Supplementary Material (ESI) for *Chemical Communications*

Supplementary Information

An organopalladium chromogenic chemodosimeter for the selective naked-eye detection of Hg^{2+} and $MeHg^{+}$ in water-ethanol 1:1 mixture.

Olga del Campo, Arancha Carbayo, José V. Cuevas, Asunción Muñoz, Gabriel García-Herbosa,* Daniel Moreno, Eduardo Ballesteros, Sara Basurto, Teresa Gómez and Tomás Torroba*[a]

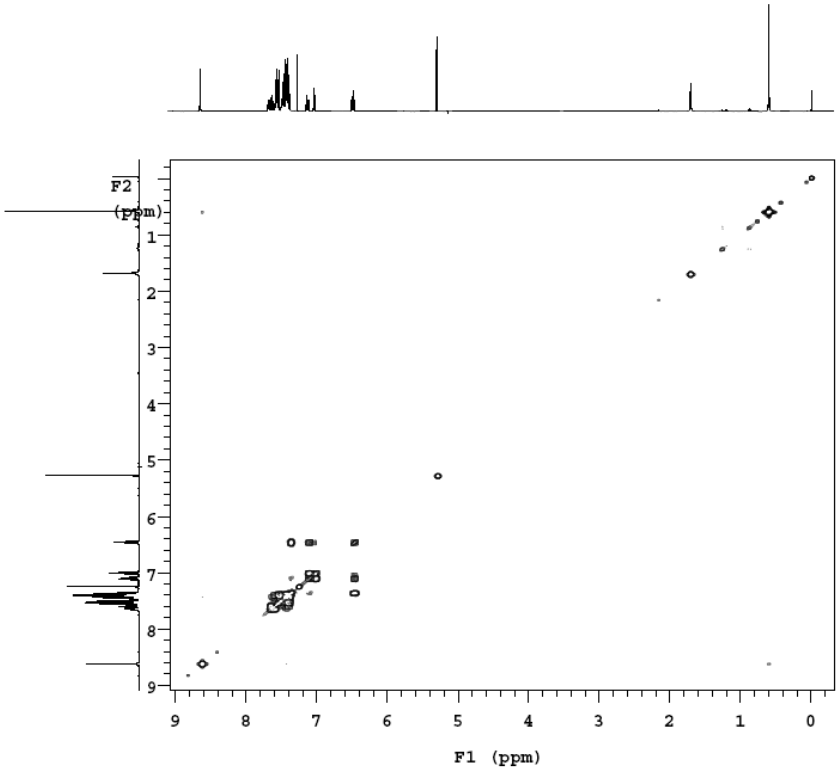
Departamento de Química, Facultad de Ciencias, Universidad de Burgos, 09001 Burgos, Spain. Fax: +34947258831; Tel: +34947258088; E-mail: ttorroba@ubu.es; gherbosa@ubu.es

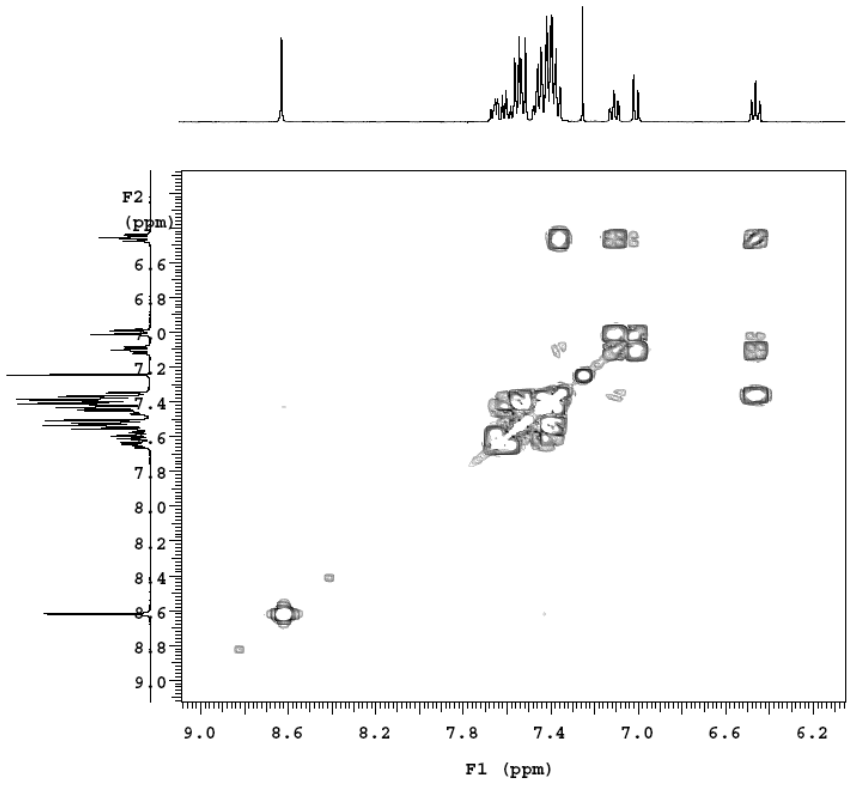
Contents:

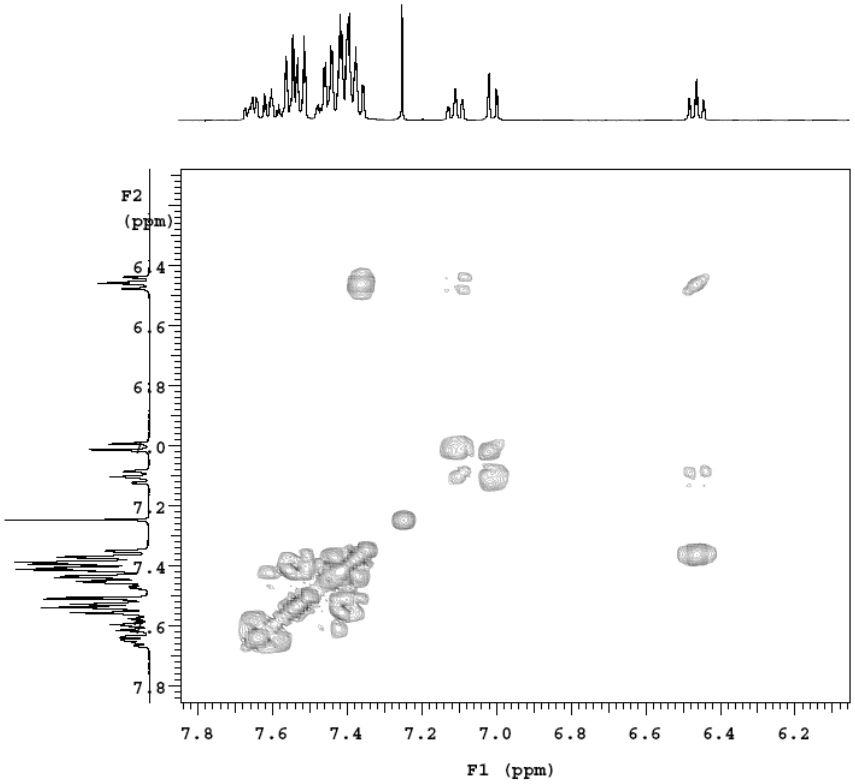
Materials and methods: The reactions performed with air sensitive reagents were conducted under dry nitrogen. The solvents were previously distilled under nitrogen over calcium hydride or sodium filaments. Infrared spectra were registered in a Nicolet Impact 410 spectrometerin potassium bromide tablets. NMR spectra were recorded in Varian Mercury-300 and Varian Unity Inova-400 machines, in DMSO-d_6, $CDCl_3$, CD_3CN, CD_3OD. Chemical shifts are reported in ppm with respect to residual solvent protons, coupling constants ($J_{X\text{-}X'}$) are reported in Hz. Elemental analyses of C, H and N were taken in a Leco CHNS-932. X-ray diffraction was performed with a Bruker single crystal X-ray diffractometer, area detector Smart Apex CCD, X-ray generator X Kristalloflex K760-80. Structural resolution and refinement of structures were performed with the Shelxtl V5 program. Quantitative measures were performed with a Varian, Cary Eclipse 300 UV spectrophotometer. As a general procedure, to a 5000 µl solution of complex, the corresponding amount (µL) of solution of the corresponding salt (5×10^{-2} M, 5×10^{-3} M, 5×10^{-4} M solutions) was added, using the minor amount of solvent. General procedure for the ^{1}H NMR titrations: a 0.007733 M solution of the compound under study was prepared (3 mg in 0.75 ml) in the NMR tube (Norell, 509-UP, 178 mm, ultra precision). For the NMR titrations performed with Hg^{2+} solely, aliquots of 20µl of a 2.9×10^{-5} M solution of Hg^{2+} were employed. For the reversed titrations, aliquots of 10 µl of dithiol (0.145 M solution) and of Hg^{2+} (0.290 M solution) were employed. Normal titrations were performed with the Varian Mercury-300 and reversed titrations were performed with the Varian Unity Inova-400 machines.

[Pd{2-[(2-diphenylphosphanylbenzylidene)(*o*-phenol)amine}ClMe] (2). [PdClMe(cod)] (0.130 g, 4.90 mmol) and ligand **1** (0.188 g, 4.92 mmol) were disolved in dichlorometane (15 mL) and stirred for 1 hour at room temperature. Then the solvent was evaporated, the residue was filtered under reduced pressure and washed with ether. A yellow solid (0.223 g, 4.15 mmol, 85%) was obtained. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.71 (d, 3H, $J_{H\text{-}P}$= 2.7 Hz, Pd-CH_3), 6.79 (br, -OH), 7.14 (m, 2H), 7.19 (m, 1H), 7.46 (m, 10H, Ph_2), 7.54 (m, 3H), 7.65 (m, 2H), 8.31 (br, 1H, HCN); ^{31}P NMR (400 MHz, $CDCl_3$) δ 39.38; IR (KBr) $\tilde{\nu}$ = 1622 (C=N), 3606 cm^{-1} (OH); elemental analysis calcd (%) for $C_{26}H_{23}ClNOPPd$: C, 58.01; H, 4.31; N, 2.60; found: C, 57.84; H, 4.47; N, 2.59.

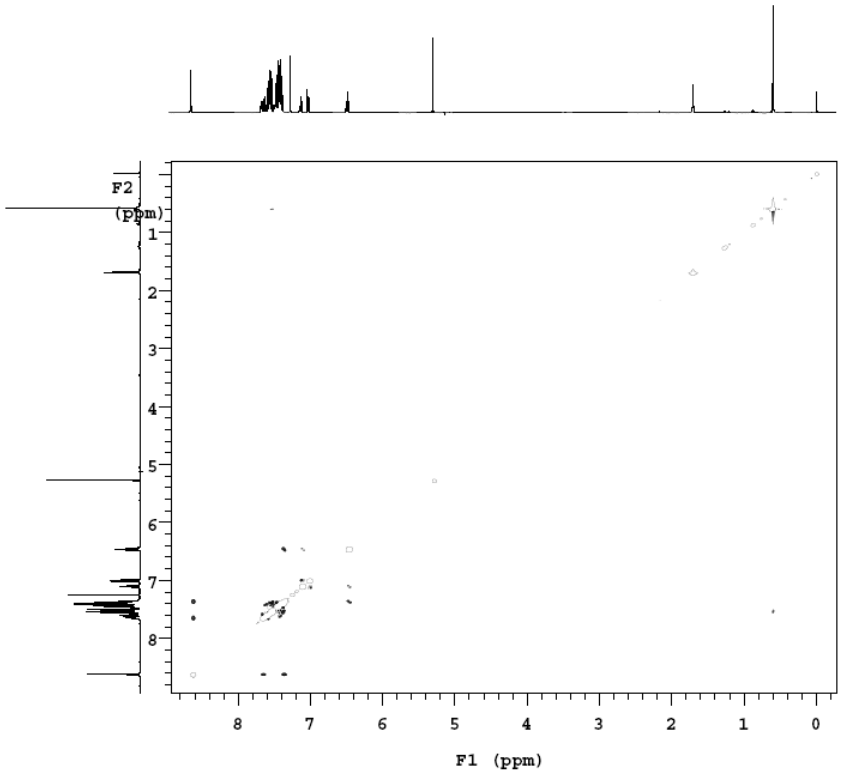
[Pd{2-[(2-diphenylphosphanylbenzylidene)(*o*-phenolate)amine}Me] (3): Complex **2** (0.101 g, 1.88 mmol) was dissolved in dichlorometane (10 mL). A 0.29 M solution of NaMeO in MeOH (0.65 mL, 1.89 mmol) was added under stirring. Then the solvent was evaporated and the residue dissolved in dichlorometane and filtered through Kieselgur. The filtrate was concentrated under reduced pressure and precipitated with hexane. The precipitate was filtered under reduced pressure and washed with ether. A red solid (0.058 g, 1.16 mmol, 62%) was obtained. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.60 (d, 3H, $J_{H\text{-}P}$ = 2.7 Hz, CH_3), 6.47 (ddd, 1H, $J_{H\text{-}H}$ = 1.4, 6.9 Hz), 7.02 (dd, 1H, $J_{H\text{-}H}$ = 1.5, 8.4 Hz), 7.12 (m, 1H), 7.43 (m, 9H), 7.55 (m, 4H), 7.61 (m, 1H), 7.66 (m, 1H), 8.63 (s, 1H, HCN); ^{31}P NMR (400 MHz, $CDCl_3$): δ = 41.35; IR (KBr): $\tilde{\nu}$ = 1099 (C-O), 1581 cm^{-1} (C=N); elemental analysis calcd (%) for $C_{25}H_{19}ClNOPPd$: C, 62.23; H, 4.42; N, 2.79; found: C, 62.09; H, 4.23; N, 2.72.

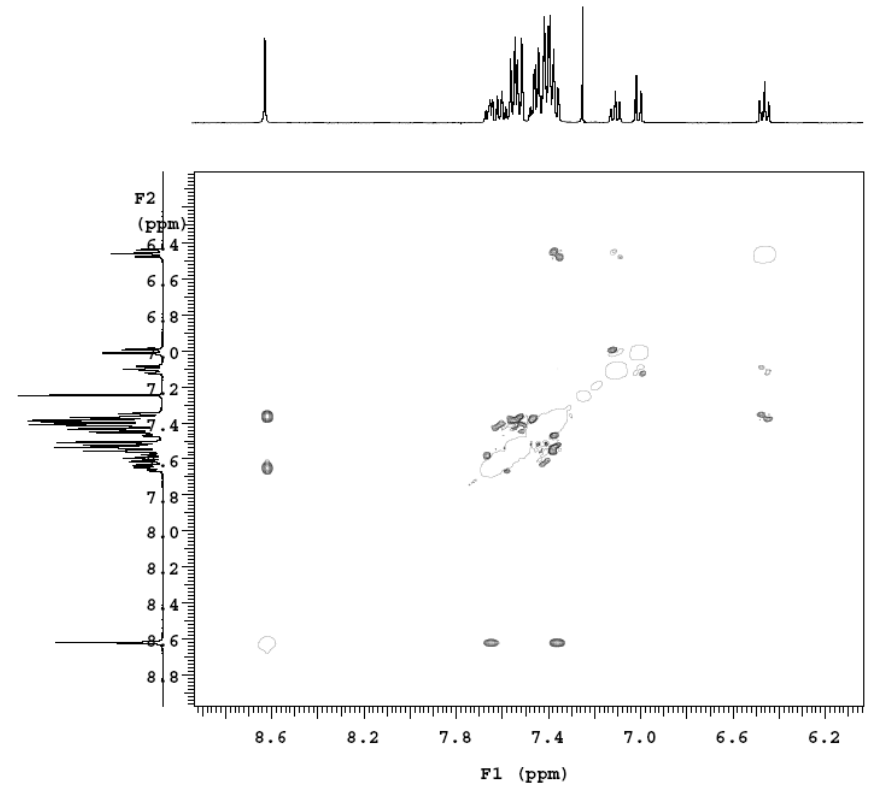


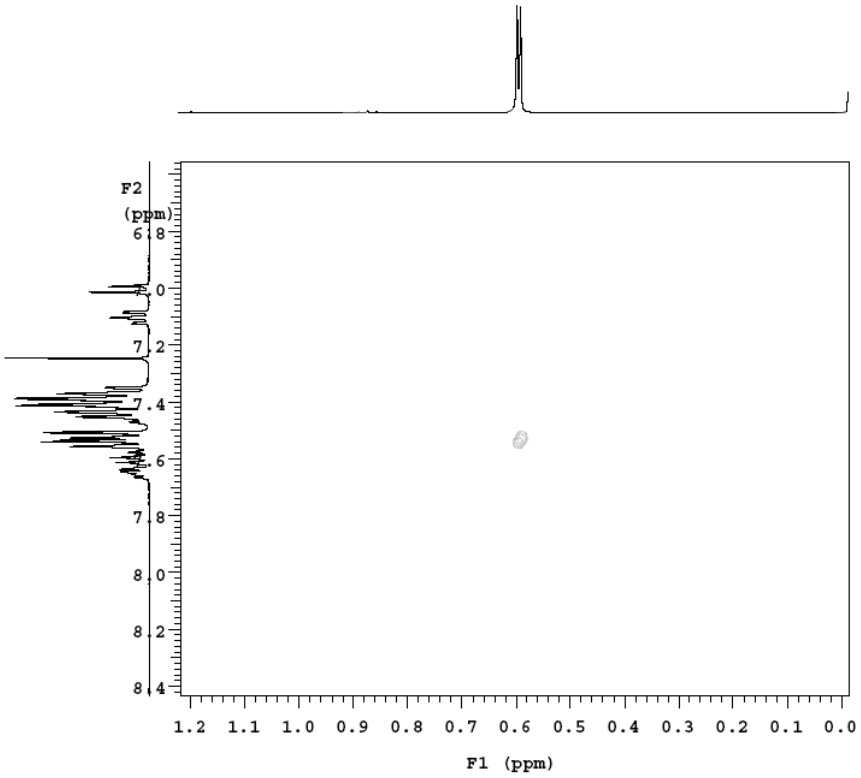




COSY spectra of **3**.



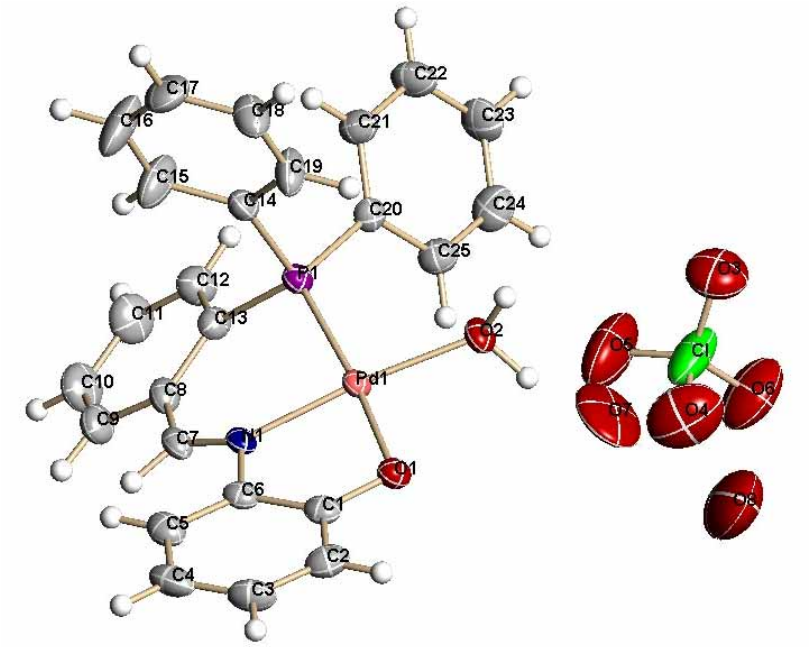




NOESY spectra of **3**.

[Pd{2-[(2-diphenylphosphanylbenzylidene)(*o*-phenolate)amine}H_2O] ClO_4 [4(H_2O)]ClO_4: Complex **3** (0.014 g, 0.028 mmol) was dissolved in MeOH (2 mL). A solution of $Hg(ClO_4)_2$ (0.013 g, 0.03 mmol) in MeOH (1 mL) was added dropwise and left for 12 days until red needles crystallized. Alternatively, complex **3** (0.015 g, 0.030 mmol) and $Hg(ClO_4)_2$ (0.016 g, 0.039 mmol) were dissolved in acetonitrile (3 mL) and left for 12 days until a purple solid was obtained. Single crystals, suitable for X-ray diffraction, were grown by slow diffusion in ether/methanol from a solution of the complex [**6**(H_2O)]ClO_4 in methanol. ^{1}H NMR (400 MHz, CD_3OD): δ = 8.89 (s, 1H), 8.22 (m, 1H), 7.94 (t, 1H, J_{H-H} = 5.3 Hz), 7.72 (m, 13H), 7.17 (t, 1H, J_{H-H} = 5.3 Hz), 6.82 (d, 1H, J_{H-H} = 6.5 Hz), 6.62 (t, 1H, J_{H-H} = 7.1 Hz); ^{1}H NMR (400 MHz, CD_3CN): δ = 8.89 (s, 1H), 8.27 (m, 1H), 7.95 (m, 1H), 7.70 (m, 13H), 7.05 (m, 1H), 6.60 (d, 1H, J_{H-H} = 4.2 Hz), 6.43 (d, 1H, J_{H-H} = 4.2 Hz); ^{31}P NMR (400 MHz, CD_3OD): δ = 32.26; elemental analysis calcd (%) for $C_{25}H_{21}ClNO_6PPd(2H_2O)$: C, 46.89; H, 3.94; N, 2.19; found: C, 46.68; H, 4.12; N, 2.06. Crystal data for [**3**(H_2O)]ClO_4, $C_{25}H_{21}ClNO_{7.50}PPd$, M = 628.25, monoclinic, C2/c, a = 18.345(2) Å, b = 22.576(3) Å, c = 14.7100(17) Å, α = 90º, β = 122.192(2)º, γ = 90º; V = 5155.7(11) Å^3, Z = 8, D_{calc} = 1.619 gcm^{-1}, μ(Mo-K$_\alpha$) = 0.933 mm^{-1}. Purple prism, (0.30 x 0.20 x 0.20) mm^3. 24303 measured reflections, 4531 independent (R_{int} = 0.0428), 3884 observed ($I > 2\sigma(I)$). R_1 = 0.0596, wR_2 = 0.1529 (all data). CCDC 675181.

Crystal Structure determination for compound [4(H_2O)]ClO_4 (CCDC 675181). A single crystal of **[4(H_2O)]ClO_4** was mounted on a glass fibre. X-ray measurements were made using a Bruker SMART CCD area-detector diffractometer with Mo-K$_\alpha$ radiation (λ = 0.71073 Å).[1] Intensities were integrated[2] from several series of exposures, each exposure covering 0.3° in ω, and the total data set being a sphere. Absorption corrections were applied, based on multiple and symmetry-equivalent measurements.[3] The structure was solved by direct methods and refined by least squares on weighted F^2 values for all reflections (see Table 1).[4] All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints. Hydrogen atoms **H(2A)** and **H(2B)** were located in the electron density difference map, assigned isotropic displacement parameters and refined with positional constraints. All other hydrogen atoms were constrained to ideal geometries and refined with fixed isotropic displacement parameters. Oxygen atoms **O7** and **O8** were refined without hydrogen atoms. Refinement proceeded smoothly to give the residuals shown in Table 1. Complex neutral-atom scattering factors were used.[5]

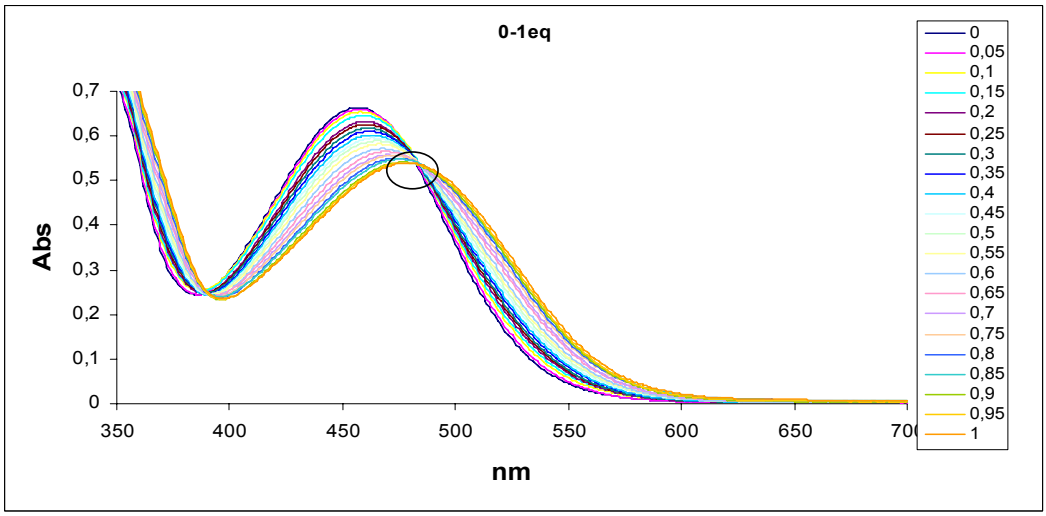


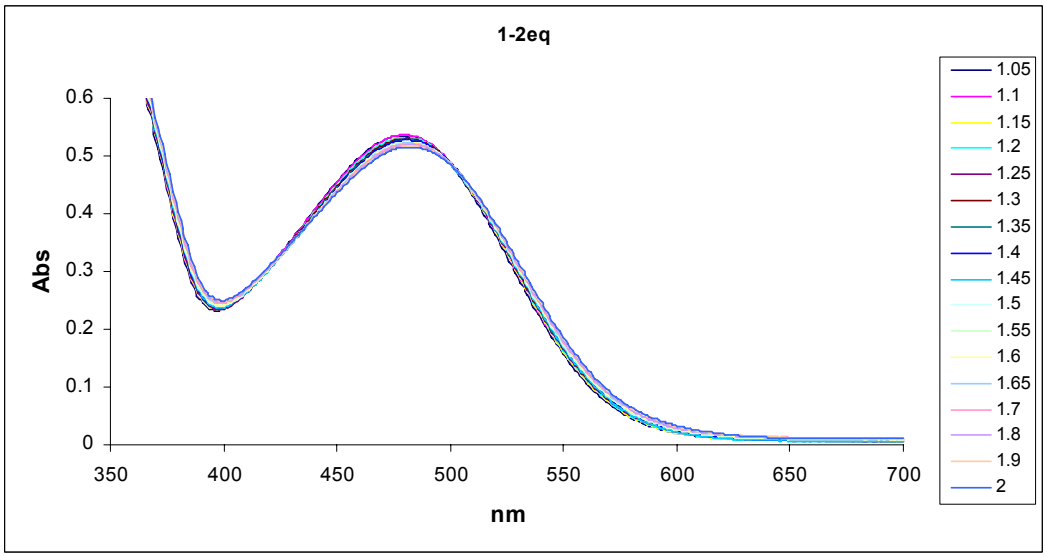
References

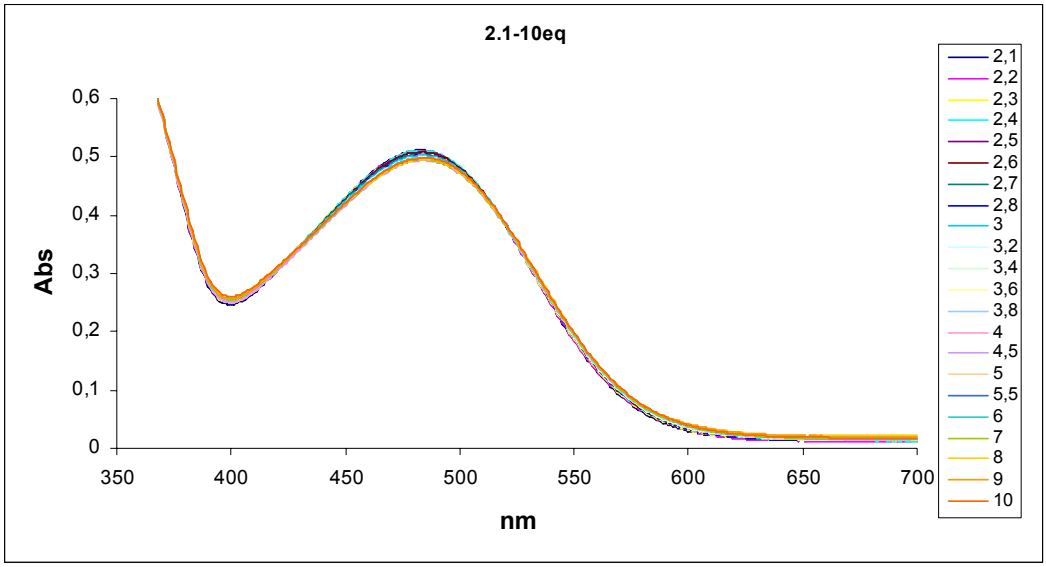
1. SMART diffractometer control software, Bruker Analytical X-ray Instruments Inc., Madison, WI, 2000.
2. SAINT integration software, Siemens Analytical X-ray Instruments Inc., Madison, WI, 2000.
3. G. M. Sheldrick. *SADABS: A program for absorption correction with the Siemens SMART system;* University of Göttingen: Germany, 2001.
4. *SHELXTL program system version 6.1;* Bruker Analytical X-ray Instruments Inc., Madison, WI, 1998.
5. *International Tables for Crystallography*, Kluwer, Dordrecht, 1992, vol. C.

COLORIMETRIC STUDIES

UV-visible titration of 3 with Hg^{2+} in EtOH/H_2O 1:1:

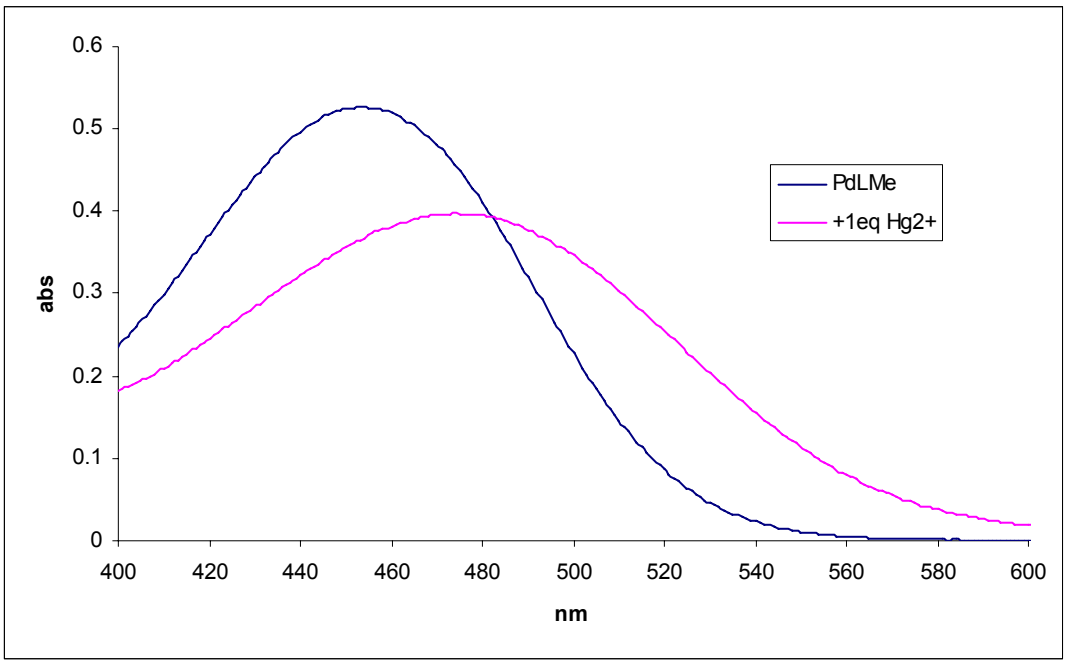




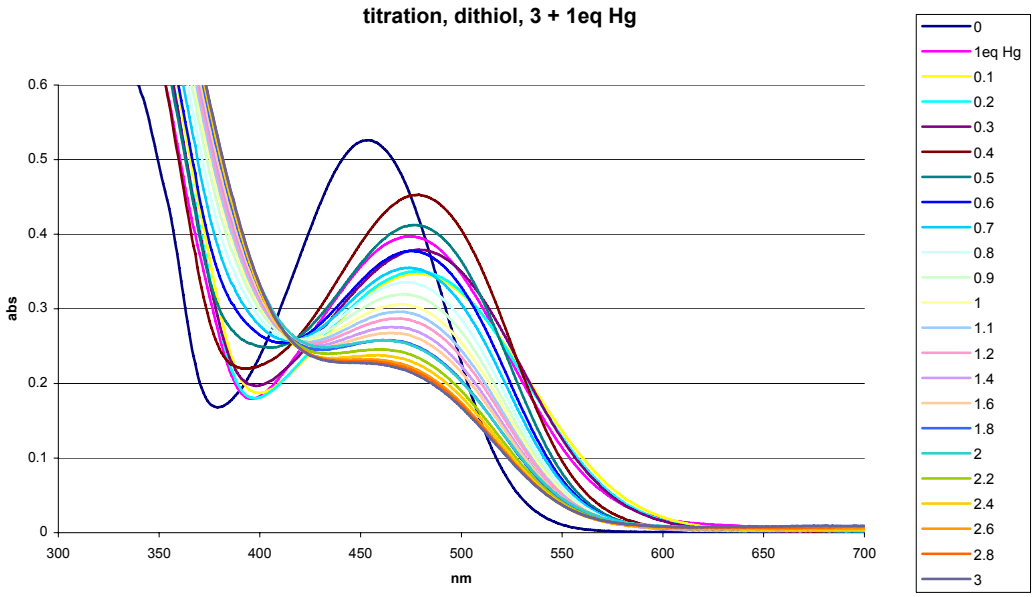


Isosbestic points in the titration curves of a 10^{-4} M solution of **3** in EtOH/H_2O 1:1 with Hg^{2+}.

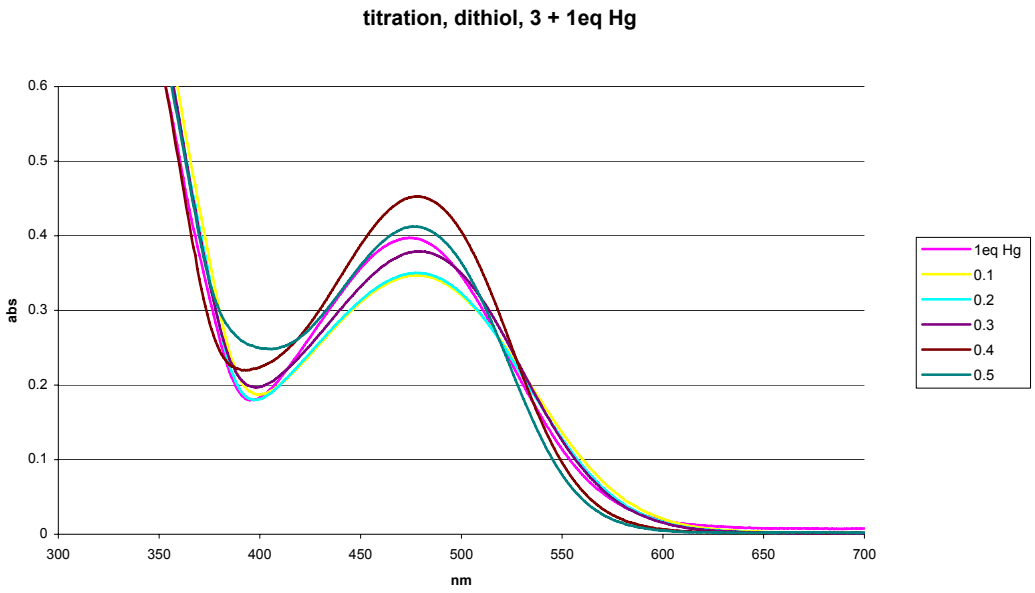
Repeated detection of Hg^{2+} in EtOH/H_2O 1:1:



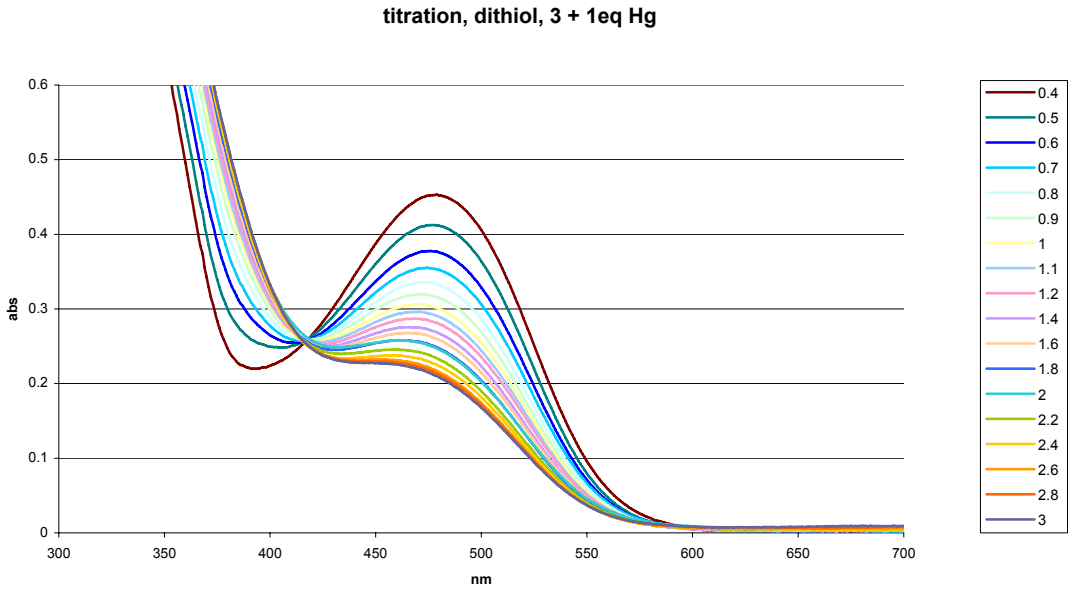
UV curves of the addition of 1 equiv Hg^{2+} to a 10^{-4} M solution of **3** (blue line) in EtOH/H_2O 1:1 with formation of **4** (purple line)



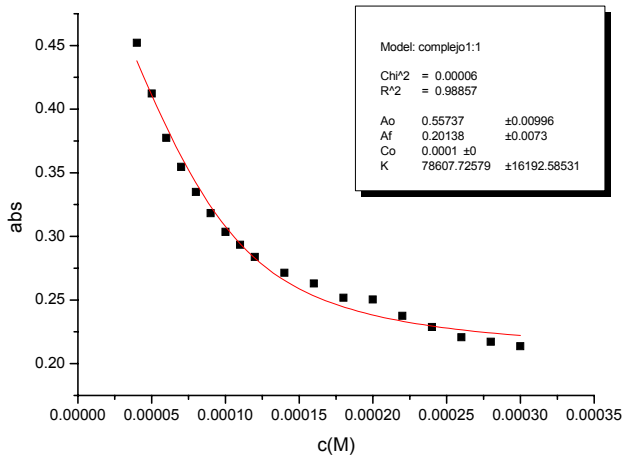
UV titration curves of a 10^{-4} M solution of **3**/Hg^{2+} in EtOH/H_2O 1:1 and **5**. The figures correspond to molar concentrations of **5**



First part of the UV titration curves of a 10^{-4} M solution of **3**/Hg^{2+} in EtOH/H_2O 1:1 and **5**. The figures correspond to molar concentrations of **5** (0.2 to 1 equiv **5**).

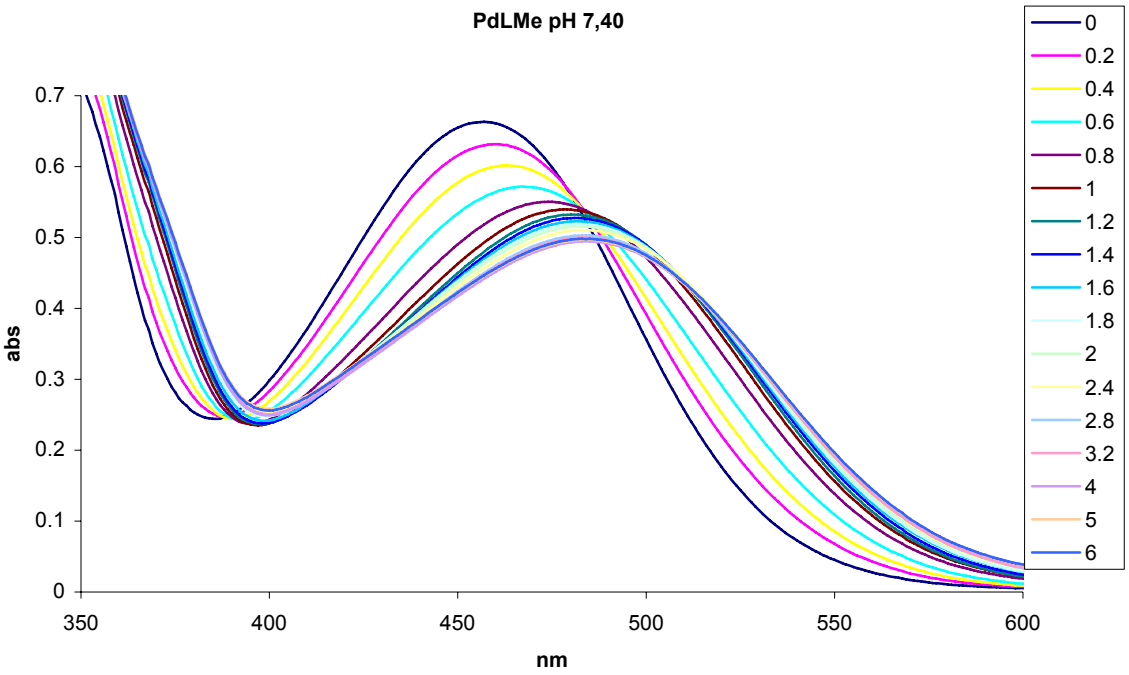


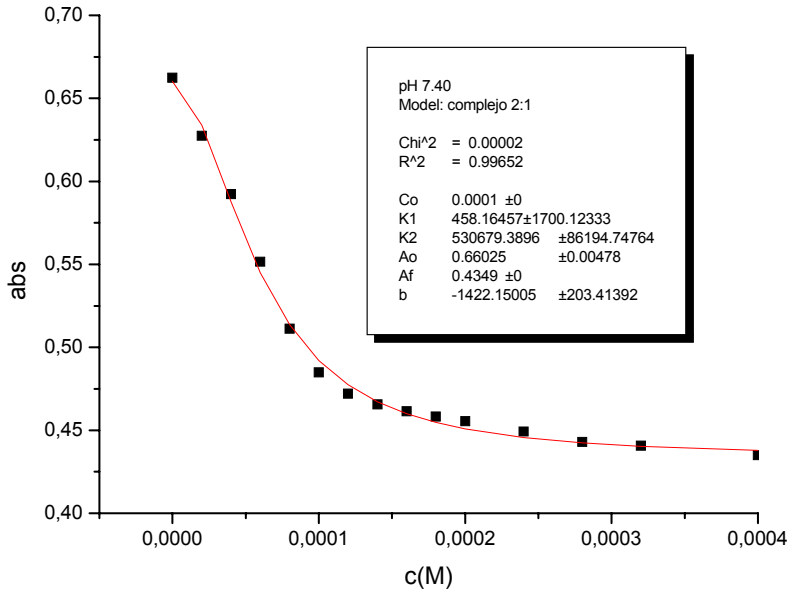
Second part of the UV titration curves of a 10^{-4} M solution of **3**/Hg^{2+} in EtOH/H_2O 1:1 and **5**. The figures correspond to molar concentrations of **5** (0.8 to 6 equiv **5**).



Titration profile from the UV titration curves of a 1:1 solution of **3**/Hg^{2+} in EtOH/H_2O and **5**. It was represented after addition of the first equivalent Hg^{2+} and adjusted to a 1:1 model, from which the titration constant was obtained: log K =4.90 ± 0.08

UV-visible titration of 3 with Hg^{2+} in EtOH/H_2O 1:1, pH = 7.40

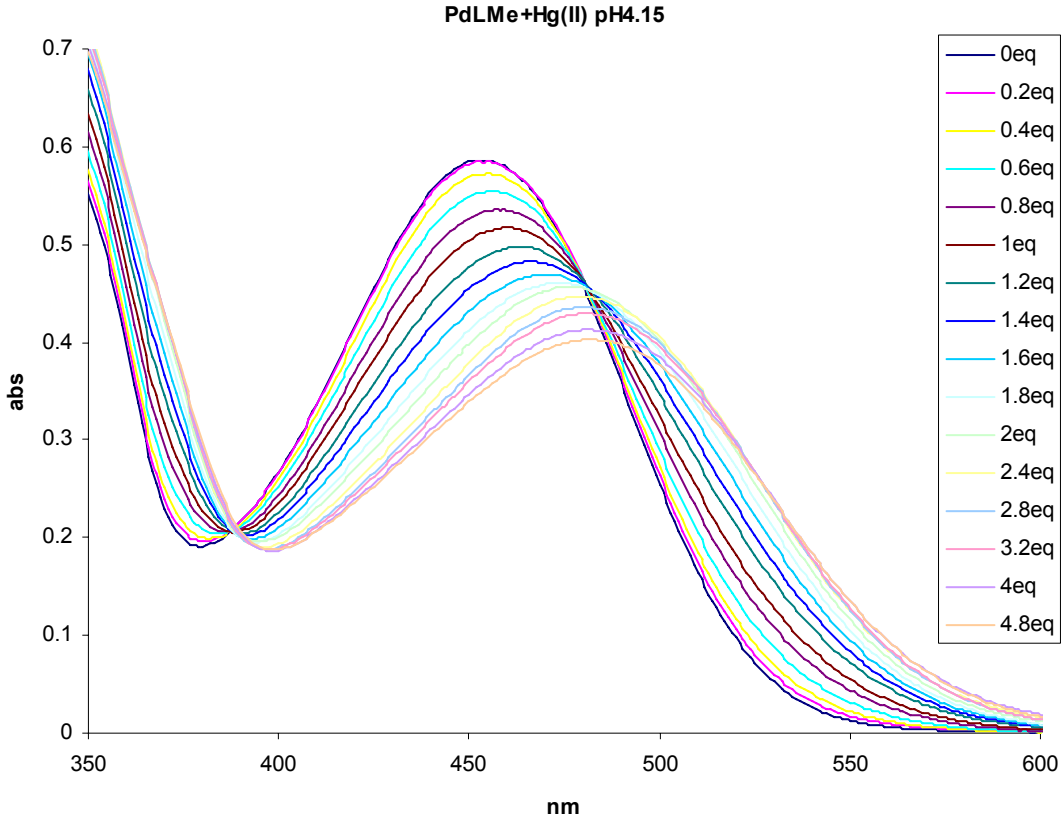


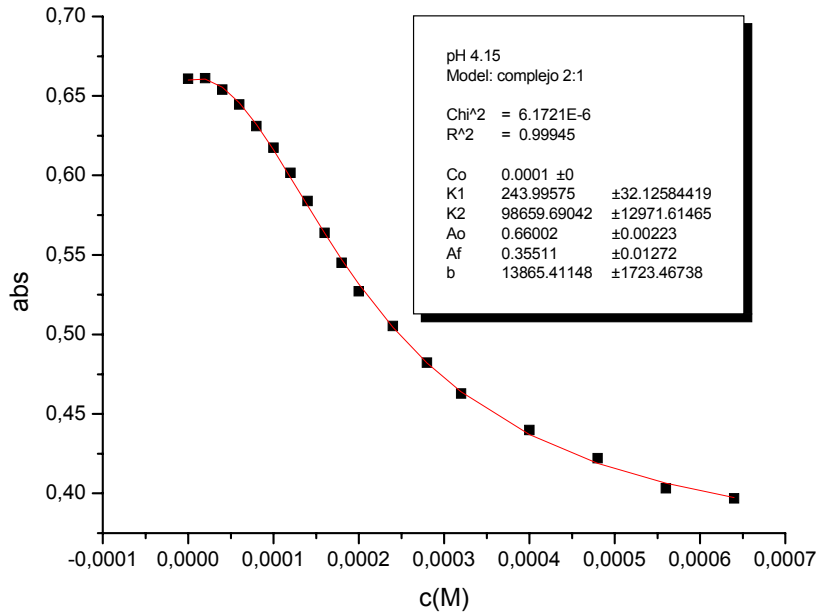


log K1= 2.661± 0.063

log K2= 5.725± 0.065

UV-visible titration of 3 with Hg^{2+} in EtOH/H_2O 1:1, pH = 4.15

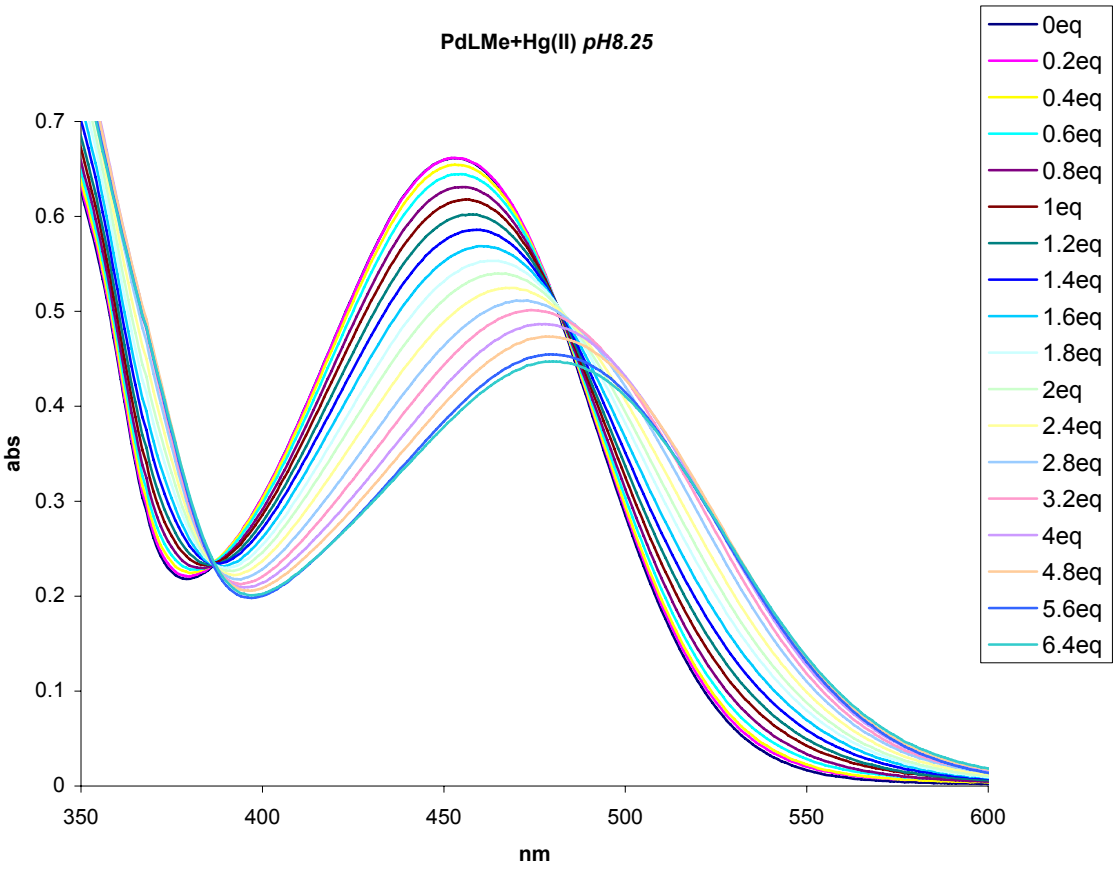


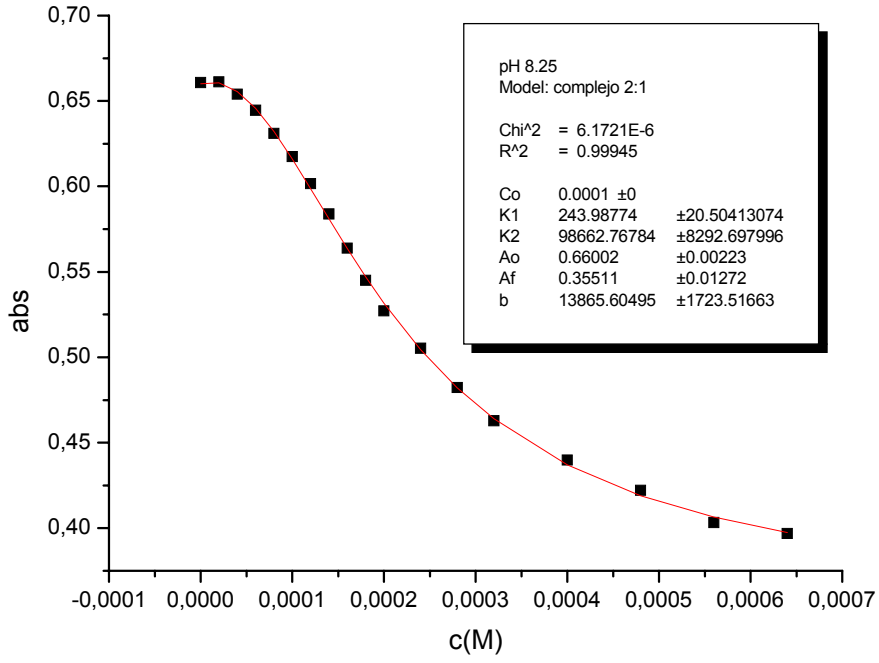


log K1= 2.387± 0.054

log K2= 4.994± 0.054

UV-visible titration of 3 with Hg^{2+} in EtOH/H_2O 1:1, pH = 8.25



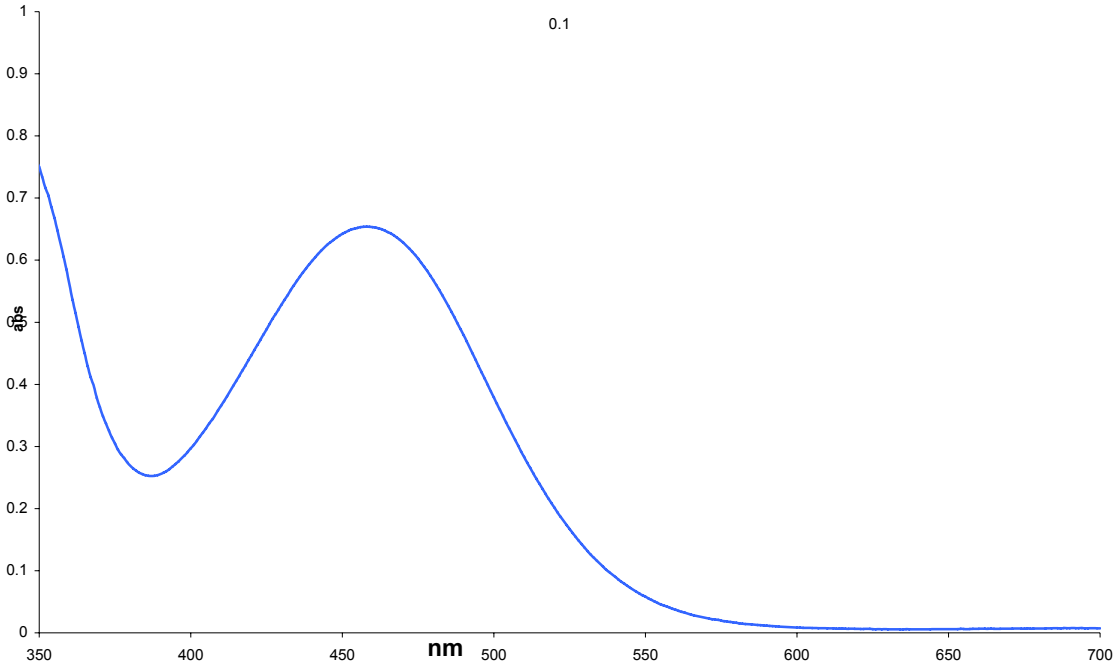


log K1= 2.387± 0.035

log K2= 4.994± 0.0350

Calculation of the Detection Limit of 3 in EtOH/H_2O 1:1:

The method used for the calculations is the blank variability as described in the *Handbook of Chemometrics and Qualimetrics*[1]. For this purpose, first a calibration plot is performed, then it is validated and then, in the same conditions, several blank replicates are measured. In this case, the solution of the complex **3** gives a signal without the presence of the analyte, therefore this signal is taken as the blank. 10 replicates of the blank were measured. The UV-visible absorption spectrum of **3** shows a maximum of absorbance at 455 nm, therefore the calibrate measures are taken at this wavelength.

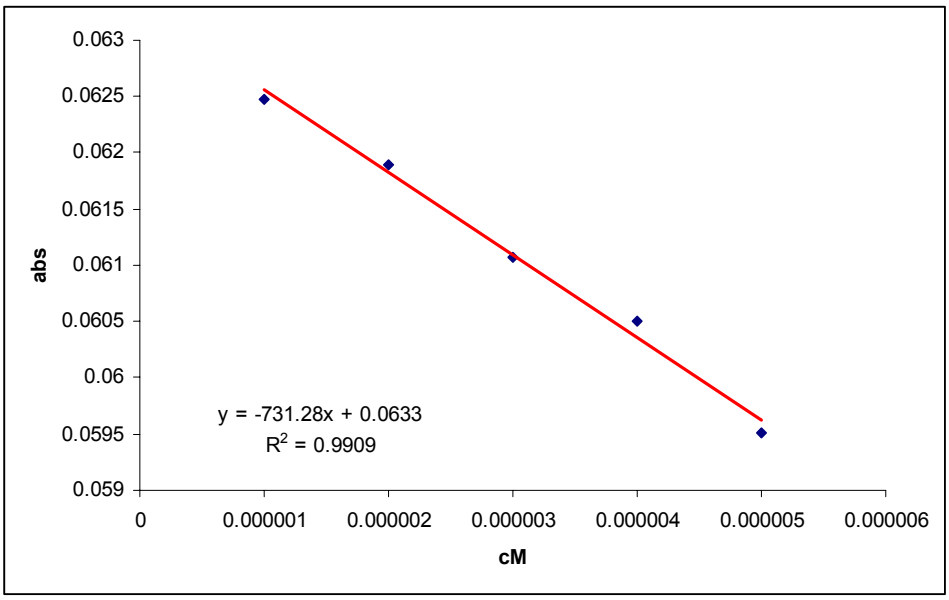


A calibration with 5 measures and 10 replicates for the blank were taken from a 10^{-5} M solution of **3**

c(M) Hg^{2+}	Abs
0.000001	*0.06247*
0.000002	*0.0619*
0.000003	*0.06107*
0.000004	*0.060507*
0.000005	*0.05951*

With these values the calibration curve was drawn:

[1] Massart, D. L.; Vandeginste, B. G. M.; Buydens, L. M. C.; De Jong, S.; Lewi, P. J.; Smeyers-Verbeke, J. *Handbook of Chemometrics and Qualimetrics: Part A*, Chapt. 13, Eselvier, Amsterdan, The Netherlands, 1997.



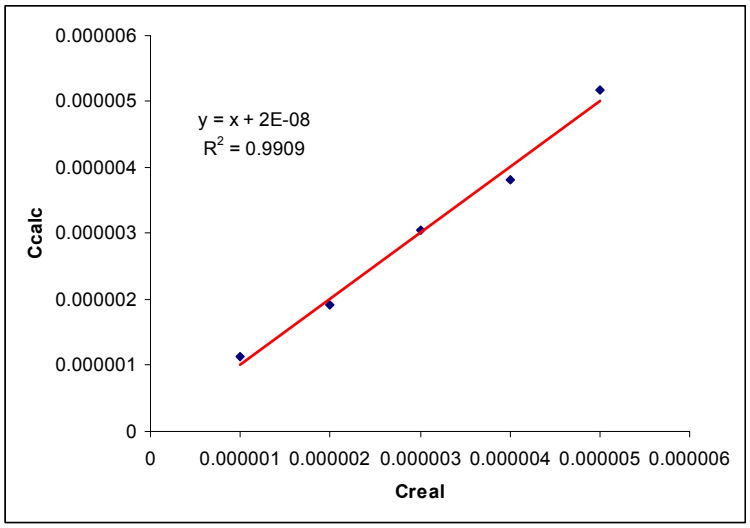
Calibration plot for **3** in EtOH/H_2O 1:1

With the least squares fit of the calibration curve, the detection limit may be calculated. First a plot of positive rate is performed by calculating the Hg^{2+} concentrations from the equation obtained from the calibration curve [6] and representing $[Hg^{2+}]_{calc}$ versus $[Hg^{2+}]$ and then calculating the detection limit taking in account the false positive (α) and false negative (β) probabilities.

$$y = -731.28 \cdot x + 0.0633 \qquad [6]$$

c $(M)_{real}$	c$(M)_{cal}$
0.000001	*1.135E-06*
0.000002	*1.91445E-06*
0.000003	*3.04945E-06*
0.000004	*3.8191E-06*
0.000005	*5.1028E-06*

With these values the new calibration curve was drawn:



The adjusted equation by least squares is obtained.

$$y = x + -2E^{-8} \qquad [7]$$

The measured blank absorbance values, from a solution of **3**, and the values of the concentration calculated from equation [6] are detailed.

replicate	Abs	$c(M)_{calc}$
1	*0.06301221*	*3.93543E-07*
2	*0.06305022*	*3.41567E-07*
3	*0.06289086*	*5.59483E-07*
4	*0.06292664*	*5.10553E-07*
5	*0.06310029*	*2.73102E-07*
6	*0.06289059*	*5.59855E-07*
7	*0.06274491*	*7.59069E-07*
8	*0.06305707*	*3.32205E-07*
9	*0.06270713*	*8.10724E-07*
10	*0.06290989*	*5.33467E-07*

The mean ($\bar{x}$) and the standard deviation (s) from the Hg^{2+} concentrations, calculated from the blank replicates, are calculated.

$$\bar{x} \pm s = (4.63229 \pm 0.82069) \cdot 10^{-7} \qquad [8]$$

For a probability level of 5% (α=β=0.05), the value of t_C=t_D from bibliography[2], for 9 freedom degrees ($GL = N - 1 = 10 - 1 = 9$) is 1.833.

Therefore, the decision limit is given by the ecuation:

$$L_C = t_C \times s \times \sqrt{1 + \frac{1}{N}} \qquad [10]$$

Being N the number of blank replicates (10), therefore:

$$L_C = t_C \times s \times \sqrt{1 + \frac{1}{N}} = 1.833 \times 0.82069 \cdot 10^{-7} \times \sqrt{1 + \frac{1}{10}} = 1.5777 \cdot 10^{-7}$$

The detection limit corresponds to the double of the decision limit, consequently:

$$L_D = 2L_C = 3.1555 \cdot 10^{-7}$$

The detection limit is given in terms of concentration by:

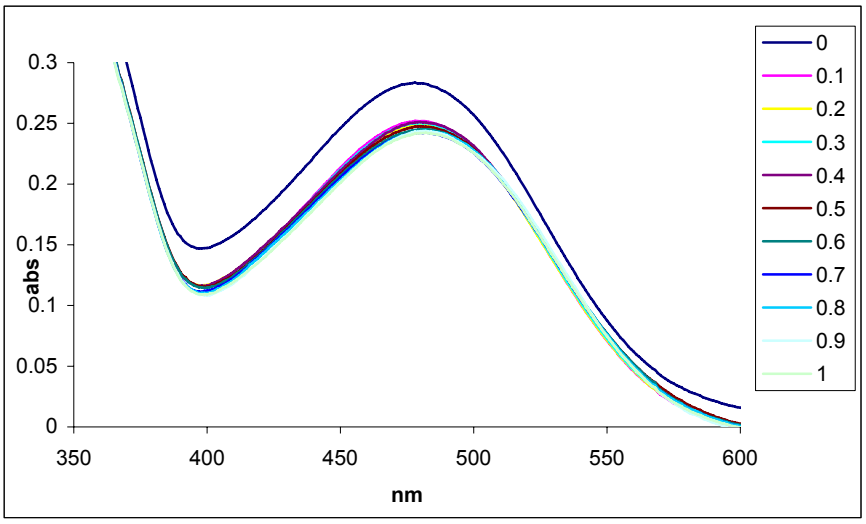
$$x_D = 2x_C = \frac{2L_C}{b} \qquad [11]$$

Where b is the slope of the calibration plot [7], therefore:

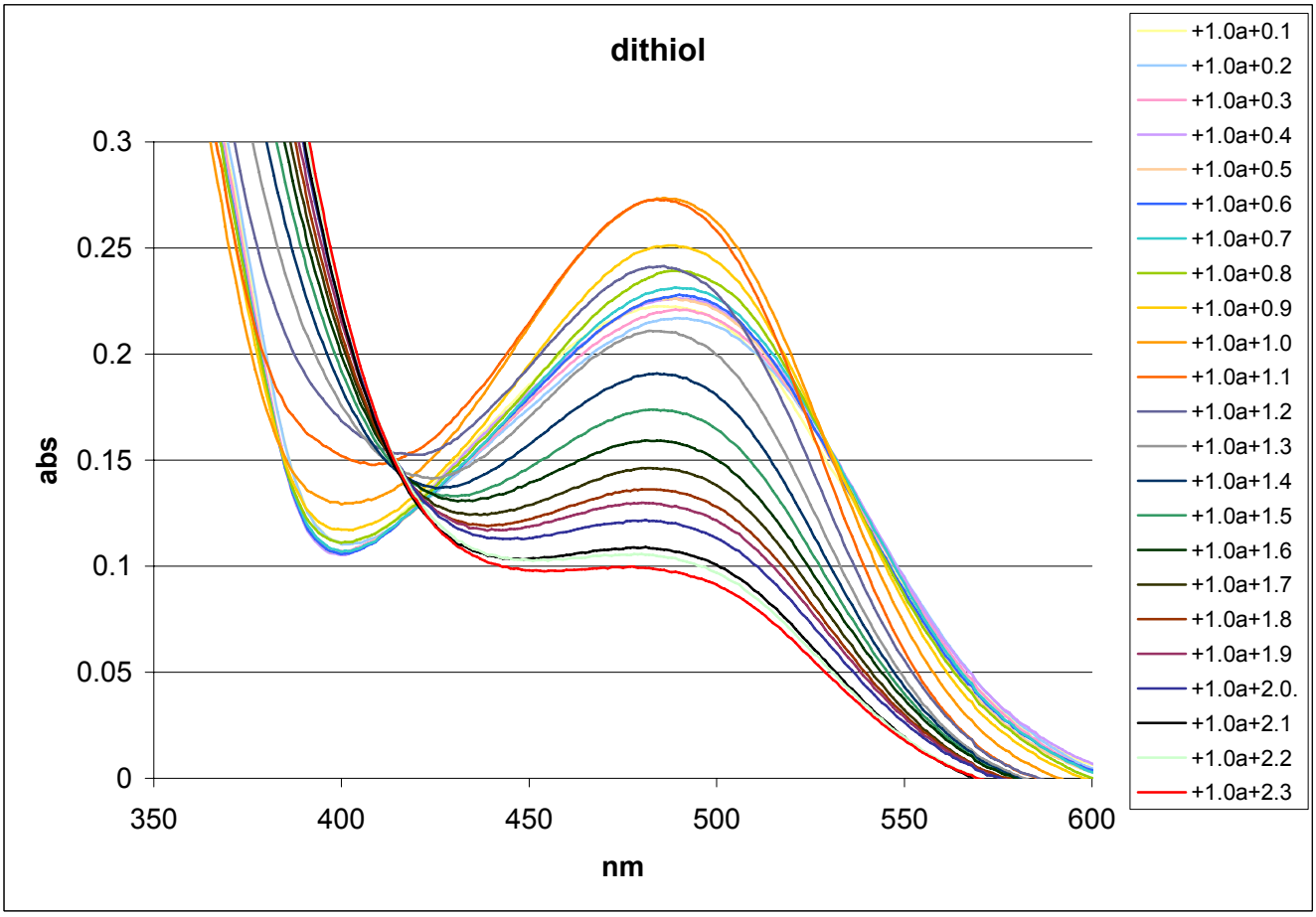
$$x_D = \frac{2L_C}{b} = \frac{2 \times 1.5777 \cdot 10^{-7}}{1} = 3.1555 \cdot 10^{-7}$$

Consequently, the detection limit of **3** at the concentration of C_L=10^{-5} M in EtOH/H_2O 1:1, corresponds to $3.16 \cdot 10^{-7}$ M.

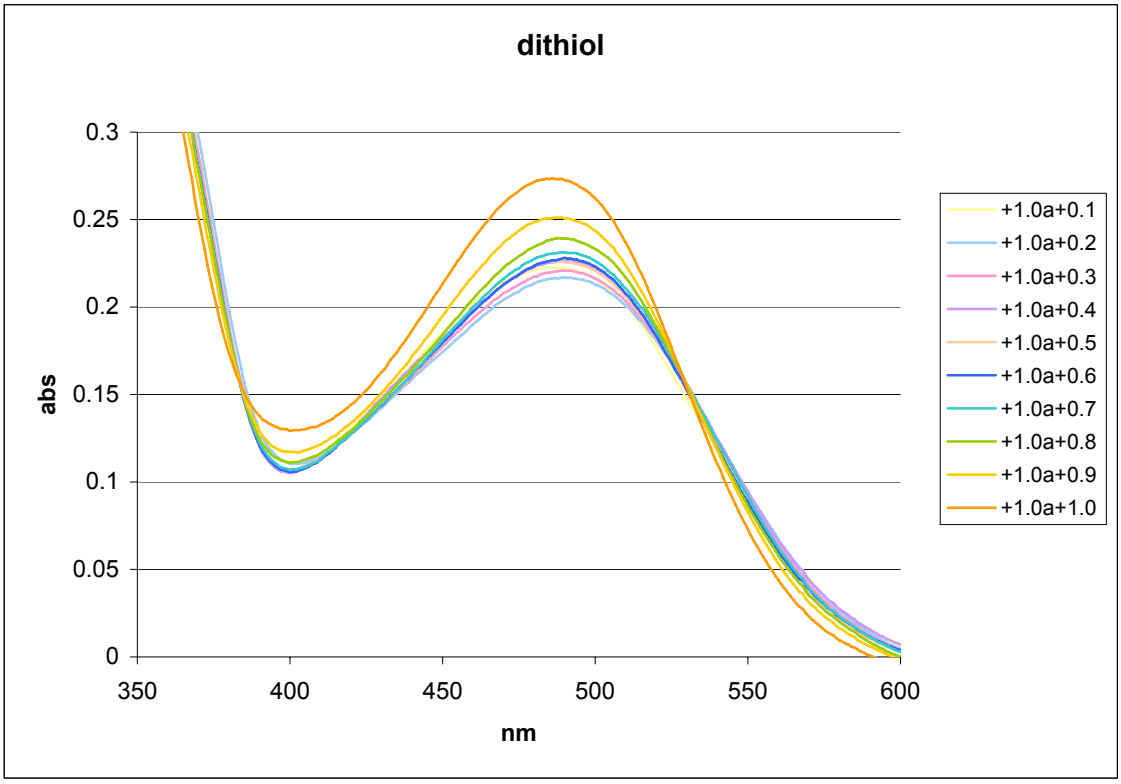
Titration of 4 and $MeHg^+$ with 5 in EtOH:H_2O 1:1



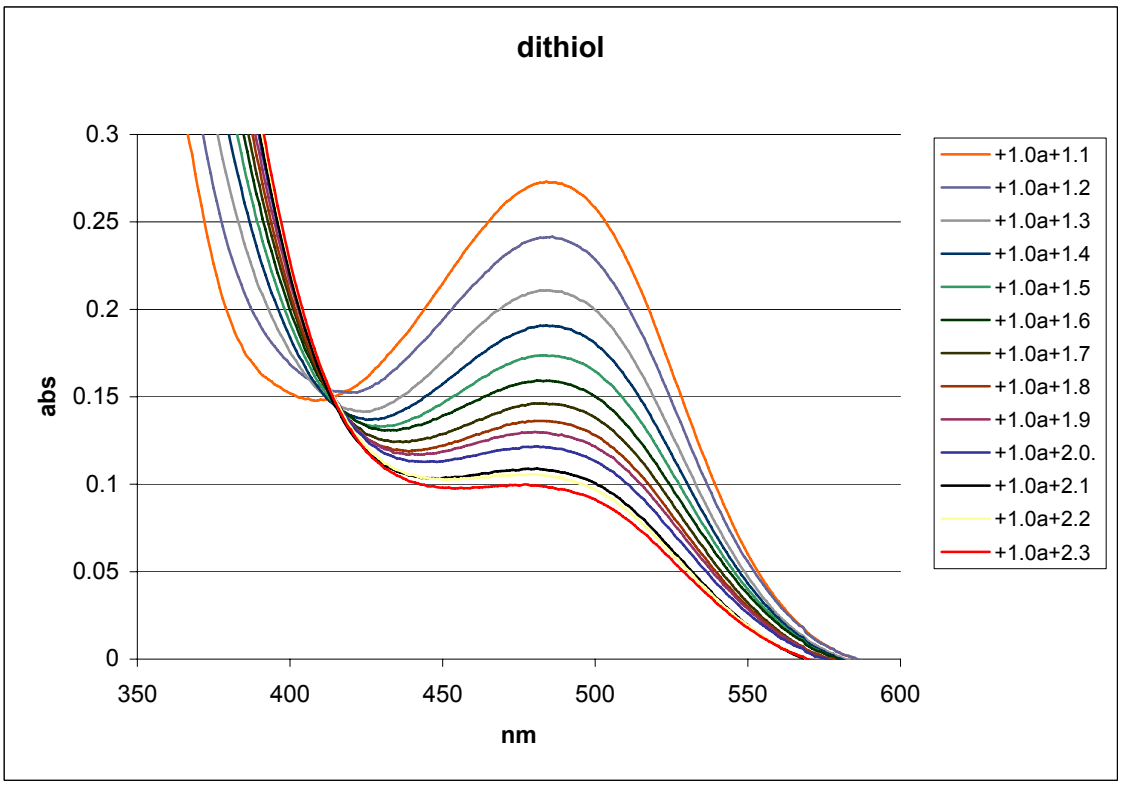
UV-visible successive addition of $MeHg^+$ to a 10^{-4} M solution of **4**.



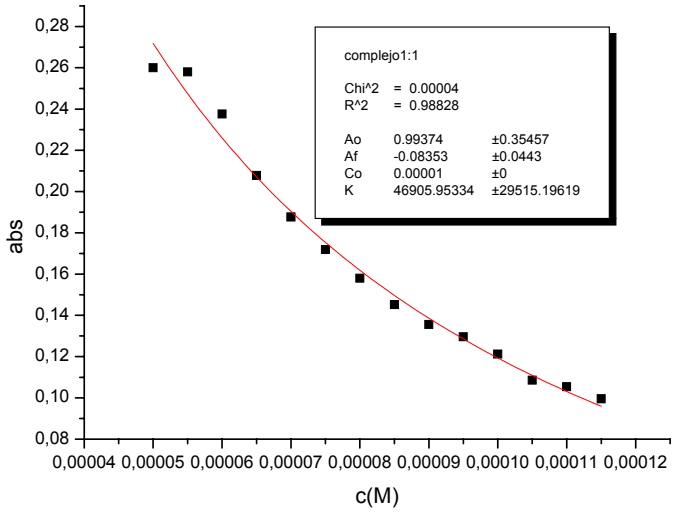
UV-visible titration of an equimolecular solution of **4** and $MeHg^+$ (10^{-4} M in EtOH/H_2O 1:1) with **5** (5×10^{-3} M in MeCN). The figures correspond to equivalents of **5**.



First part of the UV-visible titration of an equimolecular solution of **4** and $MeHg^+$ (10^{-4} M in EtOH/H_2O 1:1) with **5** (5×10^{-3} M in MeCN). The figures correspond to equiv of **5** from 0.2 to 1 equiv **5**.



Second part of the UV-visible titration of an equimolecular solution of **4** and $MeHg^+$ (10^{-4} M in EtOH/H_2O 1:1) with **5** (5×10^{-3} M in MeCN). The figures correspond to equiv of **5** from 1.1 to 2.3 equiv **5**.



Titration profile from the UV titration curves of an equimolecular solution of **4** and $MeHg^+$ (10^{-4} M in $EtOH/H_2O$ 1:1) with **5** (5×10^{-3} M in MeCN). It was represented after addition of the first equivalent **5** and adjusted to a 1:1 model, from which the titration constant was obtained: log K =4.67 ± 0.21

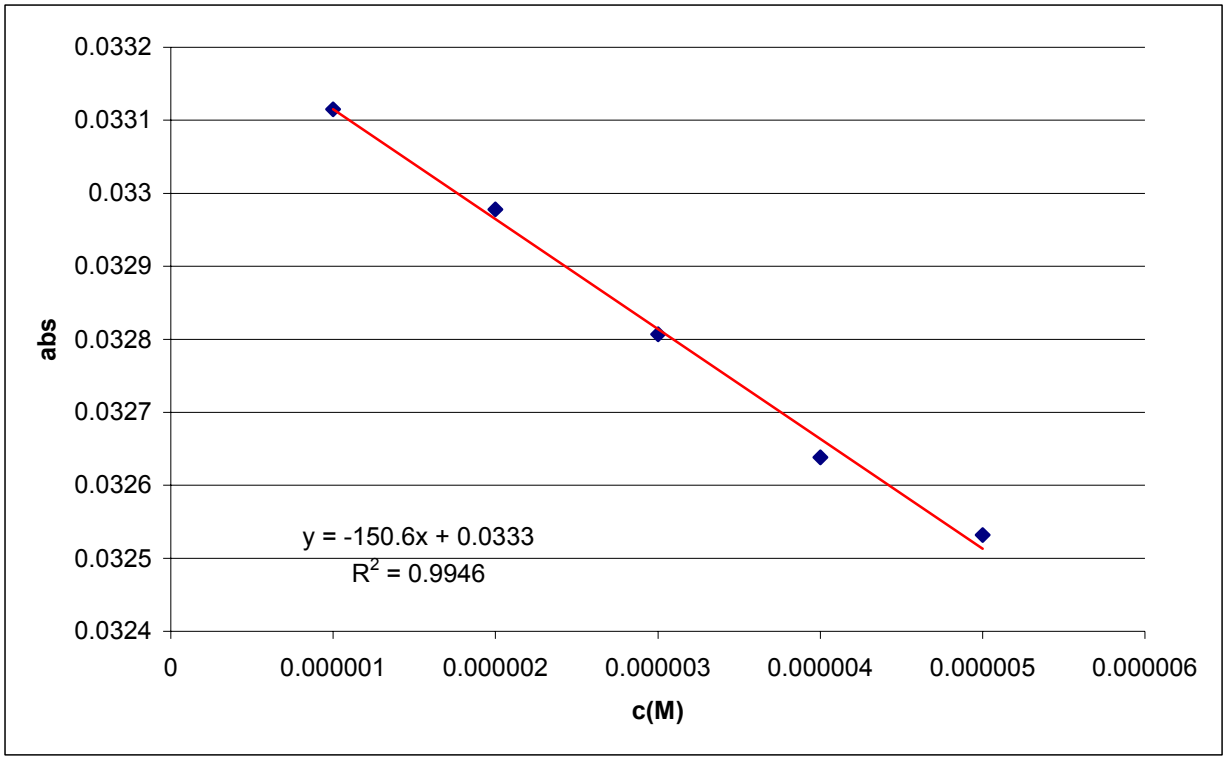
Calculation of the Detection Limit of 3 in EtOH/H_2O 1:1:

The method used for the calculations is the blank variability as described in the *Handbook of Chemometrics and Qualimetrics*[2]. For this purpose, first a calibration plot is performed, then it is validated and then, in the same conditions, several blank replicates are measured. In this case, the solution of the complex **4** gives a signal without the presence of the analyte, therefore this signal is taken as the blank. 10 replicates of the blank were measured.

A calibration with 5 measures and 10 replicates for the blank were taken from a 10^{-5} M solution of **4**

c(M) Hg^{2+}	Abs
0.000001	0.033115
0.000002	0.032978
0.000003	0.032807
0.000004	0.032638
0.000005	0.032532

With these values the calibration curve was drawn:



Calibration plot for **4** in EtOH/H_2O 1:1

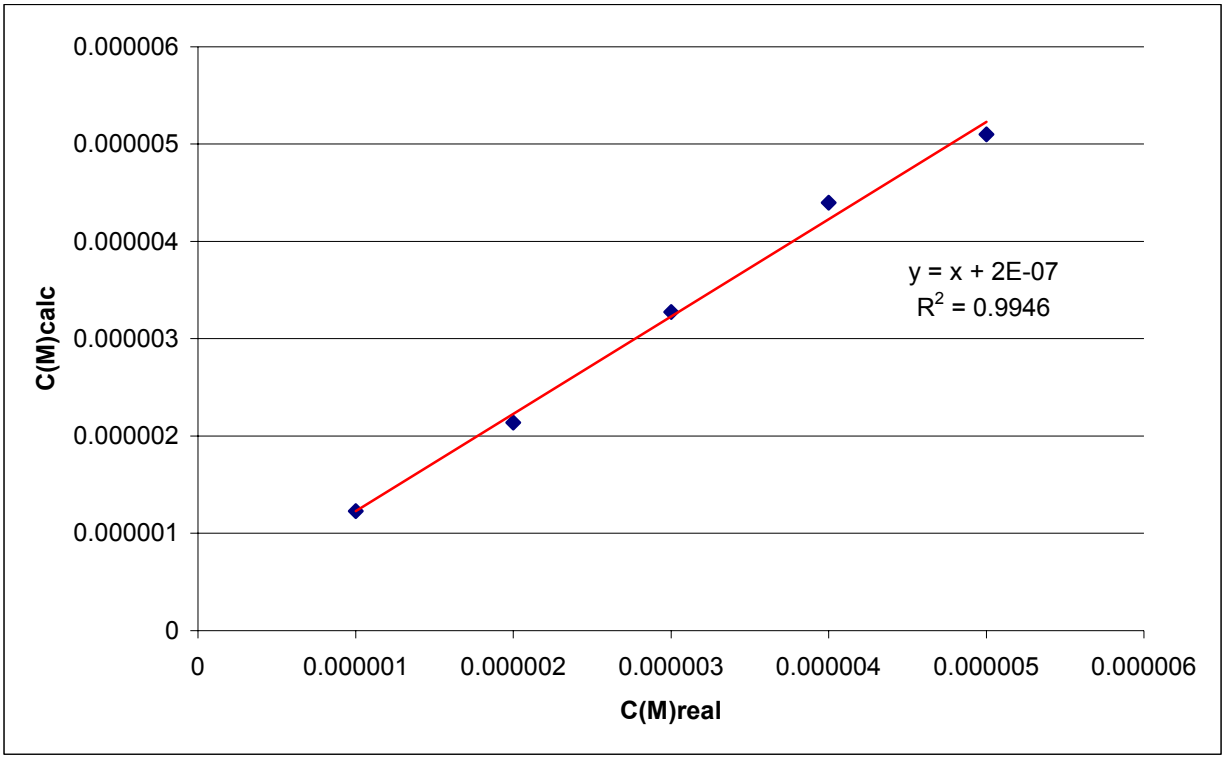
[2] Massart, D. L.; Vandeginste, B. G. M.; Buydens, L. M. C.; De Jong, S.; Lewi, P. J.; Smeyers-Verbeke, J. *Handbook of Chemometrics and Qualimetrics: Part A*, Chapt. 13, Eselvier, Amsterdan, The Netherlands, 1997.

With the least squares fit of the calibration curve, the detection limit may be calculated. First a plot of positive rate is performed by calculating the Hg^{2+} concentrations from the equation obtained from the calibration curve [6] and representing $[MeHg^{+}]_{calc}$ versus $[MeHg^{+}]$ and then calculating the detection limit taking in account the false positive (α) and false negative (β) probabilities.

$$y = -147.62 \cdot x + 0.0332 \qquad [6]$$

$c\ (M)_{real}$	$c(M)_{cal}$
0.000001	1.22842E-06
0.000002	2.13811E-06
0.000003	3.27357E-06
0.000004	4.39575E-06
0.000005	5.0996E-06

With these values the new calibration curve was drawn:



The adjusted equation by least squares is obtained.

$$y = x + -2E^{-7} \qquad [7]$$

The measured blank absorbance values, from a solution of **4**, and the values of the concentration calculated from equation [6] are detailed.

réplicas	Abs	$c(M)_{calc}$
1	0.03326660	2.2178E-07
2	0.03326048	2.62388E-07
3	0.03327552	1.62562E-07
4	0.03328139	1.23557E-07
5	0.03327147	1.8942E-07
6	0.03325991	2.66204E-07
7	0.03325780	2.80195E-07
8	0.03327393	1.73094E-07
9	0.03328285	1.13884E-07
10	0.03326484	2.33482E-07

The mean ($\bar{x}$) and the standard deviation (s) from the Hg^{2+} concentrations, calculated from the blank replicates, are calculated.

$$\bar{x} \pm s = (2.0266 \pm 0.5937) \cdot 10^{-7} \qquad [8]$$

For a probability level of 5% (α=β=0.05), the value of t_C=t_D from bibliography[2], for 9 freedom degrees ($GL = N - 1 = 10 - 1 = 9$) is 1.833.

Therefore, the decision limit is given by the ecuation:

$$L_C = t_C \times s \times \sqrt{1 + \frac{1}{N}} \qquad [10]$$

Being N the number of blank replicates (10), therefore:

$$L_C = t_C \times s \times \sqrt{1 + \frac{1}{N}} = 1.833 \times 0.5937 \cdot 10^{-7} \times \sqrt{1 + \frac{1}{10}} = 1.1414 \cdot 10^{-7}$$

The detection limit corresponds to the double of the decision limit, consequently:

$$L_D = 2L_C = 2.2829 \cdot 10^{-7}$$

The detection limit is given in terms of concentration by:

$$x_D = 2x_C = \frac{2L_C}{b} \qquad [11]$$

Where b is the slope of the calibration plot [7], therefore:

$$x_D = \frac{2L_C}{b} = \frac{2 \times 1.1414 \cdot 10^{-7}}{1} = 2.2829 \cdot 10^{-7}$$

Consequently, the detection limit of **3** at the concentration of $C_L=10^{-5}$ M in EtOH/H_2O 1:1, corresponds to **$2.2829 \cdot 10^{-7}$ M**.

Titration Materials and Methods:

Perchlorate salts were used for some cations and triflate salts for the rest of cations:

CATION	*SALT*
Ag^{+}	$AgClO_4 \cdot xH_2O$
Ni^{2+}	$Ni(ClO_4)_2 \cdot 6H_2O$
Sn^{2+}	$Sn(CF_3SO_3)_2$
Cd^{2+}	$Cd(ClO_4)_2$
Zn^{2+}	$Zn(CF_3SO_3)_2$
Pb^{2+}	$Pb(ClO_4)_2$
Cu^{2+}	$Cu(ClO_4)_2 \cdot 6H_2O$
Fe^{3+}	$Fe(ClO_4)_3 \cdot xH_2O$
Sc^{3+}	$Sc(CF_3SO_3)_3$
Al^{3+}	$Al(ClO_4)_3 \cdot 9H_2O$
Hg^{2+}	$Hg(ClO_4)_2$

5×10^{-2} M, 5×10^{-3} M, 5×10^{-4} M solutions of every salt were prepared, then a 10^{-4} M solution of the compound under study was prepared. For qualitative experiments, 2 mL solution of the compound under study were measured and the corresponding amount of salt was added by micropipette.

Eppendorf Research micropipette characteristics:

MODEL	Ep T.I.P.S.	Volume	Systematic error of measurement	Random error of measurement (CV)
2 - 20µl	2 - 200	2 µl	± 5.0 %	≤ 1.5 %
		10 µl	± 1.2 %	≤ 0.6 %
		20 µl	± 1.0 %	≤ 0.3 %
10 - 100µl	2 - 200	10 µl	± 3.0 %	≤ 1.0 %

MODEL	Ep T.I.P.S.	Volume	Systematic error of measurement	Random error of measurement (CV)
		50 µl	± 1.0 %	≤ 0.3 %
		100 l	± 0.8 %	≤ 0.2 %
100 - 1000µl	50 - 1000	100 µl	± 3.0 %	≤ 0.6 %
		5000 µl	± 1.0 %	≤ 0.2 %
		1000 µl	± 0.6 %	≤ 0.2 %
500 - 5000µl	100 - 5000	500 µl	± 2.4 %	≤ 0.6 %
		2500 µl	± 1.2 %	≤ 0.25 %
		5000 µl	± 0.6 %	≤ 0.15 %

Quantitative studies, UV-VIS titrations:

Quantitative measures were performed with a Varian, Cary Eclipse 300 UV spectrophotometer. As a general procedure, to a 5000 µl solution of complex, the corresponding amount (µL) of solution of the corresponding salt (5×10^{-2} M, 5×10^{-3} M, 5×10^{-4} M solutions) was added, using the minor amount of solvent.

A table, corresponding to the number of equivalents and the corresponding added volumes is included:

Vtotal (µl)	*eq*	*C*
5000	0	0
5005	0.05	4.995E-06
5010	0.1	9.98E-06
5015	0.15	1.4955E-05
5020	0.2	1.992E-05
5025	0.25	2.4876E-05
5030	0.3	2.9821E-05
5035	0.35	3.4757E-05
5040	0.4	3.9683E-05
5045	0.45	4.4599E-05
5050	0.5	4.9505E-05

Vtotal (µl)	***eq***	***C***
5055	0.55	5.4402E-05
5060	0.6	5.9289E-05
5065	0.65	6.4166E-05
5070	0.7	6.9034E-05
5075	0.75	7.3892E-05
5080	0.8	7.874E-05
5085	0.85	8.3579E-05
5090	0.9	8.8409E-05
5095	0.95	9.3229E-05
5100	1	9.8039E-05
5105	1.05	0.00010284
5110	1.1	0.00010763
5115	1.15	0.00011241
5120	1.2	0.00011719
5125	1.25	0.00012195
5130	1.3	0.00012671
5135	1.35	0.00013145
5140	1.4	0.00013619
5145	1.45	0.00014091
5150	1.5	0.00014563
5155	1.55	0.00015034
5160	1.6	0.00015504
5165	1.65	0.00015973
5170	1.7	0.00016441
5180	1.8	0.00017375
5190	1.9	0.00018304
5200	2	0.00019231
5210	2.1	0.00020154
5220	2.2	0.00021073
5230	2.3	0.00021989
5240	2.4	0.00022901
5250	2.5	0.0002381
5260	2.6	0.00024715
5270	2.7	0.00025617
5280	2.8	0.00026515

Vtotal (µl)	*eq*	*C*
5300	3	0.00028302
5320	3.2	0.00030075
5340	3.4	0.00031835
5360	3.6	0.00033582
5380	3.8	0.00035316
5400	4	0.00037037
5405	4.5	0.00041628
5410	5	0.00046211
5415	5.5	0.00050785
5420	6	0.00055351
5430	7	0.00064457
5440	8	0.00073529
5450	9	0.00082569
5460	10	0.00091575

^{1}H NMR Titrations: Titrations were performed with Varian Mercury 300 MHz NMR and Varian Unity Inova 400 MHz spectrometers. In all cases, a 0.007733 M solution of the compound under study was prepared (3 mg in 0.75 ml) in the NMR tube (Norell, 509-UP, 178 mm, ultra precision). For the NMR titrations performed with Hg^{2+} solely, aliquots of 20µl of a $2.9x10^{-5}$ M solution of Hg^{2+} were employed. For the reversed titrations, aliquots of 10 µl of dithiol (0.145 M solution) and of Hg^{2+} (0.290 M solution) were employed. A table, corresponding to the number of equivalents and the corresponding added volumes is included:

Hg^{2+} only	
V added (µl)	**equiv**
20	0.1
40	0.2
60	0.3
80	0.4
100	0.5
120	0.6
140	0.7
160	0.8

dithiol + Hg^{2+}	
V added (µl)	**equiv**
20	1 eq Hg^{2+}
30	0.5 eq dithiol
40	1 eq dithiol
50	1.5 eq dithiol
60	0.5 eq Hg^{2+}
70	1 eq Hg^{2+}
80	1.5 eq Hg^{2+}
90	2 eq Hg^{2+}

180	0.9
200	1
240	1.2
280	1.4
320	1.6
360	1.8
400	2
480	2.4

110	3 eq Hg^{2+}