

Supporting Information

Cyclometallated platinum(II) complexes containing pyridyl-acetylide ligands: the selective influence of lead binding on luminescence

Pierre-Henri Lanoë,^a Hubert Le Bozec,^a

*J. A. Gareth Williams,^b Jean-Luc Fillaut,^{*a} and Véronique Guerchais^{*a}*

^a Sciences Chimiques de Rennes UMR 6226 CNRS-Université de Rennes 1, ^b Department of Chemistry, University of Durham, South Road, Durham, DH1 3LE, United Kingdom.

jean-luc.fillaut@univ-rennes1.fr, veronique.guerchais@univ-rennes1.fr

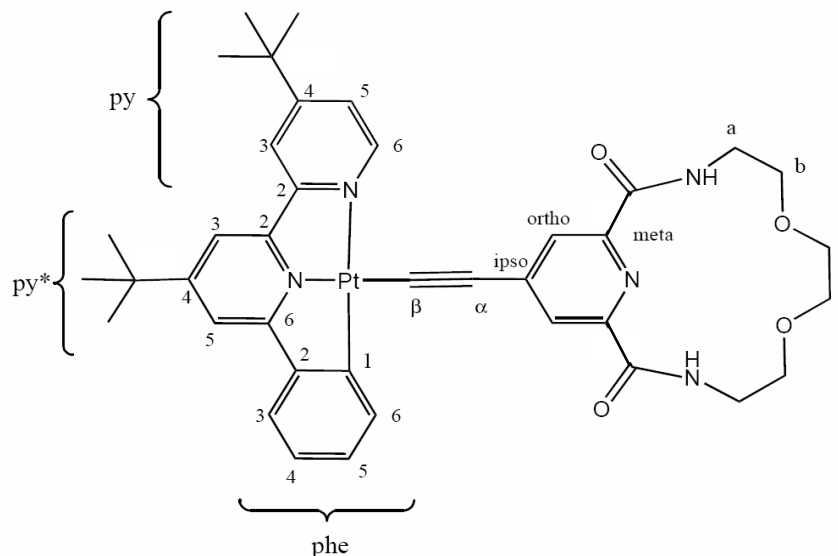
Experimental

General Procedure. All manipulations were performed using Schlenk techniques under an Ar atmosphere. All solvents were dried and purified by standard procedures. NMR spectra were recorded on Bruker DPX-200, AV 300 or AV 500 MHz spectrometers. ¹H and ¹³C chemical shifts are given versus SiMe₄ and were determined by reference to residual ¹H and ¹³C solvent signals. Assignments of carbon atoms were based on HMBC, HMQC and COSY experiments. Elemental analyses and High resolution mass spectra (HRMS) were performed on a MS/MS ZABSpec TOF (Bruker) at the CRMPO (Centre de Mesures Physiques de l'Ouest) in Rennes. UV/vis absorption spectra were recorded using a UVIKON 9413 or Biotek Instruments XS spectrophotometer using quartz cuvettes of 1 cm pathlength.

Steady-state luminescence spectra were measured using a Jobin Yvon FluoroMax-2 or Tau-3 spectrofluorimeter, fitted with a red-sensitive Hamamatsu R928 photomultiplier tube. The spectra shown are corrected for the wavelength dependence of the detector, and the quoted emission maxima refer to the values after correction. The 77K spectra were acquired using an Oxford Instruments Cryostat model D1704. Luminescence quantum yields were determined using the method of continuous dilution, using $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ as the standard ($\Phi = 0.028$ in air-equilibrated aqueous solution) and correcting for the refractive index. Fluorescence and phosphorescence lifetimes were measured by time-correlated single-photon counting (TCSPC) following excitation at 374.0 nm with an EPL-375 pulsed diode laser. The emitted light was detected at 90° using a Peltier cooled R928 PMT after passage through a monochromator.

The stoichiometry and complexation constants were determined by global analysis of the evolution of all absorption and fluorescence spectra by using Specfit Global analysis system V3.0 for 32-bit Windows system.

Numbering



4-ethynylpyridine¹ and 4-iodo-2,6- pyridinedicarboxylic acid dimethyl ester (**4**)² were synthesized according to literature procedures.

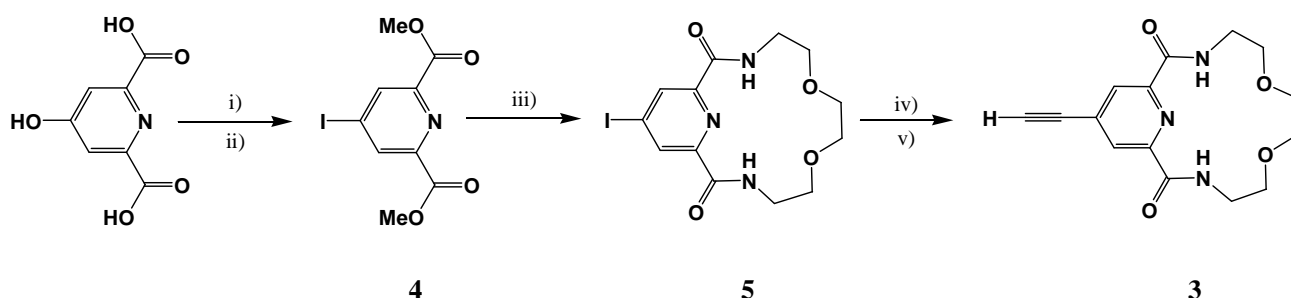
Preparation of (2): In a Schlenk tube, 4-ethynylpyridine (200 mg, 0.23 mmol) was added to a solution of [Pt(^tBu₂-C^NN)Cl]³ (445 mg, 0.78 mmol) in a mixture of anhydrous CH₂Cl₂/*i*-Pr₂NH (20 mL, 1 : 1). The solution was degassed by freeze-pump-thaw technique, then CuI (12 mg, 0.06 mmol) was added and the solution was stirred at 40°C overnight. After cooling the reaction mixture at r.t., solvents were removed by vacuum. A column chromatography (SiO₂, CH₂Cl₂/Ethyl Acetate, 7/3) yielded **2** as a yellow powder. Yield: 108 mg, 53 %. ¹H NMR – 300 MHz (CDCl₃): δ 9.02 (dd, 1H, ³J_{H-H} = 5.7 Hz, ³J_{Pt-}

¹ Ziessel, R.; Suffert, J.; Youinou, M.-T. *J. Org. Chem.* **1996**, *61*, 6535-6546.

² a) Nakatsuji, Y.; Bradshaw, J. S.; Tse, P.-K.; Arena, G.; Wilson, B. E.; Dalley, N. K.; Izatt, R. M. *J. Chem. Soc., Chem. Commun.* **1985**, 749-751. b) Picot, A.; Feuvrie, C.; Barsu, C.; Malvolti, F.; Le Guennic, B.; Le Bozec, H.; Andraud, C.; Toupet, L.; Maury, O. *Tetrahedron* **2008**, *64*, 399-411:

³ Lu, W.; Mi, B.-X.; Chan, M. C. W.; Hui, Z.; Che, C.-M.; Zhu, N.; Lee, S.-T. *J. Am. Chem. Soc.* **2004**, *126*, 4958-4971

$H = 18$ Hz, H^{6py}); 8.46 (d, 2H, $^3J = 6.1$ Hz, H^{meta}); 7.86 (ddd, 1H, $^3J_{H-H} = 7.4$ Hz, $^3J_{Pt-H} = 64$ Hz, $^4J_{H-H} = 1.1$ Hz, H^{6phe}); 7.84 (d, 1H, $^4J_{H-H} = 1.0$ Hz, H^{3py}); 7.57 (s, 1H, H^{5py*}); 7.56 (s, 1H, H^{3py*}); 7.52 (dd, 1H, $^3J_{H-H} = 5.7$ Hz, $^4J_{H-H} = 1.8$ Hz, H^{5py}); 7.38 (m, 3H, H^{ortho} , H^{3phe}); 7.16 (ddd, 1H, $^3J_{H-H} = 7.3$ Hz, $^3J_{H-H} = 6$ Hz, $^4J_{H-H} = 1.3$ Hz, H^{5phe}); 7.06 (ddd, 1H, $^3J_{H-H} = 7.5$ Hz, $^3J_{H-H} = 6.2$ Hz, $^4J_{H-H} = 1.4$ Hz, H^{4phe}); 1.46 (s, 9H, $tBupy^*$); 1.43 (s, 9H, $tBupy$). ^{13}C [1H] NMR – 75 MHz ($CDCl_3$): δ 165.1 (C^{6py*}); 163.8 (C^{4py*}); 163.7 (C^{4py}); 158.1 (C^{2py}); 154.4 (C^{2py*}); 151.5 (C^{6py}); 149.2 (C^{meta}); 147.1 (C^{2phe}); 141.9 (C^{1phe}); 138.4 (C^{6phe}); 136.9 (C^{ipso}); 131.3 (C^{5phe}); 126.3 (C^{ortho}); 124.6 (C^{5py}); 124.2 (C^{3phe}); 123.7 (C^{4phe}); 119.2 (C^{3py}); 115.6 (C^{5py*}); 114.8 (C^β); 114.5 (C^{3py*}); 104.1 (C^α); 36.0 (C^{tBupy^*}); 35.7 (C^{tBupy}); 30.6 (C^{tBupy*}); 30.3 (C^{tBupy}). Elemental Analysis Calcd.(%) for $C_{31}H_{31}N_3Pt$, C, 58.12, H, 4.88, N, 6.56; Found: C, 58.18, H, 5.01, N, 6.43.



16-iodo-6,9-dioxo-3,12,18-triazabicyclo[12.3.1]octadeca-1(18),14,16-triene-2,13-dione (5): 2,2'-(ethylenedioxy)-bis-ethylamine (222 mg, 1.5 mmol) was added to a solution of **4** (482 mg, 1.5 mmol) in anhydrous MeOH (15 mL) and the mixture was then stirred during 7 days. After evaporation of the solvent, a column chromatography (SiO_2 , $CHCl_3/MeOH/C_6H_5CH_3$, from 99/0.5/0.5 to 97.5/2/0.5) of the crude product yielded to **5** as a white solid. Yield: 412 mg, 70 %. 1H NMR – 200 MHz ($CDCl_3$): δ 8.78 (2H, s, NH); 8.64 (2H, s, H^{ortho}); 3.77 (4H, s-broad, CH_2^c); 3.71 (4H, m, CH_2^b), 3.67 (4H, m, CH_2^a). ^{13}C [1H] NMR – 75 MHz ($CDCl_3$): δ 116.2 (C=O); 148.7 (C^{meta}); 133.4 (C^{ortho}); 109.1 (C^{ipso}); 71.11 (C^c); 68.8 (C^b); 39.3 (C^a). HRMS: m/z calcd. for $[C_{13}H_{16}IN_3O_4+H]^+$: 406.0243; found 406,0244. Elemental

Analysis Calcd. (%) for C₉H₈O₄IN: C, 38.54, H, 3.98, N, 10.37; Found: C, 38.34, H, 3.97, N, 10.36.

16-ethynyl-6,9-dioxa-3,12,18-triazabicyclo[12.3.1]octadeca-1(18),14,16-triene-2,13-dione (3):

TMSA (60 mg, 0.61 mmol) was added to a degassed solution of **5** (60 mg, 0.61 mmol), Pd(PPh₃)₂Cl₂ (18 mg, 0.03 mmol) and CuI (10 mg, 0.05 mmol) in a mixture of THF/Et₃N (5 mL, 4/1). After stirring overnight, the mixture was filtrated on SiO₂ and the solvents were removed under vacuum. The crude product was extracted in CH₂Cl₂ (25 mL), washed with brine and dried. The black solution was concentrated (5 mL). Afterwards, a saturated aqueous solution of K₂CO₃ (2 mL) was added to this solution. After stirring (2 h.), brine was added to the mixture, layers were separated and the aqueous layer was extracted with CH₂Cl₂ (3 x 20 mL). The combined organic layers were dried with MgSO₄ and concentrated under vacuum. A column chromatography (SiO₂, CH₂Cl₂/MeOH/C₆H₅CH₃, 98.5/1/0.5) yielded to **3** as a white powder. Yield: 112 mg, 80 %. ¹H NMR – 500 MHz (CDCl₃): δ 8.82 (s, 2H, NH); 8.31 (s, 2H, H^{ortho}); 3.77 (s, 4H, CH₂^c); 3.75 (m, 4H, CH₂^b); 3.68 (m, 4H, CH₂^a); 3.47 (s, 1H, H^β). ¹³C [¹H] NMR – 125 MHz (CDCl₃): δ 162.1 (C=O); 148.5 (C^{meta}); 134.2 (C^{ipso}); 126.1 (C^{ortho}); 84.1 (C^β); 80.2 (C^α); 70.7 (C^c); 68.5 (C^b); 38.8 (C^a). HRMS: m/z calcd. for [C₁₅H₁₇N₃O₄+Na]⁺: 326.1116; found: 326.1116. Elemental Analysis Calcd. (%) for C₁₅H₁₇N₃O₄: C, 59.40, H, 5.65, N, 13.85; Found: C, 59.08, H, 5.72, N, 13.65.

(1): [Pt(^tBu₂-C[^]N[^]N)Cl] (144 mg, 0.25 mmol) was added to a solution of **3** (154 mg, 0.53 mmol) in a mixture of anhydrous CH₂Cl₂/*i*-Pr₂NH (1/1, 20 mL). The solution was degassed using freeze-pump-thaw technique, then CuI (5 mg, 2.5·10⁻⁴ mmol) was added and the solution was stirred at 40°C overnight. (TLC SiO₂: CH₂Cl₂/CH₃OH/C₆H₅CH₃, 91/8/1). Solvents were removed under vacuum, the crude product was dissolved in CH₂Cl₂, washed with brine and dried with MgSO₄. A column chromatography (SiO₂, CH₂Cl₂/CH₃OH/C₆H₅CH₃, 94.5/5/0.5) yielded **1** as a brown solid. Yield: 154 mg, 73%. ¹H NMR – 300 MHz (CDCl₃): δ 8.97 (d, 1H, ³J = 5.7 Hz, H^{6py}); 8.92 (dd, 2H, ³J = 4.4 Hz, N-H); 8.28 (s, 2H, H^{ortho}); 7.85 (m, 2H, H^{3py} and H^{phe6}); 7.56 (m, 3H, H^{5py}, H^{3py*} and H^{5py*}); 7.37 (dd, 1H,

$^3J = 7.7$ Hz, $^4J = 1.2$ Hz, H^{phe3}); 7.18 (ddd, 1H, $^3J = 7.4$ Hz, $^4J = 1.2$ Hz, H^{phe4}); 7.07 (ddd, 1H, $^3J = 7.5$ Hz, $^4J = 1.2$ Hz, H^{phe5}); 3.78 (s, 4H, CH_2^c); 3.76 (m, 4H, CH_2^b); 3.68 (m, 4H, CH_2^a); 1.47 (s, 9H, $tBupy^*$); 1.46 (s, 9H, $tBupy$). ^{13}C [1H] NMR – 75 MHz ($CDCl_3$): δ 165.0 (C^{6py^*}); 163.9 (C^{4py^*}); 163.64 (C^{4py}); 163.4 (C=O); 158.1 (C^{2py}); 154.4 (C^{2py^*}); 151.2 (C^{py6}); 147.7 (C^{meta}); 147.1 (C^{2phe}); 141.8 (C^{1phe}); 140.7 (C^{ipso}); 138.4 (C^{6phe}); 131.3 (C^{4phe}); 126.2 (C^{ortho}); 124.7 (C^{5py}); 124.2 (C^{3phe}); 123.7 (C^{5phe}); 120.3 (C^β); 119.3 (C^{3py}); 115.6 (C^{5py^*}); 114.7 (C^{3py^*}); 103.8 (C^α); 70.8 (CH_2^c); 68.7 (CH_2^b); 38.8 (CH_2^a); 36.0 (C^{tBupy^*}); 35.7 (C^{tBupy}); 30.5 (C^{tBupy^*}); 30.4 (C^{tBupy}). m/z calcd. for $[C_{39}H_{43}N_5O_4Pt-H]^+$: 839.2921; found: 839.2925. Elemental Analysis Calcd. (%) for $C_{39}H_{43}N_5O_4Pt, H_2O$: C, 54.54, H, 5.28, N, 8.15; Found: C, 54.32, H, 5.04, N, 7.89.

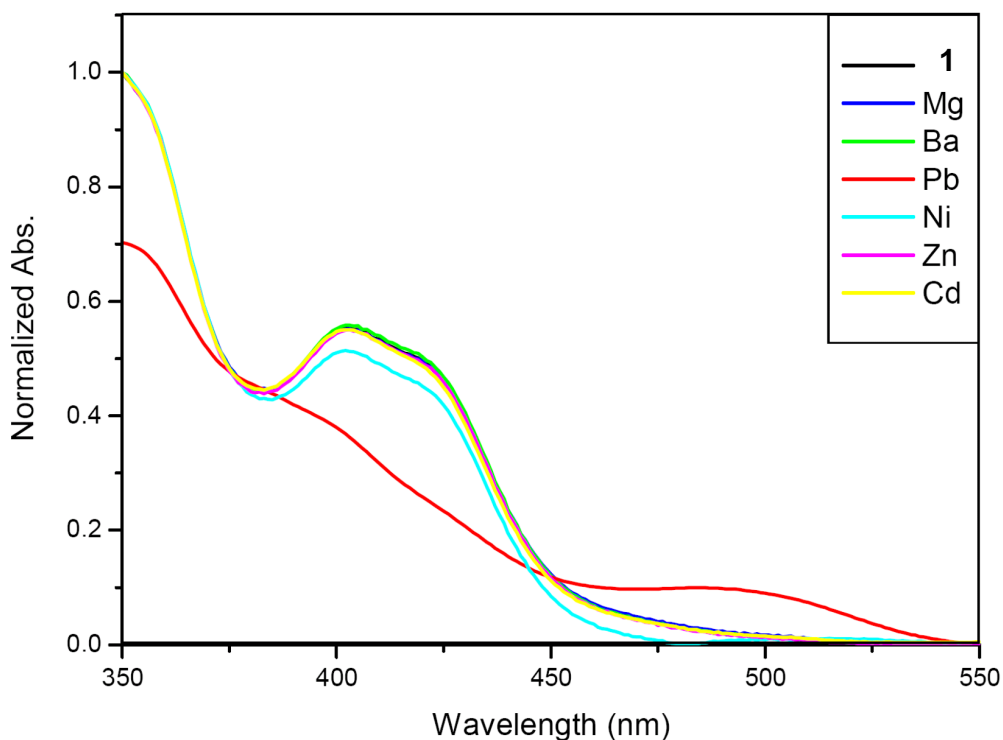


Figure S1. Absorption spectrum of **1** after addition of 50 equiv. $M(ClO_4)_2$, $[1] = 10^{-5}$ M, CH_3CN , 298 K.

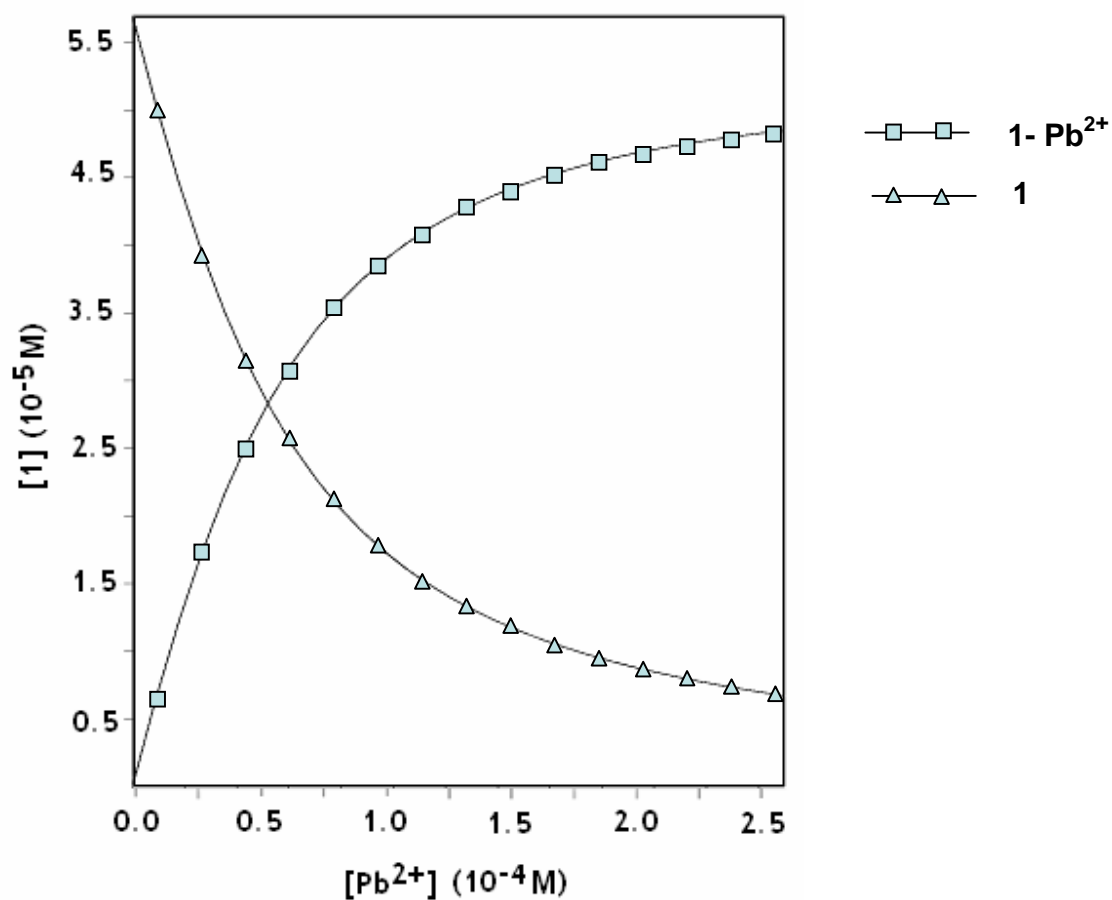


Figure S2. Evolution of the concentration of the free **1** and lead-complexed **1-Pb²⁺** species in CH_3CN , as a function of added Pb^{2+} cations, calculated from absorption spectra.

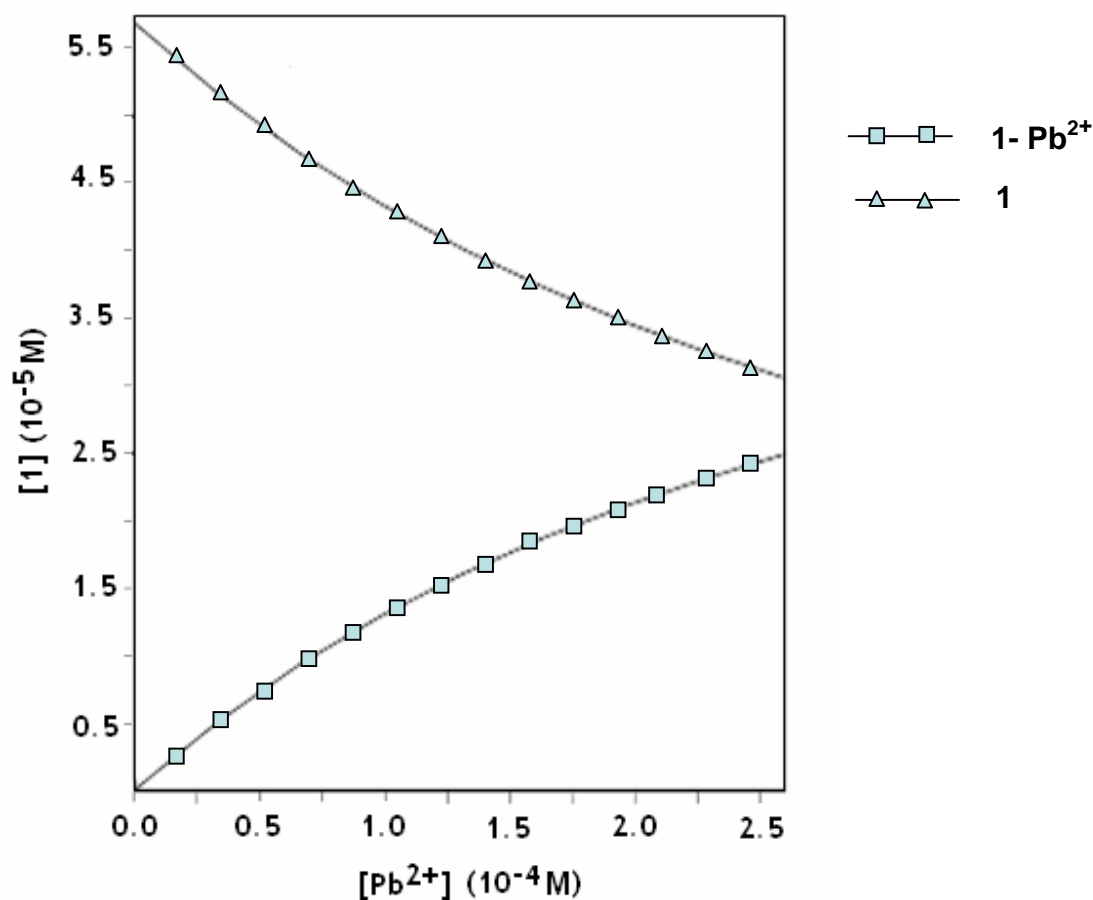


Figure S3. Evolution of the concentration of the free **1** and lead-complexed **1-Pb²⁺** species in CH₃CN, as a function of added Pb²⁺ cations, calculated from emission spectra.

High resolution electrospray ionization mass spectrometry (HR-ESI-MS) analysis of **1-Pb²⁺**

Pb(ClO₄)₂·H₂O (5 mg, 10 × 10⁻³ mmol) was added to a solution of **1** (2 mg, 2.4 × 10⁻³ mmol) in CH₃CN (5 mL). The sample was left standing without stirring overnight.

ESI (PEGNa ref): calculated for [C₃₉H₄₂N₅O₄¹⁹⁴Pt²⁰⁸Pb]⁺ 1046.26300 found 1046.2633 ; calculated for [C₃₉H₄₂N₅O₄¹⁹⁵Pt²⁰⁸Pb]⁺ 1047.26511 found 1046.2651. (The given value represents the largest peak).