Supporting Information

Organometallic Derivative of BAPTA Ligand: Towards Electrochemically Controlled Cation Release in Biocompatible Media

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Table of contents:

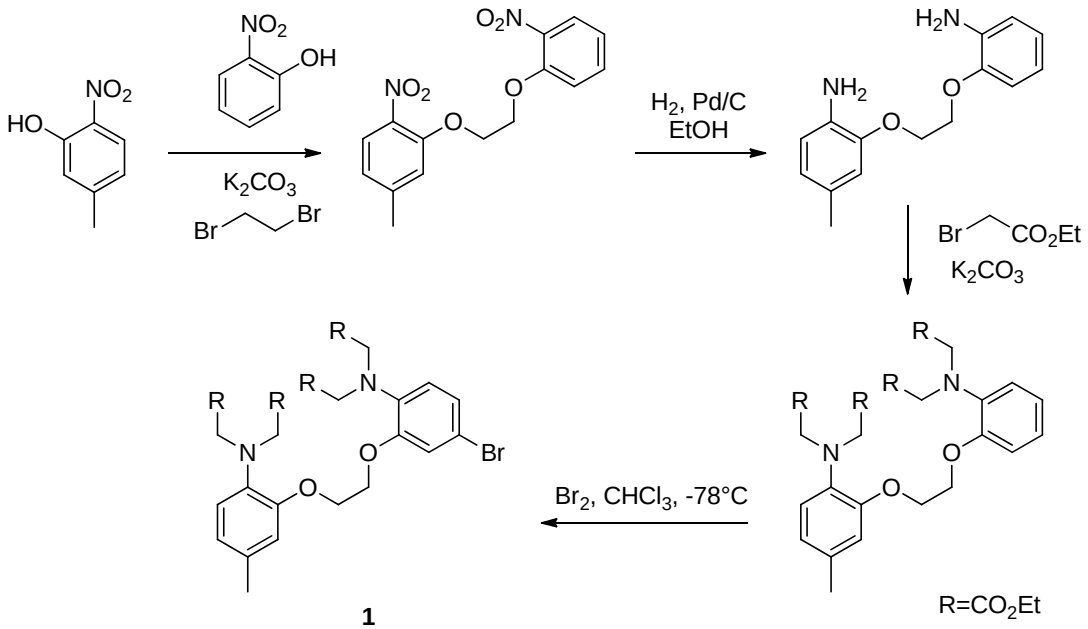
I- Experimental section

I-1- General considerations: All reactions were performed under argon if not stated otherwise. EGTA (ethylene glycol bis (2-aminoethylether)-N,N,N',N'-tetraacetic acid), MOPS (4-morpholinepropanesulfonic acid), and all chemicals were purchased from Sigma/Aldrich (France) or Alfa Aesar (France). Bromomethyl-BAPTA tetraester **1** was synthesized in 4 steps according to the published procedure.[1]

^{1}H and ^{13}C-NMR spectra were recorded on Bruker AC-250 spectrometer in the solvents indicated at 298 K. Chemical shifts are reported using the deuterated (^{13}C NMR) or the residual monoprotonated (^{1}H NMR) solvent signals as reference. Mass spectra were recorded using a Jeol JMS-700 Spectrometer. Elemental analysis were conducted at the Service de Microanalyses- ICSN (Gif sur Yvette, France). Thin layer chromatography (TLC) was performed on aluminium sheets precoated with 60 F_{254} silica gel. Preparative flash chromatography was performed on silica gel 60 (0.040-0.063 mm, Merck).

I-2- Synthesis:

I-2-1- Synthesis of 5-bromo-5'-Methyl-BAPTA ethyl ester (**1**). (BAPTA = 1,2-bis(2aminophenoxy)-ethane- N,N,N',N'-tetraacetic acid). For synthesis details of **1** see [1]



1

Scheme S1: *Synthesis of the bromo-BAPTA tetra-ester **1***

I-2-2- Synthesis of Methyl mono(acetylferrocenyl)BAPTA tetraester ***2***

An Ar-flushed round-bottomed Schlenk flask was charged with CuI (6.9 mg, 0.036 mmol), $PdCl_2(PPh_3)_2$ (25.3 mg, 0.036 mmol), PPh_3 (38.1 mg, 0.145 mmol), and an Ar-purged mixture of 1:1 DMF: *i*-Pr_2NH (5 mL). The mixture was stirred under Ar at 0 °C for 15 min. Ethynylferrocene (69.3 mg, 0.33 mmol) and bromomethyl-BAPTA tetraester **1** (225. mg, 0.33) were added under Ar flow. The reaction was warmed to RT slowly, whereupon it was heated to 120°C and stirred at reflux for 18 h. It was cooled to RT and dried on the Rotavap. The crude was purified on a silica gel column in petroleum ether with increasing volumes of ethyl acetate to yield **2** (100 mg, 38 %) as an orange crystalline solid. ^{1}H-NMR (250 MHz, $CDCl_3$): δ 7.06-6.93 (m, 2H, Ph), 6.79-6.62 (m, 4H, Ph), 4.48 (m, 2H, CH of Cp-≡), 4.19-4.30 (m, 11H, 5H of Cp + 2H of Cp-≡ and 4H of CH_2O_{ether}), 3.99-4.17 (m, 16H, CH_2N and CH_2O_{ester}), 2.26 (s, CH_3-Ph), 1.17 (t, $^3J_{HH}$=7.2 Hz, 6H, CH_3), 1.15 (t, $^3J_{HH}$=7.2 Hz, 6H, CH_3); ^{13}C-NMR (62.5 MHz, $CDCl_3$): δ 171.4 (C=O), 150.2 and 149.6 (C^{Ar}-O_{ether}), 139.3 and 136.9 (C^{Ar}-N), 132.0 (C^{Ar}-CH_3), 125.1 (C^{Ar}-H), 121.8 (C^{Ar}-H), 119.2 (C^{Ar}-H), 118. 3(C^{Ar}-H), 115.8 (C^{Ar}-H), 114.3 (C^{Ar}-H), 116.9 (C^{Ar}-≡), 86.9, 85.8, 71.3 and 67.3 (CH of mono-substituted Cp ring), 69.9 (CH of unsubstituted Cp ring), 67.3 and 66.9 (CH_2-N), 65.7, 60.8 and 60.7 (CH_3-**C**H_2), 53.6 and 53.5 (CH_2-O_{ether}), 20.9 (CH_3-Ar), 14.1 and 14.0 (**C**H_3-CH_2) ; Elemental Analysis: calc.for $C_{43}H_{50}FeN_2O_{10}$.$CHCl_3$: C 56.82, H 5.53, N 3.01, found:. C 57.28, H 5.43, N 2.92.

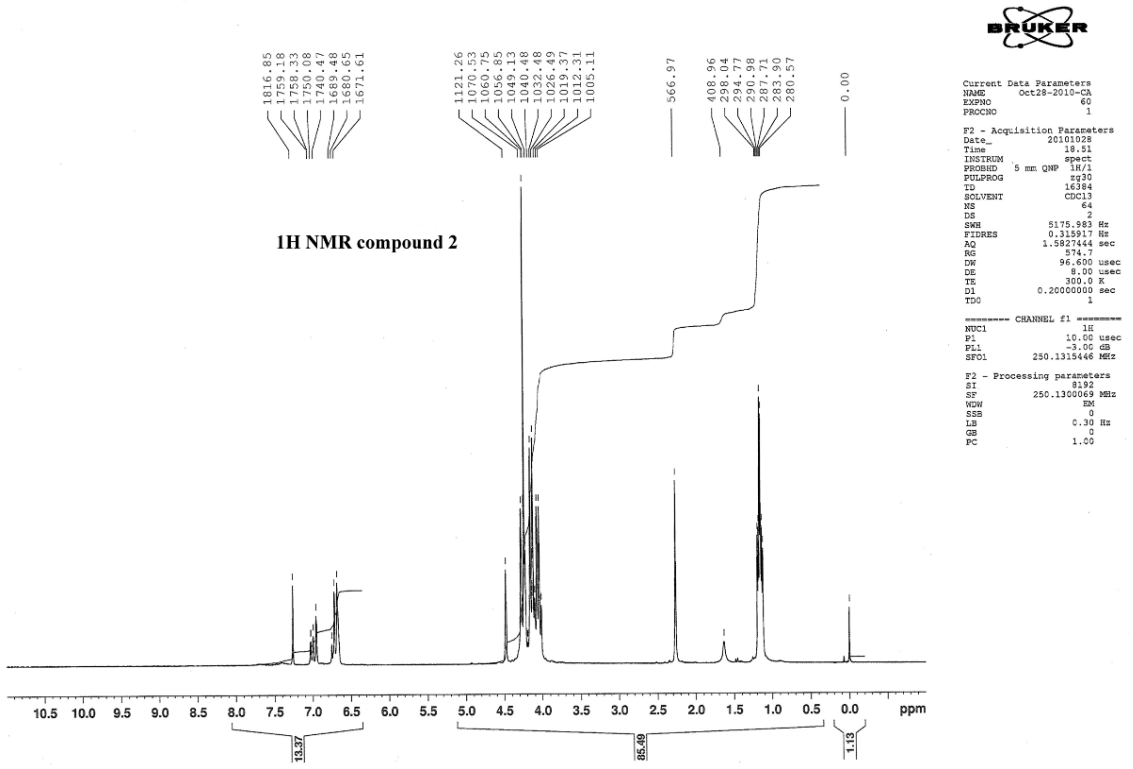


Figure S1: *^{1}H NMR spectrum ($CDCl_3$) of compound* ***2***

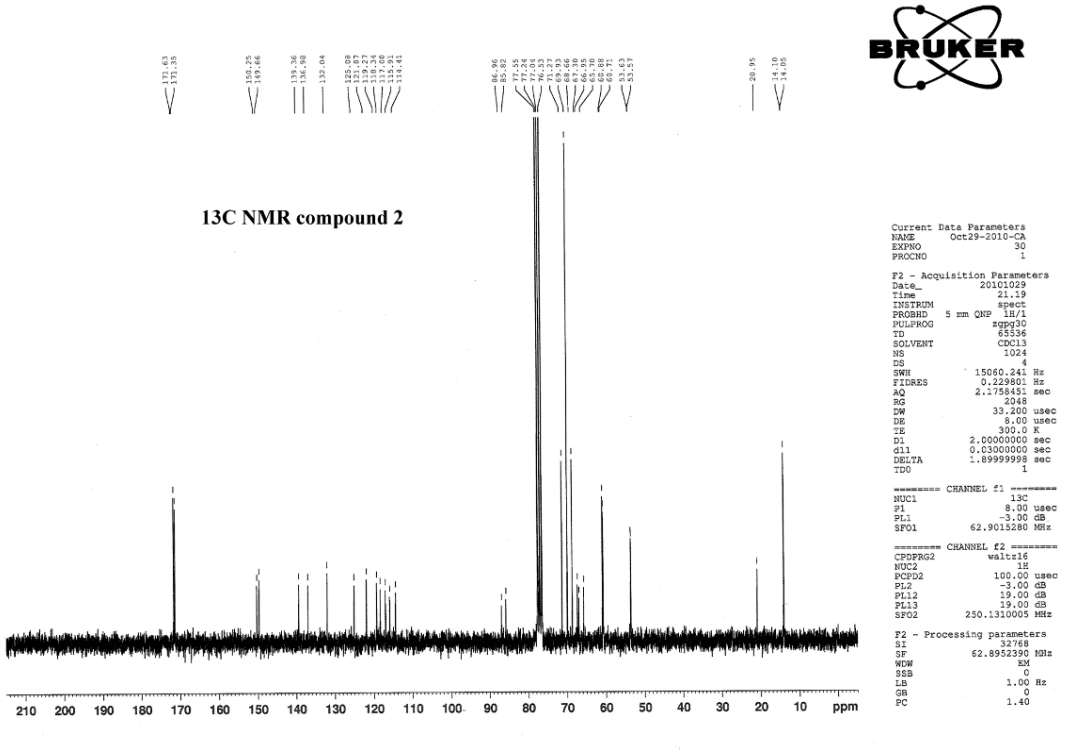


Figure S2: *^{13}C NMR spectrum ($CDCl_3$) of compound* ***2***

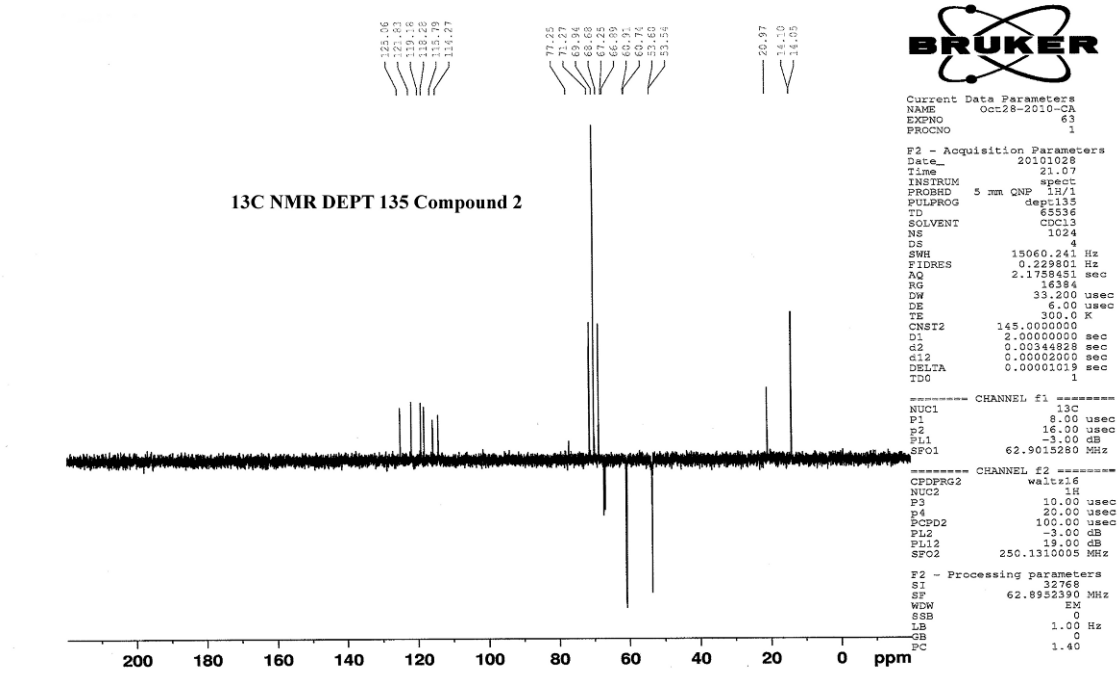


Figure S3: *^{13}C NMR spectrum (DEPT 135 experiment, $CDCl_3$) of compound* ***2***

I-2-3- Synthesis of Methyl mono(acetylferrocenyl)BAPTA potassium salt ***3***

A round-bottomed flask was charged with **2** (36 mg, 0.044 mmol), dissolved in THF (5 mL). A solution of KOH (18 mg, 0.321 mmol) in H_2O (500 µL) was added, and the solution was

stirred at RT for 18 h. The light-colored liquid phase above was decanted, and the oily residue was dried to a crystalline solid **3** (>98%). The solid was redissolved in MeOH, filtered, and dried again on the Rotavap. ESI-MS (m/z): 735.8 ([M^{4-}, K^+, $2H^+$]: z=1); 697.6 ([M^{4-}, $3H^+$]: z=1), 367.4 ([M^{4-}, K^+, H^+]: z=2), 348.5 ([M^{4-}, $2H^+$]: z=2).

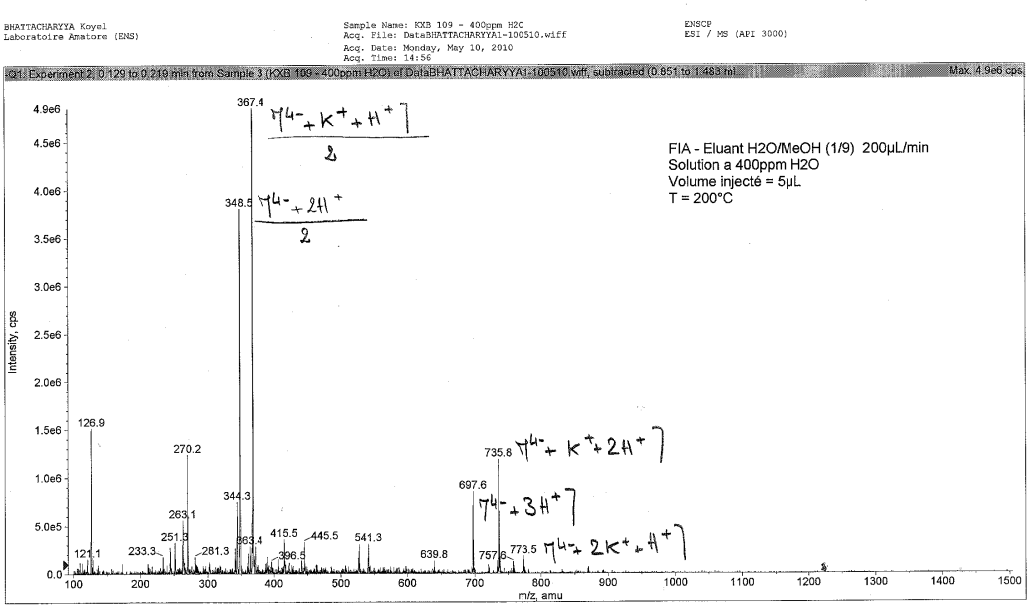


Figure S4: *Mass spectrometry characterization by ESI-MS for compound* ***3***

I-3- Electrochemistry: The electrochemical experiments in aqueous electrolyte were conducted in an air-tight three electrodes glass cell under argon atmosphere, controlled by a computer-controlled potentiostat (Autolab PGSTAT 30, Eco-Chemie, the Netherlands). A large platinum wire and a saturated calomel electrode were used as a counter electrode and a reference electrode, respectively. A glassy carbon electrode with a disk radius of 0.5 mm, was used as working electrode. The working electrode was polished to a mirror finish before each experiment. The supporting electrolyte employed was prepared from ultra-pure water (<18MΩ/cm) and contained 0.1 M KCl, 10 mM MOPS, pH=7.2. Cyclic Voltammograms (CV) were recorded at room temperature (22 ±2°C) at a potential sweep rate of $0.1 V.s^{-1}$.

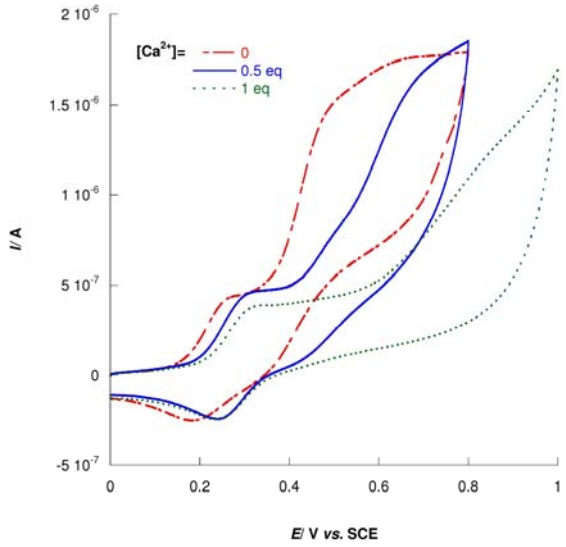
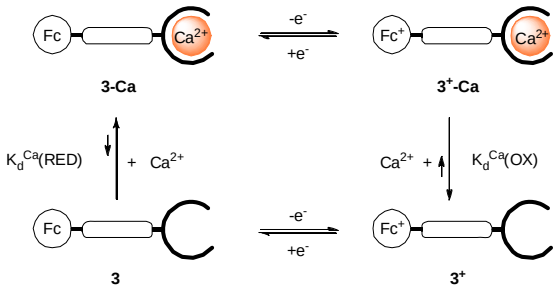


Figure S5: *Effect of Ca^{2+} on the electrochemical response of 3 (0.9 mM) in aqueous solutions (0.1 M KCl, 30mM MOPS pH=7,4). Scan rate: 100 mV.s^{-1}.*

The commercial voltammetric simulation package DigiSim (version 3.05, Bioanalytical Systems, USA) was used to model the cyclic voltammograms at 100 mV.s^{-1}) for 1 mM of compound **3** on electrode of diameter 1 mm. The reversible square scheme mechanism (see Scheme S2) was modelled as follows:

Charge transfer reactions:
reaction[1]: A + e = B with E0[1] (V): 0.2
reaction[2]: D + e = F with E0[2] (V): 0.28
Homogeneous chemical reactions:
reaction[1]: B + C = F with Keq[1]: 3E+006
reaction[2]: A + C = D with Keq[2]: 1.3338E+005 (TSR)



Scheme S2: *Square scheme mechanism*

I-4- UV-Visible spectroscopy: All spectra were recorded on a computer-controlled Lambda 45-Perkin Elmer spectrophotometer. Spectroscopic measurements were performed in aqueous solutions containing 0.1 M KCl, 10 mM MOPS pH=7.2 adjusted with KOH. The affinity constant of chelator **3** for Ca^{2+} was obtained by titration in pH and buffered Ca^{2+} (with 10 mM EGTA as calcium buffer [2,3]) aqueous media and data processed in Hill plot. The latter represents $\log[(A-A_{min})/(A_{max}-A)]$ vs. $\log[Ca^{2+}]_{free}$ at two different wavelengths (266 and 326 nm). A_{min} is the absorbance of the free ligand **3** ($[Ca^{2+}]_{free}$= 0), A_{max} the absorbance of the Ca^{2+} complex ($[Ca^{2+}]_{free}$= 39µM), and A the absorbance at a given free Ca^{2+} concentration.
Affinity constant of **3** for Mg^{2+} was obtained by direct titration with magnesium chloride in buffered (in pH) aqueous solutions. Data were fitted to the Benesi-Hildebrand equation ($\Delta A = l.\Delta\varepsilon.[L].K_a.[M^{2+}]/(1+K_a.[M^{2+}])$, were l: optical path, $\Delta\varepsilon=\varepsilon_{ML}-\varepsilon_L$ as the difference in extinction coefficients between the free ligand L and the complex ML, $\Delta A=A-A_0$ as the change in absorbance on gradual addition of M^{2+} and $K_a=./K_d^{M2+}$ as the affinity constant).

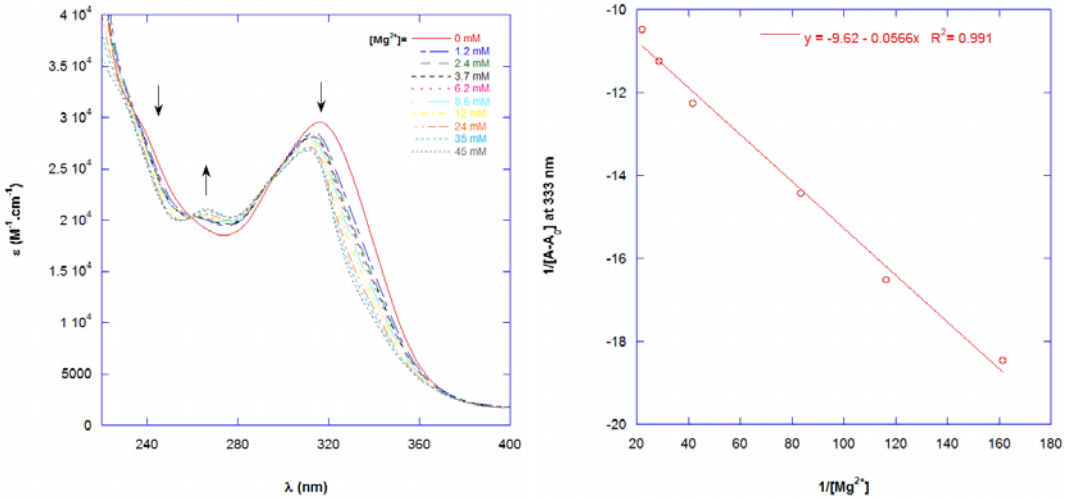


Figure S5: *UV-Vis Studies: Magnesium effect on compound* ***3.***

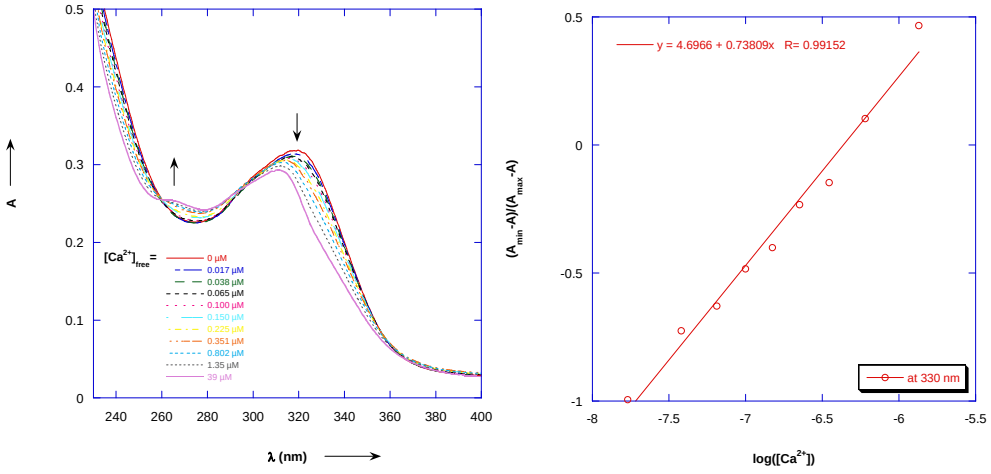
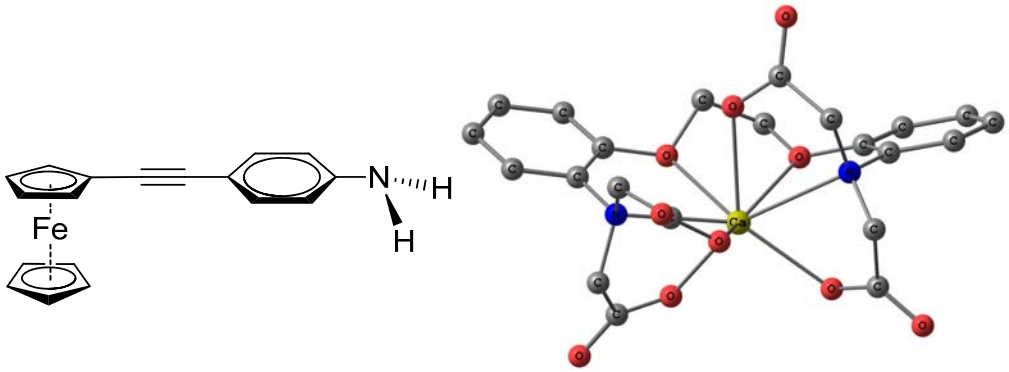


Figure S6: *UV-Vis Studies: calcium effect on the oxidized form of compound* ***3.***

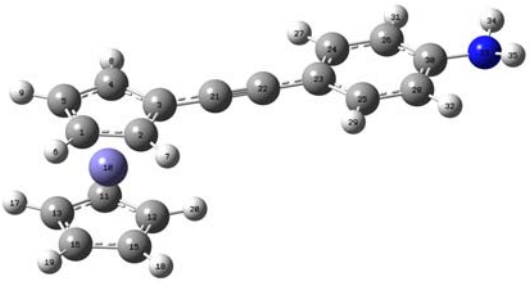
II. Computational details



Scheme S3: *model systems for the ligand (on left) and the complex (on the right)*

All calculations were carried out using the Gaussian 03 set of programs [4] with the B3PW91 functional[5] the 6-31+G* basis set for all non metallic atoms (H, C, O, N, Ca) and LANL2DZ [6] basis set with pseudopotentials for iron. The structures were optimized without symmetry constraint and frequency calculations performed.

II-1- Optimized geometry, three lower frequencies for neutral ferrocenyl ligand



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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4	6	0	2.195501	-0.028343	0.693752
5	6	0	1.346839	-0.033474	-0.449681
6	1	0	-0.888270	-0.056450	-0.629468
7	1	0	-0.868699	-0.023260	2.074377
8	1	0	3.277400	-0.055419	0.696122
9	1	0	1.674389	-0.076664	-1.480886
10	26	0	0.973624	-1.674523	0.729470
11	6	0	2.183802	-3.331865	0.739819
12	6	0	1.356570	-3.313196	1.902963
13	6	0	1.332680	-3.346765	-0.407359
14	1	0	3.266085	-3.298886	0.729270
15	6	0	-0.005569	-3.316063	1.476032
16	6	0	-0.020713	-3.337170	0.047710
17	1	0	1.656979	-3.329279	-1.440411
18	1	0	-0.873735	-3.270107	2.121617
19	1	0	-0.902852	-3.311916	-0.580059
20	1	0	1.701883	-3.243560	2.927044
21	6	0	1.812868	0.040532	3.213853
22	6	0	2.197035	0.096097	4.368982
23	6	0	2.642016	0.170740	5.717739
24	6	0	4.014095	0.157166	6.035298
25	6	0	1.724314	0.262497	6.782168
26	6	0	4.447857	0.233156	7.351410
27	1	0	4.742811	0.088571	5.232071
28	6	0	2.155925	0.338656	8.098875
29	1	0	0.659936	0.276447	6.563591

30	6	0	3.526723	0.327068	8.408613
31	1	0	5.514485	0.214991	7.567973
32	1	0	1.423977	0.403206	8.901985
33	7	0	3.958933	0.345856	9.731075
34	1	0	4.905446	0.670591	9.879662
35	1	0	3.312821	0.745453	10.399079

	1			2			3		
	A			A			A		
Frequencies --	18.5137			26.8140			31.6975		
Red. masses --	3.6948			6.0460			3.5927		
Frc consts --	0.0007			0.0026			0.0021		
IR Inten --	0.4836			0.8150			0.1086		
Atom AN	X	Y	Z	X	Y	Z	X	Y	Z
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3 6	-0.04	-0.01	0.02	-0.03	0.10	-0.07	0.04	0.00	-0.01
4 6	-0.05	0.03	0.02	-0.04	0.05	-0.08	0.01	0.00	-0.04
5 6	-0.06	0.03	0.02	-0.04	-0.05	-0.07	-0.02	0.00	-0.01
6 1	-0.06	-0.03	0.04	-0.04	-0.12	-0.06	-0.03	0.00	0.05
7 1	-0.04	-0.08	0.04	-0.03	0.05	-0.07	0.04	0.01	0.05
8 1	-0.05	0.07	0.01	-0.03	0.08	-0.08	0.01	0.00	-0.07
9 1	-0.06	0.06	0.02	-0.04	-0.10	-0.07	-0.05	-0.01	-0.02
10 26	0.00	0.00	-0.01	0.01	0.02	0.04	0.01	0.00	0.00
11 6	0.05	0.03	-0.02	0.07	0.06	0.18	0.00	0.00	-0.19
12 6	0.04	-0.01	-0.03	0.05	0.12	0.17	0.19	0.00	-0.06
13 6	0.06	0.03	-0.03	0.08	-0.06	0.17	-0.18	0.00	-0.06
14 1	0.05	0.06	-0.01	0.06	0.09	0.19	0.00	-0.01	-0.37
15 6	0.04	-0.04	-0.05	0.06	0.05	0.15	0.12	0.00	0.16
16 6	0.06	-0.02	-0.05	0.07	-0.06	0.15	-0.11	0.00	0.16
17 1	0.07	0.06	-0.03	0.09	-0.13	0.17	-0.35	-0.01	-0.11
18 1	0.03	-0.08	-0.06	0.05	0.07	0.14	0.23	0.01	0.30
19 1	0.06	-0.03	-0.06	0.08	-0.14	0.14	-0.21	0.00	0.31
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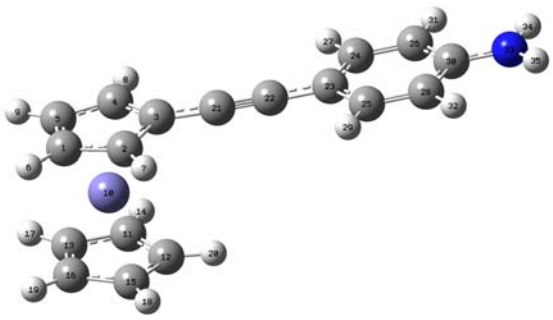
35 1	0.08	0.19	-0.03	0.00	-0.27	-0.04	-0.11	0.01	0.01

II-2- Optimized geometry, three lower frequencies for oxidized ferrocenyl ligand



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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5	6	0	0.800091	0.091162	-0.279617
6	1	0	-1.376121	-0.457203	-0.347123
7	1	0	-1.151094	-0.704150	2.333486
8	1	0	2.753949	0.446144	0.765543
9	1	0	1.048547	0.255241	-1.320779
10	26	0	0.911853	-1.745591	0.637263
11	6	0	2.474760	-3.143768	0.381698
12	6	0	1.699691	-3.549270	1.502843
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14	1	0	3.526842	-2.887427	0.394961
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21	6	0	1.494716	-0.046566	3.330836
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27	1	0	4.460050	0.631958	5.147039
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32	1	0	1.505830	-0.332347	9.026376
33	7	0	4.005490	0.297258	9.653747
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35	1	0	3.421184	0.142677	10.461210

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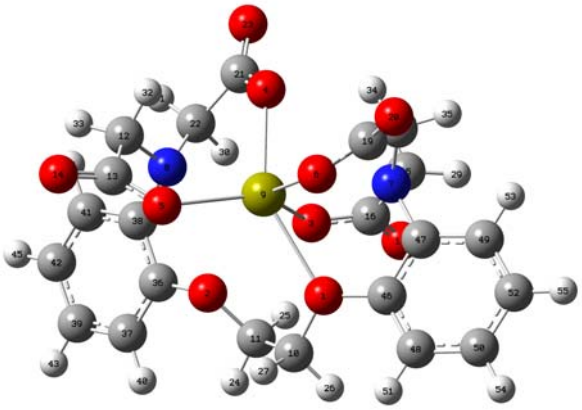
	A			A			A		
Frequencies --	18.1145			24.6042			37.0266		
Red. masses --	3.5018			6.2183			3.7955		
Frc consts --	0.0007			0.0022			0.0031		
IR Inten --	0.0172			0.6846			0.2290		
Atom AN	X	Y	Z	X	Y	Z	X	Y	Z
1 6	-0.02	-0.01	0.00	-0.01	-0.03	-0.09	-0.02	-0.02	0.00
2 6	-0.02	-0.01	0.00	-0.05	0.06	-0.08	-0.04	-0.04	0.00
3 6	-0.03	0.00	0.01	-0.06	0.10	-0.07	-0.06	-0.02	0.02
4 6	-0.02	0.00	0.01	-0.04	0.05	-0.06	-0.04	0.01	0.04
5 6	-0.02	0.00	0.01	-0.01	-0.03	-0.08	-0.02	0.01	0.02
6 1	-0.02	-0.01	0.00	0.01	-0.08	-0.11	-0.01	-0.03	-0.02
7 1	-0.02	-0.01	0.00	-0.06	0.08	-0.08	-0.05	-0.06	-0.02
8 1	-0.02	0.01	0.01	-0.04	0.07	-0.05	-0.05	0.03	0.06

9	1	-0.02	0.00	0.01	0.02	-0.09	-0.08	-0.01	0.03	0.03
10	26	-0.01	0.00	0.01	0.01	0.02	0.04	0.00	0.00	0.00
11	6	0.00	0.01	0.21	0.06	0.05	0.16	0.05	0.05	-0.02
12	6	-0.19	-0.04	0.07	0.06	0.12	0.19	0.06	0.02	-0.02
13	6	0.19	0.05	0.07	0.06	-0.06	0.15	0.04	0.04	-0.02
14	1	0.00	0.00	0.40	0.05	0.08	0.15	0.04	0.08	-0.02
15	6	-0.11	-0.03	-0.17	0.07	0.05	0.20	0.07	-0.02	-0.02
16	6	0.12	0.02	-0.16	0.07	-0.07	0.18	0.05	-0.01	-0.02
17	1	0.35	0.08	0.13	0.06	-0.14	0.13	0.03	0.06	-0.02
18	1	-0.22	-0.05	-0.31	0.08	0.07	0.21	0.08	-0.05	-0.02
19	1	0.22	0.05	-0.31	0.08	-0.14	0.17	0.06	-0.03	-0.02
20	1	-0.36	-0.08	0.13	0.06	0.21	0.20	0.06	0.02	-0.02
21	6	-0.03	0.00	0.01	-0.08	0.13	-0.06	-0.07	-0.02	0.03
22	6	-0.02	0.00	0.00	-0.07	0.11	-0.06	-0.06	-0.02	0.02
23	6	0.00	0.00	0.00	-0.05	0.05	-0.07	-0.04	-0.01	0.02
24	6	0.00	0.02	-0.02	-0.04	0.01	-0.08	0.02	-0.22	-0.03
25	6	0.02	-0.01	0.01	-0.03	0.00	-0.07	-0.07	0.20	0.05
26	6	0.02	0.02	-0.03	-0.01	-0.08	-0.08	0.05	-0.22	-0.04
27	1	-0.02	0.02	-0.03	-0.06	0.05	-0.08	0.05	-0.39	-0.05
28	6	0.04	-0.01	0.00	0.00	-0.09	-0.07	-0.04	0.22	0.03
29	1	0.02	-0.02	0.02	-0.04	0.03	-0.06	-0.11	0.37	0.08
30	6	0.04	0.00	-0.02	0.01	-0.14	-0.08	0.02	0.01	-0.01
31	1	0.02	0.02	-0.04	0.00	-0.11	-0.09	0.10	-0.38	-0.08
32	1	0.05	-0.02	0.01	0.01	-0.13	-0.07	-0.06	0.39	0.06
33	7	0.05	0.00	-0.03	0.04	-0.24	-0.09	0.05	0.02	-0.02
34	1	0.05	0.01	-0.04	0.05	-0.26	-0.09	0.10	-0.13	-0.06
35	1	0.07	-0.01	-0.02	0.05	-0.26	-0.09	0.04	0.18	0.00

II-3- Optimized geometry, three lower frequencies for complex ***BAPTA-Ca***



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	1.425601	1.462124	-0.751181
2	8	0	-1.360476	1.665167	-0.560232
3	8	0	0.101972	0.573318	1.682056
4	8	0	-0.444512	-2.560242	0.761038
5	8	0	-1.537635	-0.708687	-2.396351
6	8	0	1.846058	-1.524126	-1.835989
7	7	0	2.425309	-0.717381	0.710946
8	7	0	-2.546696	-0.829450	0.194044
9	20	0	0.009285	-0.610159	-0.547147
10	6	0	0.749339	2.743381	-0.885768
11	6	0	-0.499569	2.728776	-0.038515
12	6	0	-3.049470	-1.749739	-0.863272
13	6	0	-2.709721	-1.245586	-2.287968
14	8	0	-3.567082	-1.446797	-3.194742
15	6	0	2.128584	-0.601980	2.160793
16	6	0	1.135299	0.536160	2.467291
17	8	0	1.379473	1.304674	3.441816
18	6	0	2.828774	-2.077299	0.269801
19	6	0	2.805917	-2.187832	-1.274440
20	8	0	3.675672	-2.924230	-1.819254

21	6	0	-1.423021	-2.615317	1.609245
22	6	0	-2.455214	-1.461969	1.536834
23	8	0	-1.607219	-3.467673	2.522525
24	1	0	-0.989898	3.706060	-0.121851
25	1	0	-0.271558	2.461776	1.000861
26	1	0	1.403846	3.548964	-0.533393
27	1	0	0.510511	2.890725	-1.944370
28	1	0	1.649138	-1.543203	2.453389
29	1	0	3.039460	-0.459782	2.762569
30	1	0	-2.115008	-0.687120	2.233301
31	1	0	-3.423741	-1.856604	1.883762
32	1	0	-2.538050	-2.707646	-0.712582
33	1	0	-4.134686	-1.916583	-0.786231
34	1	0	2.073173	-2.766388	0.669745
35	1	0	3.819427	-2.381136	0.642032
36	6	0	-2.691005	1.640036	-0.146608
37	6	0	-3.451819	2.817728	-0.133509
38	6	0	-3.283611	0.412666	0.213122
39	6	0	-4.791131	2.801671	0.252685
40	1	0	-2.997719	3.751452	-0.447270
41	6	0	-4.635386	0.424042	0.590882
42	6	0	-5.389949	1.596412	0.623670
43	1	0	-5.361657	3.726860	0.254562
44	1	0	-5.091697	-0.521220	0.867758
45	1	0	-6.432850	1.567466	0.927341
46	6	0	2.793950	1.413853	-0.515177
47	6	0	3.297310	0.318598	0.216581
48	6	0	3.654396	2.395991	-1.017438
49	6	0	4.679481	0.265633	0.435528
50	6	0	5.028046	2.318631	-0.778243
51	1	0	3.257802	3.201193	-1.626704
52	6	0	5.545168	1.250331	-0.046445
53	1	0	5.075126	-0.576393	0.993743
54	1	0	5.686581	3.083917	-1.180458
55	1	0	6.612783	1.175310	0.140026

		1			2			3	
		A			A			A	
Frequencies --		21.7692			25.9881			46.4704	
Red. masses --		7.8550			5.3167			8.7772	
Frc consts --		0.0022			0.0021			0.0112	
IR Inten --		0.3046			0.2899			2.8491	
Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	8	-0.02	-0.01	0.04	-0.01	0.05	0.15	-0.01	-0.04	-0.08
2	8	-0.02	0.00	0.04	0.01	0.02	0.08	0.00	-0.05	0.06
3	8	-0.05	-0.01	0.01	0.00	-0.07	0.08	0.15	0.06	0.06
4	8	-0.01	-0.05	-0.04	-0.01	0.01	0.02	-0.06	0.01	0.12
5	8	0.07	0.06	-0.02	0.01	0.05	0.02	0.05	0.00	0.06
6	8	0.04	-0.07	0.09	-0.02	0.02	0.01	-0.03	-0.03	0.04
7	7	0.02	0.04	0.06	0.03	-0.01	0.00	0.07	0.02	0.01
8	7	-0.01	-0.02	-0.04	-0.01	0.00	0.00	-0.05	0.00	0.02
9	20	0.01	-0.01	0.03	0.00	0.02	0.03	0.01	-0.02	0.10
10	6	-0.01	-0.01	0.01	0.00	0.07	0.23	-0.03	-0.05	-0.10
11	6	-0.01	0.01	0.01	-0.03	0.00	0.18	0.02	-0.03	-0.02
12	6	0.01	0.03	-0.10	0.03	-0.02	0.00	-0.02	0.01	-0.01
13	6	0.06	0.09	-0.07	0.03	-0.01	0.00	0.04	0.04	0.01
14	8	0.07	0.17	-0.10	0.05	-0.05	-0.01	0.06	0.08	-0.02
15	6	0.02	0.14	0.05	0.06	0.00	0.00	0.13	0.00	0.02
16	6	-0.02	0.12	-0.02	0.05	-0.01	0.02	0.10	-0.05	0.11
17	8	-0.02	0.24	-0.12	0.10	0.04	-0.04	0.03	-0.22	0.26
18	6	0.00	0.01	0.13	-0.01	-0.02	-0.01	0.10	0.04	-0.01
19	6	0.02	-0.06	0.14	-0.04	-0.01	-0.01	0.04	0.03	-0.01
20	8	0.01	-0.10	0.19	-0.06	-0.03	-0.03	0.07	0.10	-0.05
21	6	-0.05	-0.09	-0.09	-0.01	0.03	0.03	-0.14	-0.04	0.02
22	6	-0.05	-0.09	-0.07	-0.02	0.02	0.01	-0.11	-0.01	0.02
23	8	-0.09	-0.14	-0.14	0.01	0.06	0.06	-0.26	-0.12	-0.07
24	1	-0.01	0.01	-0.02	-0.04	0.00	0.23	0.01	-0.03	-0.02
25	1	-0.02	0.05	0.02	-0.06	-0.07	0.17	0.08	0.00	-0.03
26	1	-0.01	0.00	-0.01	0.00	0.03	0.33	-0.02	-0.03	-0.17
27	1	-0.02	-0.03	0.01	0.04	0.17	0.23	-0.10	-0.10	-0.09
28	1	0.07	0.14	0.12	0.08	0.00	0.02	0.17	-0.03	0.03

29	1	0.02	0.21	0.03	0.08	0.02	-0.02	0.15	0.01	-0.01
30	1	-0.07	-0.12	-0.02	-0.03	0.03	0.00	-0.11	-0.03	0.04
31	1	-0.06	-0.11	-0.12	-0.02	0.02	0.00	-0.13	0.01	-0.02
32	1	0.00	0.02	-0.13	0.06	0.00	0.00	-0.03	0.01	0.00
33	1	0.01	0.04	-0.14	0.04	-0.05	-0.02	-0.02	0.02	-0.05
34	1	-0.02	0.05	0.15	-0.02	0.00	0.00	0.15	0.00	0.03
35	1	-0.01	0.01	0.16	-0.01	-0.05	-0.03	0.13	0.08	-0.05
36	6	-0.01	-0.01	0.07	-0.02	0.00	-0.01	-0.01	0.00	0.01
37	6	0.00	0.00	0.15	-0.04	-0.01	-0.07	0.01	0.01	-0.03
38	6	-0.01	-0.02	0.01	-0.02	-0.01	-0.04	-0.04	0.01	-0.01
39	6	0.00	-0.02	0.16	-0.06	-0.03	-0.16	-0.01	0.03	-0.09
40	1	-0.01	0.01	0.20	-0.03	-0.01	-0.06	0.03	0.00	-0.01
41	6	0.00	-0.04	0.02	-0.05	-0.03	-0.12	-0.06	0.03	-0.07
42	6	0.00	-0.04	0.10	-0.07	-0.04	-0.18	-0.04	0.04	-0.11
43	1	0.01	-0.02	0.23	-0.08	-0.04	-0.21	0.00	0.04	-0.12
44	1	0.00	-0.06	-0.02	-0.05	-0.03	-0.14	-0.09	0.03	-0.09
45	1	0.00	-0.06	0.11	-0.09	-0.05	-0.25	-0.06	0.06	-0.16
46	6	-0.01	-0.01	-0.02	0.00	0.02	0.05	-0.01	-0.01	-0.09
47	6	0.01	0.01	-0.02	0.03	-0.02	-0.03	0.02	0.05	-0.03
48	6	-0.02	-0.03	-0.10	-0.02	0.03	0.03	-0.04	-0.02	-0.16
49	6	0.02	-0.01	-0.09	0.04	-0.07	-0.15	0.03	0.11	-0.03
50	6	-0.01	-0.04	-0.16	0.00	-0.02	-0.08	-0.04	0.04	-0.16
51	1	-0.04	-0.04	-0.10	-0.05	0.06	0.10	-0.06	-0.07	-0.21
52	6	0.01	-0.03	-0.16	0.03	-0.07	-0.18	0.00	0.10	-0.09
53	1	0.04	0.00	-0.08	0.07	-0.11	-0.22	0.05	0.15	0.02
54	1	-0.02	-0.07	-0.22	-0.01	-0.02	-0.10	-0.06	0.03	-0.22
55	1	0.02	-0.05	-0.22	0.04	-0.11	-0.27	0.00	0.15	-0.08

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