Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Pb^{2+} Complexes of Small-Cavity Azamacrocyclic Ligands. Thermodynamic and Kinetic Studies.

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Fig. S1. Distribution diagram of receptor **L1**.

Fig. S2. Plot of the fluorescence intensity vs. [Pb^{2+}] for **L1.**

Fig. S3. Fluorescence spectra of [Pb**L3**]$^{2+}$ and [H_3**L3**]$^{3+}$

Fig. S4. pH effect on the electronic spectra of aqueous solutions containing **L2**

Fig. S5. pH effect on the electronic spectra of aqueous solutions containing **L2** and Pb^{2+} in 1:1 molar ratio

Fig. S6. Fluorescence spectra of [Pb**L2**]$^{2+}$ and [H_3**L2**]$^{3+}$

Fig. S7. pH effect on the electronic spectra of aqueous solutions containing **L1**.

Fig. S8. pH effect on the electronic spectra of aqueous solutions containing **L1** and Pb^{2+} in 1:1 molar ratio.

Fig. S9. Fluorescence spectra of [Pb**L1**]$^{2+}$ and [H_3**L1**]$^{3+}$

Table S1. Crystallographic data for **1** and **2**.

Fig. S1. Distribution diagram of receptor **L1**.

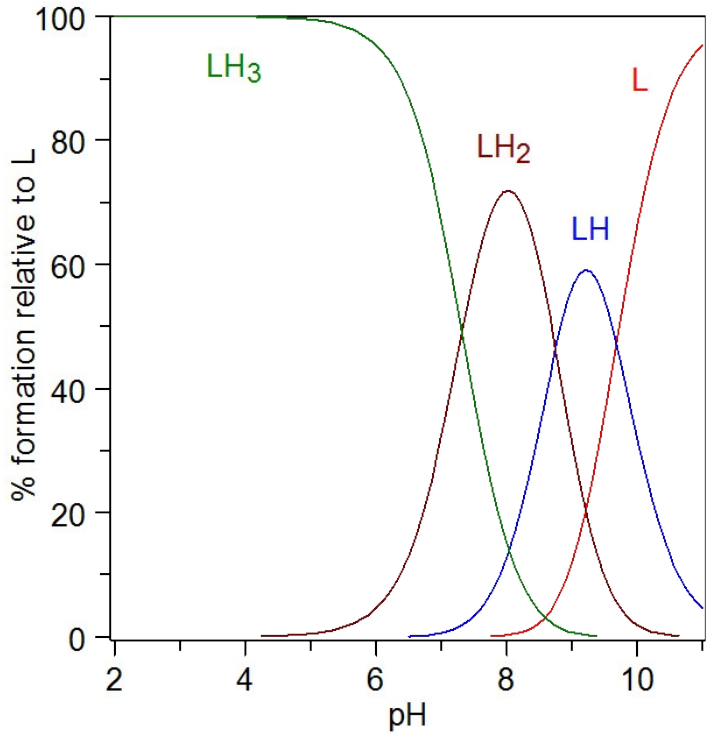
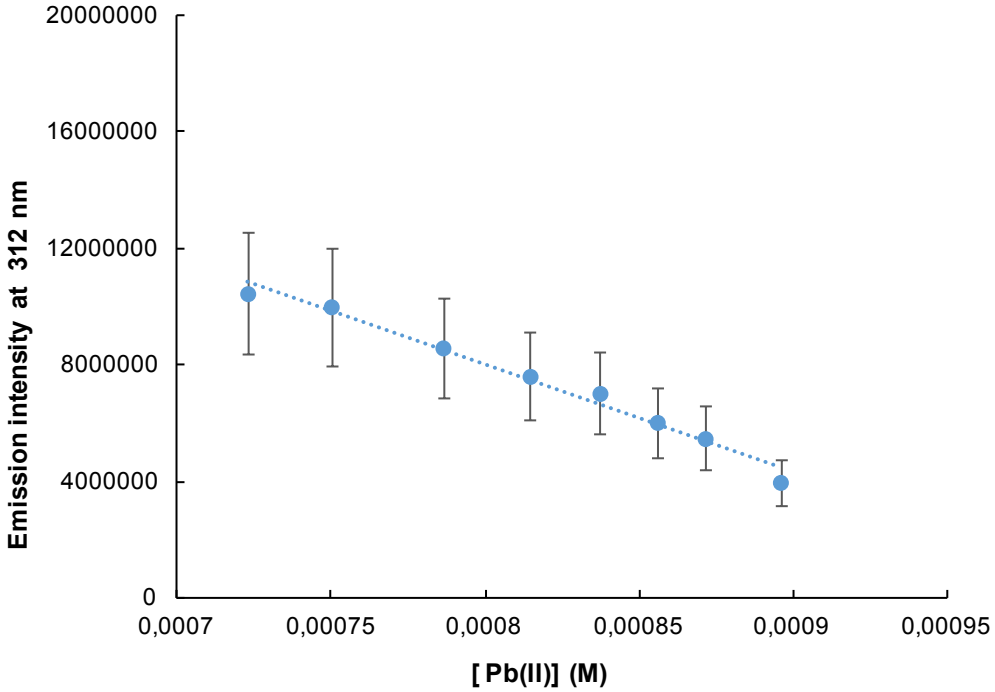


Fig. S2. Plot of the fluorescence intensity vs. [Pb^{2+}] for **L1.**



The detection limit depends on the instrumentation (i.e. the Signal-to-Noise Ratio gives you a quantitative indication of the sensitivity, in this case 352) and on the sensitivity of the ligand defined as the d(luminescence)/d[cation]. Using these two parameters, the limit of detection can then be calculated as 3* SNR/sensitivity. The mean value obtained from three independent measurements is 3.0 ± 0.2 ppb for **L1**.

Fig. S3. Fluorescence spectra of [Pb**L3**]$^{2+}$ (dotted line) and [H_3**L3**]$^{3+}$ (solid line) (excitation at 275 nm of a solution of the [Pb**L3**]$^{2+}$ complex causes fluorescence emission with a maximum at 320 nm).

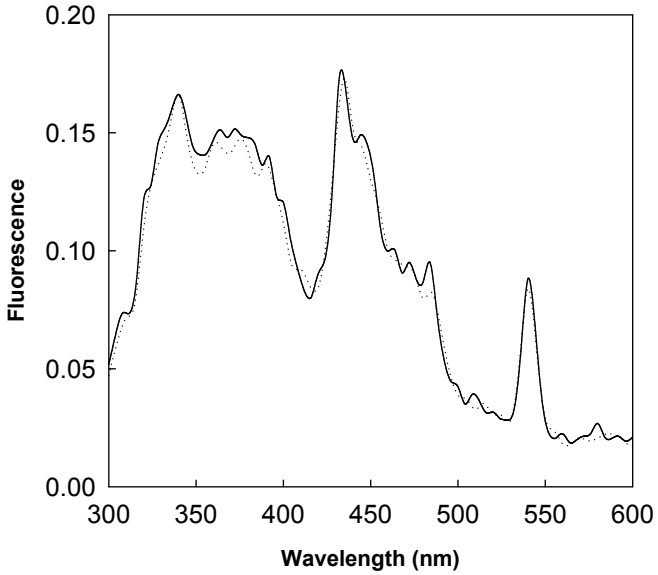


Fig. S4. pH effect on the electronic spectra of aqueous solutions containing **L2** ($[\mathbf{L2}]_0$= 1×10^{-4} M). The pH values were selected to achieve the maximum concentrations of $[H_3\mathbf{L2}]^{3+}$ (pH= 4) (solid line), $[H_2\mathbf{L2}]^{2+}$ (pH= 8.5) (dotted line), $[H\mathbf{L2}]^{+}$ (pH= 9.5) (dashed line) and **L2** (pH= 11) (dash-dotted line).

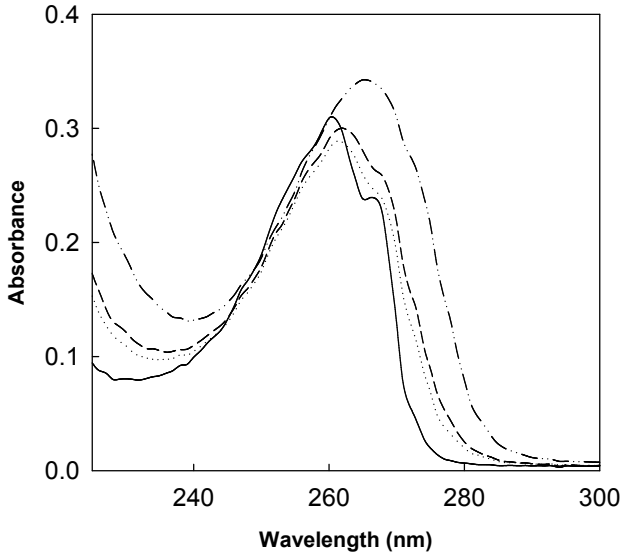


Fig. S5. pH effect on the electronic spectra of aqueous solutions containing **L2** and Pb^{2+} in 1:1 molar ratio ($[\mathbf{L2}]_0=[Pb^{2+}]_0=1\times10^{-4}$ M). The pH values were selected to achieve the maximum concentrations of $[Pb\mathbf{L2}]^{2+}$ (pH=9) (dashed line), $[PbH\mathbf{L2}]^{3+}$ (pH=5) (dotted line), and protonated ligand (pH=3) (solid line).

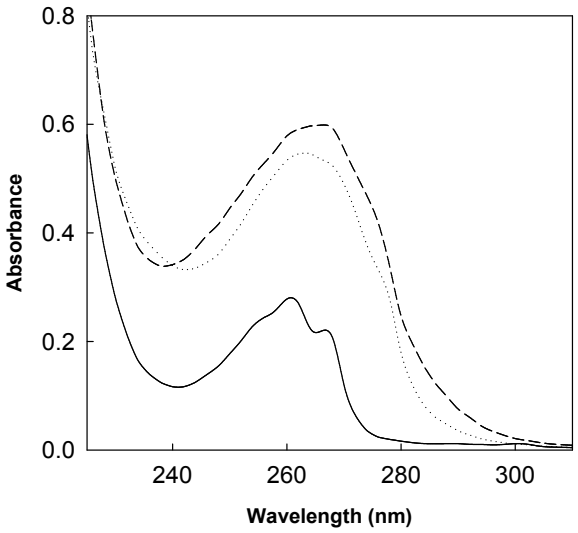


Fig. S6. Fluorescence spectra of [Pb**L2**]$^{2+}$ (dotted line) and [H_3**L2**]$^{3+}$ (solid line) (excitation at 275 nm of a solution of the [Pb**L2**]$^{2+}$ complex causes fluorescence emission with a maximum at 320 nm).

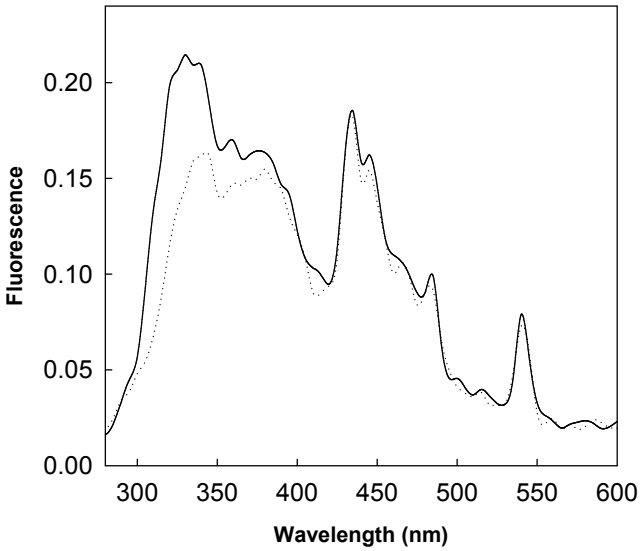


Fig. S7. pH effect on the electronic spectra of aqueous solutions containing **L1** ($[\mathbf{L1}]_0=1\times10^{-4}$ M). The pH values were selected to achieve the maximum concentrations of $[H_3\mathbf{L1}]^{3+}$ (pH=3) (solid line), $[H_2\mathbf{L1}]^{2+}$ (pH=7.5) (dotted line), $[H\mathbf{L1}]^{+}$ (pH=9) (dashed line) and **L1** (pH=11) (dash-dotted line). The mono and deprotonated species always exist as complex mixtures of species.

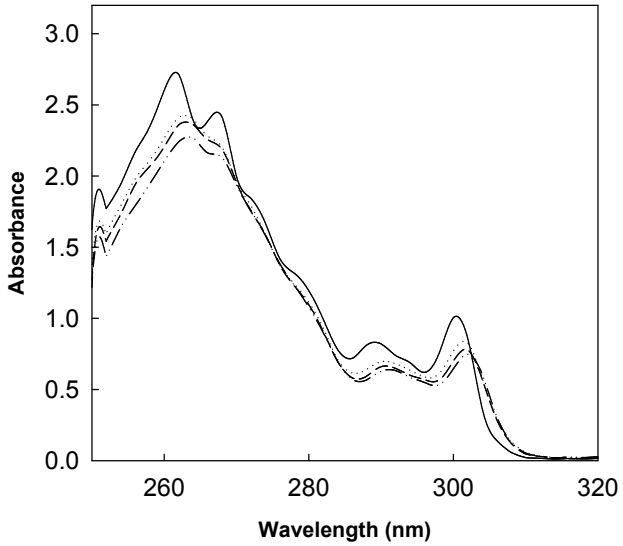


Fig. S8. pH effect on the electronic spectra of aqueous solutions containing **L1** and Pb^{2+} in 1:1 molar ratio ($[\mathbf{L1}]_0=[Pb^{2+}]_0=1\times10^{-4}$ M). The pH values were selected to achieve the maximum concentrations of $[Pb\mathbf{L1}]^{2+}$ (pH=8.3) (dashed line), $[PbH\mathbf{L1}]^{3+}$ (pH=5) (dotted line), and protonated ligand (pH=2) (solid line).

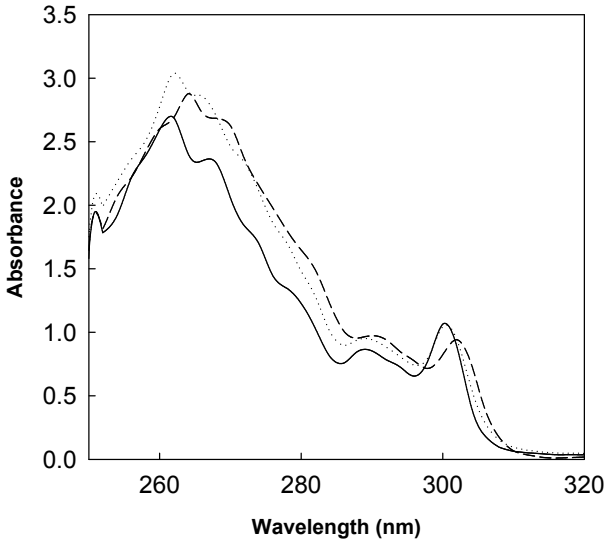


Fig. S9. Fluorescence spectra of [Pb**L1**]$^{2+}$ (dotted line) and [H_3**L1**]$^{3+}$ (solid line) (excitation at 275 nm of a solution of the [Pb**L1**]$^{2+}$ complex causes fluorescence emission with a maximum at 320 nm).

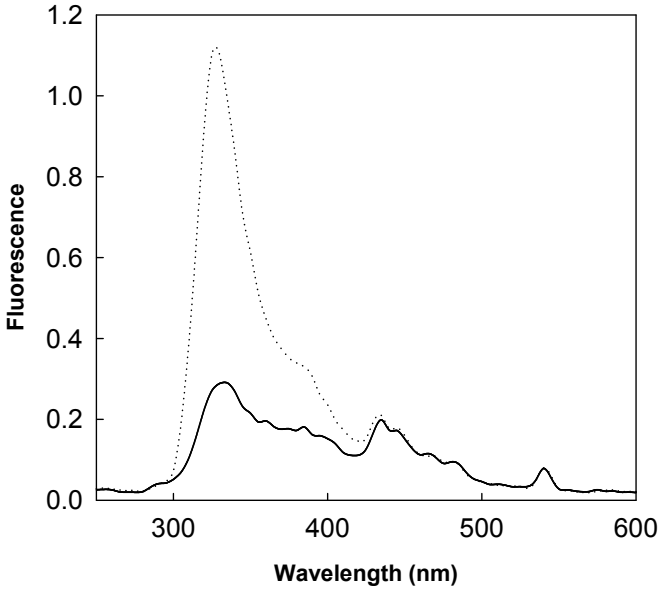


Table S1. Crystallographic data for **1** and **2**

Compound	**1**	**2**
Empirical formula	$C_{54}H_{68}Cl_3N_{11}O_7Pb_2$	$C_{11}H_{18}Cl_2N_4O_8Pb$
Formula weight	1503.92	612.38
Temperature	120(1)	293(2)
Crystal system	orthorhombic	monoclinic
Space group	Pbcn	$P2_1/c$
Unit cell dimensions		
a(Å)	13.1619(4)	8.8925(3)
b(Å)	13.0751(4)	15.1543(5)
c(Å)	33.1703(10)	13.5209(5)
α(°)	90	90
β(°)	90	101.1503(13)
γ(°)	90	90
Volume Å^3	5708.4(3)	1787.68(11)
Z	4	4
Density calc (g/cm^3)	1.75	2.275
Crystal size (mm)	0.17× 0.15 ×0.1	0.1×0.05×0.05
Wavelength	0.71073	0.71073
F(000)	2960	1168
μ (mm^{-1})	6.092	9.785
Absorption correction	Multiscan	Multiscan
Θ range	6.59 to 27.38	0.998 to 27.485
reflns collected	13519	7719
indep reflns	5006	4063
R(int)	0.0405	0.0588
data/restr/param	5006/104/445	4063/0/235
Final R indices[I >2 σ(I)]	R_1 = 0.0651,	R_1=0.0455
	wR_2 = 0.0765;	wR_2=0.1222
Final R indices [all data]	R_1 = 0.1313,	R_1=0.1077
	wR_2 = 0.1350;	wR_2=0.1612
GOF (F^2)	1.368	0.881