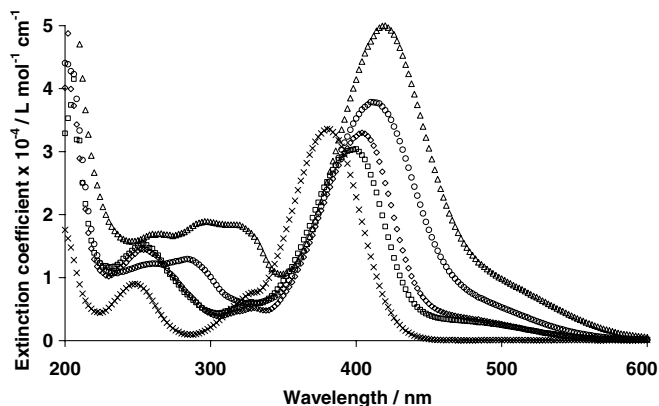


Fig. 1. Absorption spectra of compounds **1** (\diamond), **2** (\circ), **3** (Δ), **4** (\square), and **5** (\times) in CH_3CN , under the same experimental conditions.

5, which is in agreement with the extension of the conjugated system. The broad low-intensity band located above 480 nm is not present on the absorption spectrum of **5**. It can be assigned to a d–d transition of iron in ferrocene [11]. The position of this band at long wavelengths can be explained by the electron acceptor effect of the organic moiety linked to ferrocene [11e]. Actually, it has been checked that under our experimental conditions, comparable values were found for acetyl- and 1,1'-diacetyl ferrocene bearing the COCH_3 electron-withdrawing group.

The absorption spectra of compounds **2** and **3** are rather similar in shape to that of **1** (Fig. 1). As expected, the extension of the conjugated system induces a red shift of the maximum of the CT band (412 and 418 nm, respectively for **2** and **3**), while the width of this band increases (full-width at half-maximum = 3900, 3700, and 3300 cm^{-1} for **2**, **3** and **1**, respectively). These results are in agreement with those obtained by Thomas et al. with polyferrocene compounds incorporating conjugated spacers [12]. The d–d transition is now partially overlapped because of the width of the CT band. When compared to **1**, the absorption spectrum of compounds **2** and **3** also displays new short-wavelength bands of weak intensity (peaking around 284, and 296, 320 nm, respectively). These features can be explained by the extension of the conjugated system due to the presence of an additional ethylenic unit. As far as compound **4** is concerned, its absorption spectrum strongly resembles that of compound **1**, but the CT band is now slightly blue shifted by 6 nm. This phenomenon can be ascribed to the presence of the electron-withdrawing effect of the oxygen atoms in the crown ring [13].

2.2. Calcium detection by compounds 1–3. Influence of the insertion of a $-\text{CH}=\text{CH}-$ unit into the conjugated system of 1

Two different salts were used to analyze the effect of calcium upon the absorption properties of our compounds. Calcium triflate was employed in a previous work to study

their electrochemical behaviour in the presence of ions. We went on working with this salt for absorption studies, so that the results obtained by the two methods were comparable. Calcium perchlorate was also used because it dissolves easily in acetonitrile and is known not to interfere with spectrophotometric measurements. Our aim was to explore a wide range of concentration in calcium, which means that a high metal-to-ligand ratio should be attained. In most of the cases, the salt concentration was varied from 10^{-6} to 10^{-1} M.

Addition of calcium triflate to a solution of the dyes 1–3 (2×10^{-5} M) induced drastic changes in their respective spectrum. A two-step behaviour was typically observed (Fig. 2): First, until a 7×10^{-3} M salt concentration, a reddening of the solution was noted. Meanwhile, the intensity of the CT band was decreased and the absorption maximum shifted to long wavelengths as absorbance was increased around 500 nm. This phenomenon was assigned to the interaction of the carbonyl group with the cation [7,14]. This result is in perfect agreement with the NMR

analysis previously reported [8b]. Then, upon subsequent addition of salt, the solution turned clearer (very pale violet). On the spectrum, absorbance at long wavelengths vanished while a new band grew around 300 nm. An isosbestic point, around 360 nm, was only observed for high salt concentration ($>7 \times 10^{-3}$ M). This second phenomenon suggests that another type of ligand–calcium interaction is involved.

In the presence of calcium perchlorate, the behaviour of dyes 1–3 was different from that observed with triflate salt. The main feature concerned the CT band that was slightly decreased and progressively shifted to the red, while a new broad band grew up at long wavelengths (Table 1). A representative evolution of the spectrum is displayed in Fig. 3 for compound 1. It is noteworthy that for this compound isosbestic points situated at 264, 320 and 418 nm are observed, suggesting the formation of a unique species in solution. For compounds 2 and 3, only quasi-isosbestic points were observed, indicating the formation of several species in solution.

The lengthening of the unsaturated system of the ferrocenyl chalcone 1 therefore leads to small differences in the behaviour of the ligands towards calcium addition. But, it must be underlined that from a general viewpoint, compounds 1–3 share an important common feature that is they all give different absorption responses according to the nature of the calcium salt.

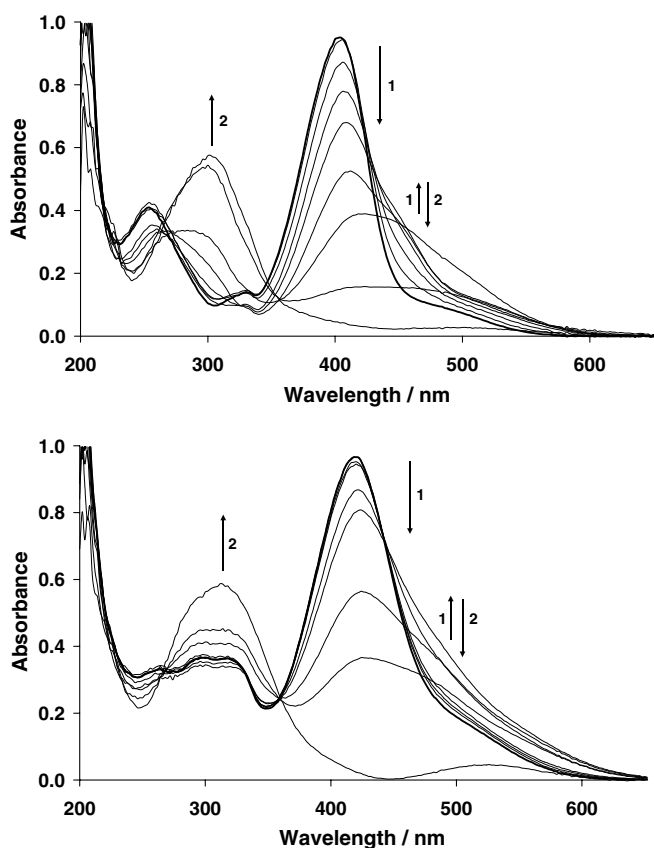


Fig. 2. (Top) Absorption behaviour of compound 1 [2.58×10^{-5} M] before (bold line) and after addition of $\text{Ca}(\text{CF}_3\text{SO}_3)_2$ in CH_3CN . (From top to bottom) $[\text{Ca}^{2+}]$ (M): 1.0×10^{-3} , 3.0×10^{-3} , 5.0×10^{-3} , 7.0×10^{-3} , 1.0×10^{-2} , 1.5×10^{-2} , 2.2×10^{-2} , 2.5×10^{-2} . (Bottom) Absorption behaviour of compound 3 [1.45×10^{-5} M] before (bold line) and after addition of $\text{Ca}(\text{CF}_3\text{SO}_3)_2$, in CH_3CN . (From top to bottom) $[\text{Ca}^{2+}]$ (M): 5.0×10^{-5} , 7.5×10^{-4} , 1.0×10^{-3} , 3.0×10^{-3} , 5.0×10^{-3} , 7.0×10^{-3} , 1.0×10^{-2} , 1.25×10^{-2} .

Table 1
Absorption maxima for compounds 1–4 ($\approx 3 \times 10^{-5}$ M) before (λ_1), and after (λ_2) addition of calcium perchlorate (10^{-1} M)

Compound	λ_1 (nm)	λ_2 (nm)	$\Delta\lambda_{\text{max}}$ (nm)
1	404	438	34
2	412	438	26
3	418	464	46
4	398	320	-78

$$\Delta\lambda_{\text{max}} = \lambda_2 - \lambda_1.$$

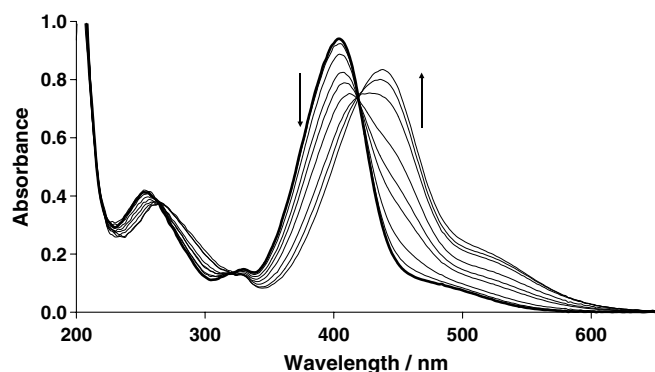


Fig. 3. Absorption behaviour of compound 1 [2.58×10^{-5} M] (bold line) upon calcium perchlorate addition, in CH_3CN ; successive Ca^{2+} concentration (M): 1.0×10^{-5} , 2.5×10^{-5} , 7.5×10^{-5} , 2.5×10^{-4} , 1.0×10^{-2} , 3.00×10^{-2} , 5×10^{-2} , 1.0×10^{-1} .

2.3. Research of an explanation for the two-step-response observed with compounds 1–3 in the presence of triflate, and in situ protonation of compounds 1–4

Previous results obtained by NMR spectroscopy with compound **1** in the presence of calcium salt have revealed that interaction with calcium triflate or calcium perchlorate involves the same interacting site, i.e. the unsaturated carbonyl moiety, in the molecule. This is in line with the effect observed by UV/vis absorption spectroscopy at low cation-to-ligand ratio. NMR analysis gives no information about what occurs at concentration higher than 10 equiv. of calcium, but absorption spectroscopy does. Thus, at high triflate salt concentration, we have previously considered the fact that a second interacting site, probably centred on the nitrogen atom, was involved with compounds 1–3. Therefore, we have suspected the presence of a side-reaction leading to the formation of a by-product: the protonated homologue. We have previously shown elsewhere that adding HBF_4 to solutions of compounds 1–4 effectively leads to their N-protonated homologues [8]. Consequently, we investigated here the absorption behaviour of compounds 1–4 upon H^+ addition. Triflic acid was added stepwise to

a 10^{-5} M solution of each compound in CH_3CN . All the solution turned clearer (orange to very pale violet) and strong modifications of the spectrum were observed. The intensity of the CT band (near 400 nm) progressively decreased while a new band appeared around 300 nm (Fig. 4). Isosbestic points were formed, located for example at 230, 260 and 322 nm for compound **4**. They indicate a single equilibrium between two species. This kind of behaviour is characteristic of the formation of the protonated species, the quaternarization of the amino group leading to the suppression of charge transfer within the molecule [15]. We noted thus some similarities between the UV/vis absorption spectrum of compounds 1–3 placed in the presence of high triflate salt concentration and that of their respective protonated homologues. In particular, for the same compound, the maximum wavelength of the two spectra was quite close (see Table 2).

To strengthen our hypothesis, a new experiment was performed, keeping the same concentrations as those used for UV/vis absorption experiments, but in a larger scale. In a schlenk flask, 1000 equiv. of triflate calcium salt were added to a solution of compound **1** (10^{-5} M) in acetonitrile. The mixture was stirred for 4 h. After filtration and evaporation of the solvent, only one compound was obtained and identified as the 1H^+ adduct by NMR and mass spectrometry. This clearly shows that protonated species are formed at high calcium triflate concentration. In conclusion, we have established that compounds 1–3 are sensitive to the experimental conditions, and in particular, to the high metal-to-ligand ratio that can be used in UV/vis absorption spectroscopy.

2.4. Calcium detection by compound 4. Substitution of the diethylamino group of 1 by an aza-15-crown-5 residue

In contrast to compounds 1–3, compound **4** was not sensitive to the nature of the calcium salt used. Actually, for both the salts the solution turned from red-orange to pink, and the same evolution of the spectrum upon salt addition was observed for calcium triflate and perchlorate: the intensity of the CT band steeply decreases until the band totally disappears at the expense of a new broad band situated at short wavelengths around 320 nm (Fig. 5). It should be added that three quasi-isosbestic points are detected at 240, 274 and 350 nm, respectively. As explained above, the changes observed are characteristic of a nitrogen–calcium interaction. The UV/vis absorption data

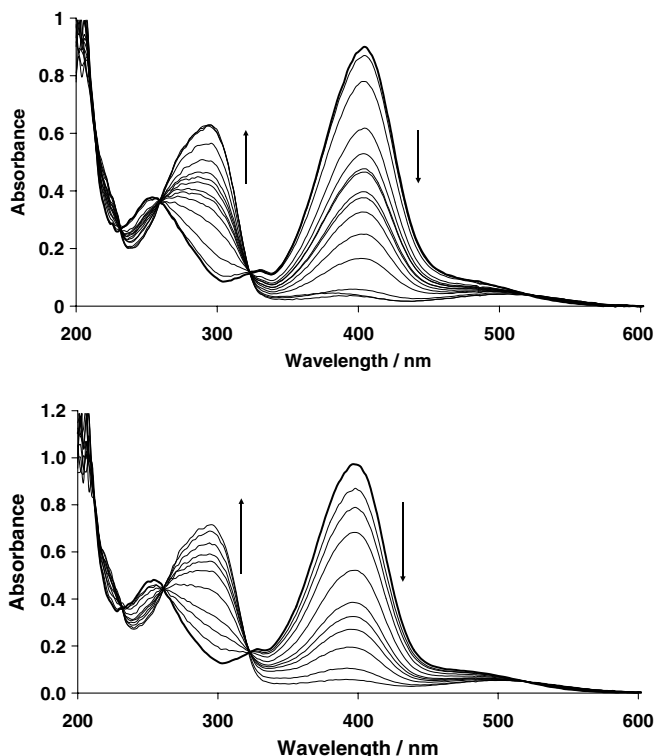


Fig. 4. (Top) Absorption behaviour of compound **1** [2.58×10^{-5} M] before (bold line) and after addition of $\text{CF}_3\text{SO}_3\text{H}$. (From top to bottom) [H^+] (M): 2.58×10^{-6} , 5.16×10^{-6} , 7.74×10^{-6} , 1.55×10^{-5} , 1.68×10^{-5} , 1.81×10^{-5} , 1.94×10^{-5} , 2.07×10^{-5} , 2.19×10^{-5} , 2.45×10^{-5} , 2.58×10^{-5} , 3.22×10^{-5} , 3.87×10^{-5} , 5.16×10^{-5} . (Bottom) Absorption behaviour of compound **4** [3.19×10^{-5} M] before (bold line) and after addition of $\text{CF}_3\text{SO}_3\text{H}$. (From top to bottom) [H^+] (M): 6.38×10^{-6} , 9.57×10^{-6} , 1.28×10^{-5} , 1.60×10^{-5} , 1.91×10^{-5} , 2.39×10^{-5} , 2.71×10^{-5} , 3.03×10^{-5} , 3.19×10^{-5} , 3.99×10^{-5} .

Table 2

Absorption maxima for compounds 1–4, before (λ_1), and after addition of triflate acid (3.0×10^{-5} M) (λ_2) or of calcium triflate ($\geq 10^{-2}$ M) (λ_3); [L] $\approx 1.4\text{--}3.0 \times 10^{-5}$ M

Compound	λ_1 (nm)	λ_2 (nm)	λ_3 (nm)
1	404	294	302
2	412	326	332
3	418	322	314
4	398	292	322

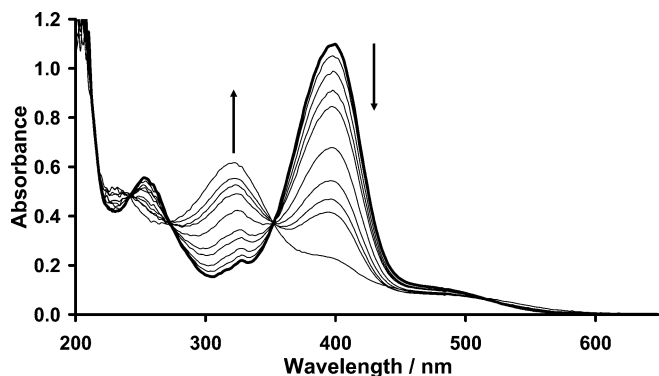


Fig. 5. Absorption behaviour of compound **4** [3.38×10^{-5} M] upon calcium perchlorate addition, in CH_3CN ; successive Ca^{2+} concentration (M): 5.0×10^{-6} , 2.5×10^{-5} , 5.0×10^{-5} , 1×10^{-4} , 2.5×10^{-4} , 5.0×10^{-4} , 7.5×10^{-4} , 1×10^{-3} , 1×10^{-2} .

clearly confirms the preferred azacrown–calcium interaction already revealed by our previous NMR analysis [8a]. However, it can be noted that under the present experimental conditions, no interaction of calcium with the ligand carbonyl group was evidenced, in contrast to what was observed under NMR conditions.

Therefore, the behaviour of **4** in the presence of cations strongly differs from that of the three other dyes. Changing the nature of the aza group in molecule **1** induced a change in the nature of the preferred calcium–ligand interaction site. This leads to a unique spectroscopic response upon calcium addition, whatever the nature of the salt used.

2.5. Proposition of a model for the ligand– Ca^{2+} interaction. Processing of the absorption data and results from mass spectrometry

To get a deeper insight into the ligand– Ca^{2+} interaction process, we wanted to determine the number, the stoichiometry, and the association constants of the calcium adducts involved. To do so, the absorbance variation was analyzed versus cation concentration. Absorbance was recorded at four different wavelengths chosen to obtain maximum information, and the absorption spectroscopic data were processed according to the global curve-fitting method described elsewhere [13,16]. Regarding the experiments performed with calcium triflate, no accurate determination of the binding constants could be achieved for compounds **2** and **3**, probably because of the competitive protonation reaction. However, a good result was obtained for compound **1**, but in a restricted range of calcium triflate

concentrations (Table 3). In this case, the data were satisfactorily fitted by taking into account only one species, LM. The data acquired with calcium perchlorate were also processed, evidencing again the formation of only one species for compound **1**. In contrast, for compounds **2** and **3**, good fits were only obtained by taking into account the existence of two species of different stoichiometries: LM and LM_2 , the first one being found in major proportion. The corresponding association constants are indicated in Table 3 (values given with a $\pm 15\%$ error). It is noteworthy that the LM association constant is nearly the same for compound **1** whatever the calcium salt used. The value of the LM association constant found for **2** and **3** is close to that of **1**. However, the fact that the two first compounds form the LM_2 species indicates that they behave on a slightly different way. It is also interesting to note that for compound **2** (see Fig. 6) the values of the association constants obtained with calcium perchlorate by absorption spectroscopy are the same than those obtained by NMR spectroscopy with calcium triflate.

Concerning ligand **4**, the association constants were first calculated for the experiments done with calcium perchlorate (Fig. 7). Three species were now necessary to obtain a good fit. Species LM and LM_2 were found again, and a new substoichiometric species, namely L_2M , appears. Let us remark that the association constants of the L_nM_m species of **4** determined by this technique are one to three orders of magnitude higher than the constants obtained for compounds **1–3** under the same experimental conditions. These results clearly indicate that complexation involves the azacrown ring. The L_2M species may correspond to the formation of a sandwich complex, as sometimes reported with organic 15-crown-5 ether derivatives in the presence of Ca^{2+} [13,17].

We noted above that the UV/vis absorption response of ligand **4** is not sensitive, qualitatively speaking, to the nature of the calcium salt. Actually, the association constants were found to be quite close for the two salts used. However, the data acquired with calcium perchlorate were easier to process than those acquired with calcium triflate. The difficulty encountered in the latter case can be attributed to discrete protonation reaction that occurs with calcium triflate, and competes with calcium complexation. Subsequently, the same set of values was used to process the ^{13}C NMR data obtained with compound **4** [1×10^{-2} M] and calcium triflate [$0.5\text{--}5 \times 10^{-2}$ M], using the same global curve-fitting method, and remarkably a good fit was obtained again [8a]. To our knowledge, this example of

Table 3

Association constants of the L_nM_m species obtained when processing the UV/vis data; L = **1–4**, M = Ca^{2+}

Compound	Calcium salt	LM, K_1 (L mol^{-1})	L_2M , K_2 (L mol^{-1})	LM_2 , K_3 (L mol^{-1})	Final $[\text{Ca}^{2+}]$ (mol^{-1})
1	$\text{Ca}(\text{CF}_3\text{SO}_3)_2$	9.2×10^1	–	–	7.0×10^{-3}
1	$\text{Ca}(\text{ClO}_4)_2$	1.3×10^2	–	–	10^{-1}
2	$\text{Ca}(\text{ClO}_4)_2$	8.1×10^1	–	3.8	10^{-1}
3	$\text{Ca}(\text{ClO}_4)_2$	1.2×10^2	–	6.1	10^{-1}
4	$\text{Ca}(\text{ClO}_4)_2$	1.99×10^3	8.09×10^4	1.07×10^3	10^{-2}

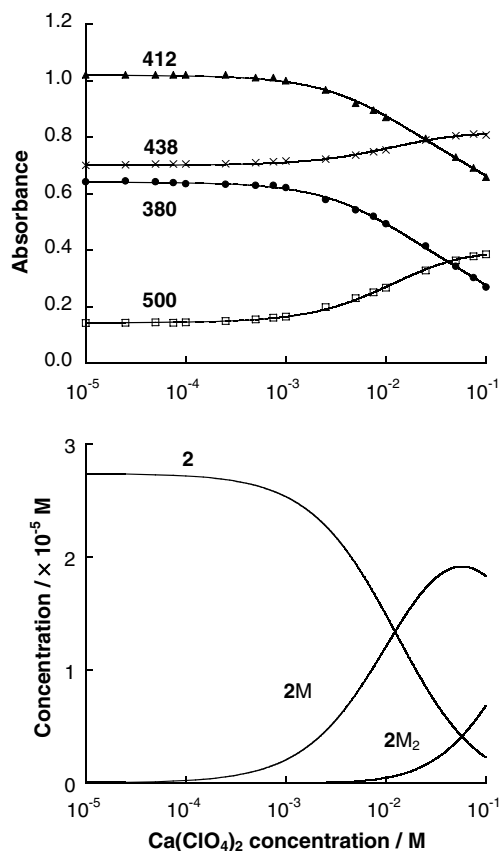


Fig. 6. Processing of the UV/vis absorption data for compound **2** (2.74×10^{-5} M) in the presence of calcium perchlorate. (Top) Absorbance versus calcium concentration at different wavelengths in nanometers. The points are experimental and the curves (lines) were calculated by fitting the data. (Bottom) Corresponding calculated concentrations of the different species.

using a unique set of association constants to fit both UV/vis absorption and NMR data is unprecedented for a ferrocenyl ligand.

Finally, to support the hypothesis that different L_nM_m adducts are involved in these ligand–calcium interactions, experiments were performed by mass spectrometry. Mass spectra were recorded with samples of compounds **1–4** (5×10^{-3} M) containing different equivalents of salts. These measurements revealed all the peaks corresponding to the expected species (Table 4), thus providing strong support for their existence in solution.

2.6. A spectroscopic behaviour specific to ferrocenyl chalcones?

To our knowledge, obtaining different optical responses according to the anion of the salt used has not been reported beforehand for the benzylideneacetone $\text{CH}_3\text{COCH}=\text{CHC}_6\text{H}_4\text{NEt}_2$ (**5**) or related compounds such as $\text{CO}(\text{CH}=\text{CHC}_6\text{H}_4\text{NEt}_2)_2$. At this point, an interesting question was as follows: Is this behaviour specific to ferrocenyl chalcones or not? To answer this question, the

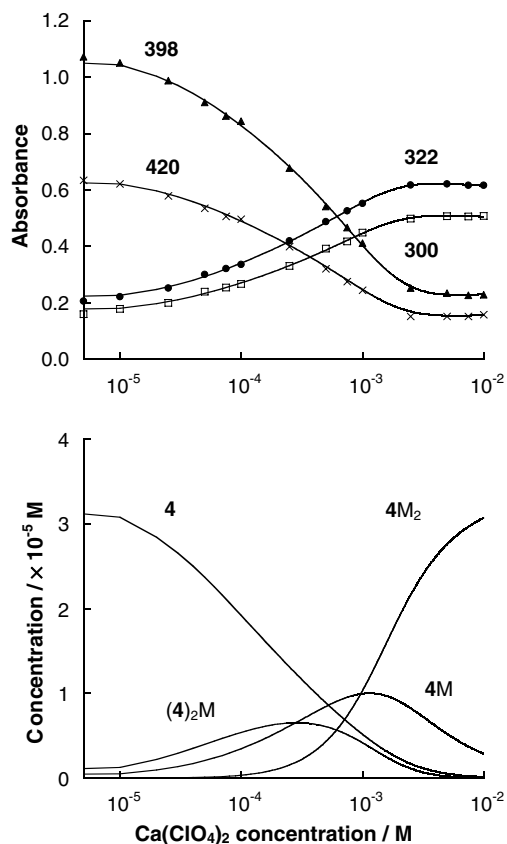


Fig. 7. Processing of the UV/vis absorption data for compound **4** (3.38×10^{-5} M) in the presence of calcium perchlorate. (Top) Absorbance versus calcium concentration at different wavelengths in nanometers. The points are experimental and the curves (lines) were calculated by fitting the data. (Bottom) Corresponding calculated concentrations of the different species.

Table 4

Assignment of the main peaks obtained by mass spectrometry using the ESI-MS technique for compounds **1–4** in the presence of calcium; $M = \text{Ca}^{2+}$, $X = \text{ClO}_4^-$

Compound	$[\text{LMX}]^+$	$[\text{L}_2\text{MX}]^+$	$[\text{LM}_2\text{X}_3]^+$	$[\text{L}_2\text{M}_2\text{X}_3]^+$
1	527	–	–	–
2	524	–	764	–
3	552	–	791	–
4	672	1205	912	1445

UV/vis absorption behaviour of the organic compound **5** was examined qualitatively under our conditions.

As illustrated in Fig. 8, the UV/vis absorption behaviour of dye **5** is reminiscent of that of compounds **1–3**. With perchlorate salt, a bathochromic shift of the CT band (26 nm) was observed. In contrast, with calcium triflate, a total decrease of the absorbance at long wavelengths occurs while a new band appears at 276 nm. We verified that in the latter case, this behaviour corresponds to the formation of the protonated species. In conclusion, the behaviour of compounds **1–3** upon calcium addition is not specific to

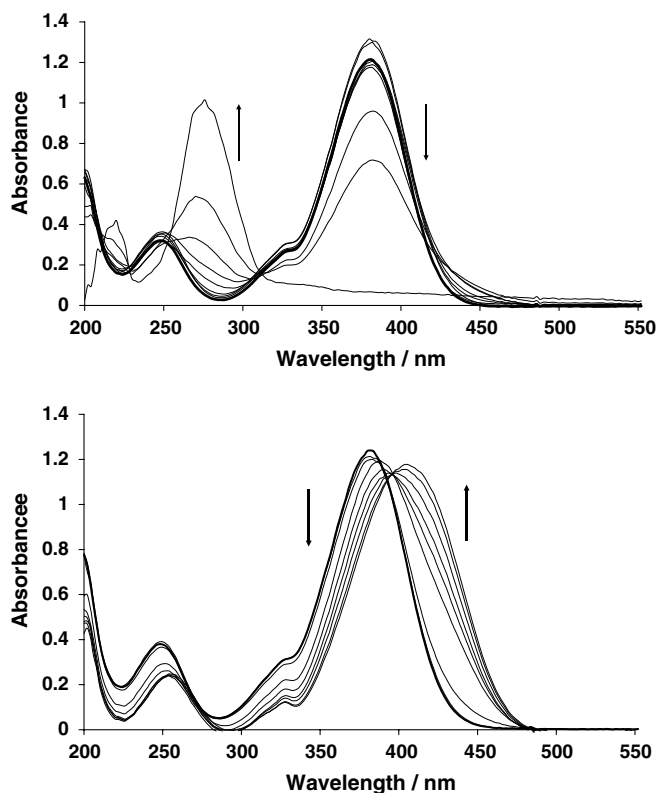


Fig. 8. (Top) Absorption behaviour of compound **5** [4.0×10^{-5} M] upon calcium triflate addition, in CH_3CN ; successive Ca^{2+} concentration (M): (From top to bottom) 3.0×10^{-3} , 1.0×10^{-3} , 5.0×10^{-3} , 2.0×10^{-5} , 8.0×10^{-3} , 7.0×10^{-3} , 1.0×10^{-2} , 3.0×10^{-2} . (Bottom) Absorption behaviour of compound **5** [3.42×10^{-5} M] upon calcium perchlorate addition, in CH_3CN ; successive Ca^{2+} concentration (M): (From top to bottom) 5.0×10^{-5} , 7.5×10^{-3} , 5.0×10^{-2} , 7.5×10^{-2} , 1.0×10^{-1} , then excess.

the ferrocenyl chalcones, but is also encountered with organic chalcone-like derivatives.

In the literature, Schmehl's team [18] has shown with a totally organic ligand containing a crown ether that a different optical signature can be obtained when changing the anion associated to the same cation. In this interesting example, the differences observed are due to the formation of adducts of different stoichiometry according to the nature of the anion used. In our case, this explanation seems unlikely. We gave evidence that the behaviour observed with ferrocenyl chalcone derivatives **1–3** is in connection with the existence of a competitive protonation reaction that occurs when using triflate salt at high concentration. Interaction with calcium, which is clearly visible at a low salt concentration, involves the carbonyl group, with quite a weak association constant. Subsequently, when rising triflate concentration, protonation occurs on the nitrogen atom of the diethylamino group. In the case of compound **4**, no difference was observed using either perchlorate or triflate salts. This can be explained by the fact that interaction with calcium involves the azacrown group. As revealed by the calculation of the association constants, the species thus formed are much more stable than those formed by

interaction with the carbonyl group on ligands **1–3**. When using calcium triflate at high concentration, it is possible that some H^+ and Ca^{2+} ions compete for the crown nitrogen. However, this is hardly noticeable on the absorption spectrum because the stability of the species formed with calcium makes the competition harder, and because the same ligand site is affected in the two types of interaction, therefore leading to small spectroscopic effects when swapping from an ion to another.

Let us consider now the origin of the H^+ source: Under our NMR experimental conditions, the salt to ligand ratio is below 15 equiv., and we have checked that there is no protonation reaction over a 48 h period [8]. In contrast, under our UV/vis conditions, the salt to ligand ratio is much higher. Consequently, the amount of impurities such as free triflic acid may increase and become a substantial source of H^+ . Another explanation could be that the proton source comes from the hydrolysis of the triflate calcium salt in spectroscopic grade acetonitrile, used without subsequent dehydration. Regarding the NMR calcium titrations experiments, we have performed them with dried deuterated acetonitrile and under inert atmosphere.

3. Concluding remarks

This study shows that ferrocenyl derivatives **1–4** are good sensors for the detection of calcium by UV/vis absorption spectroscopy. Processing the absorption data gave evidence for the different species formed in the presence of calcium perchlorate. Moreover, all these species were detected by mass spectrometry, providing strong support for our hypotheses. Interestingly, for ligand **4**, the same set of association constants could be used to fit both the UV/vis and NMR data whatever the calcium salt. Remarkable absorption behaviour was highlighted: while azacrown compound **4** is not sensitive to the nature of the calcium salt, simple dialkylamino compounds **1–3** selectively discriminate calcium triflate from calcium perchlorate as they offer in each case a specific response, visible to the naked eye. We have shown that this unprecedented behaviour of ferrocenyl chalcone derivatives **1–3** is (i) in connection with the existence of a competitive protonation reaction which occurs when using triflate salt; (ii) probably related to the stability of the L_nM_m species formed during the ferrocenyl ligand–calcium interaction process; (iii) not exclusively encountered with ferrocenyl derivatives.

Our results underline the important role of the nature of the ferrocenyl receptor but also point out the importance of considering the nature of the salt and the experimental conditions when performing cation detection experiments. Finally, these findings also suggest that other ferrocenyl chalcones may have some surprising optical properties. Work is presently underway to extend this study to disubstituted ferrocenyl ligands, a distinct advantage of which is to allow calcium detection by an additional technique, i.e. fluorescence spectroscopy.

4. Experimental

4.1. Materials

Spectroscopic grade acetonitrile (Merck) was used for absorption measurements. $\text{CF}_3\text{SO}_3\text{H}$ (98%) was from Aldrich. Calcium salts: $\text{Ca}(\text{CF}_3\text{SO}_3)_2$ (96%), $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ (99%) were from Strem and Aldrich, respectively. Triflate salt was dried, weighed, and solved in acetonitrile solutions of ligands under inert atmosphere before use of the mixtures. Warning! Perchlorate salts are hazardous because of the possibility of explosion! Compounds **1–4** were prepared according to our published procedures [8].

4.2. General instrumentation and procedures

The solutions of compounds **1–4** were light-protected before each measurement. Mass spectra were obtained at the Service Commun de Spectrométrie de Masse de l'Université Paul Sabatier et du CNRS de Toulouse. Spectra were performed on a triple quadrupole mass spectrometer (Perkin–Elmer Sciex API 365) using electrospray as the ionization mode (positive mode). The infusion rate was 5 $\mu\text{L}/\text{min}$.

4.3. Optical measurements

4.3.1. Apparatus

UV/vis absorption spectra were recorded on a Hewlett-Packard 8452 A diode array spectrophotometer. It was checked that the absorption spectra did not vary over a period of 2 h. Cuvettes of 1 cm optical path length were used. The measurements were conducted at 20 °C in a thermostated cell.

4.3.2. Curve fitting method

All the simulations and parametric adjustments were performed using a home-made software, SA version 3, as described in Refs. [7,8,13,16].

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