# A phenylbenzoxazole-amide-azacrown linkage as a selective fluorescent receptor for ratiometric sening of Pb(II) in aqueous media

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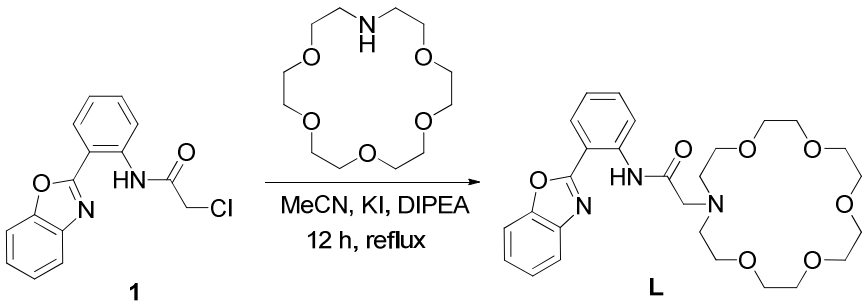
## Electronic Supplementary Information (ESI†)

## CONTENTS

## Experimental

### Materials.

All reagents were supplied from Wako, Sigma-Aldrich, and Tokyo Kasei and used without further purification. Perchlorate ($Cu^{2+}$, $Na^{+}$, $Hg^{2+}$, $Fe^{2+}$, $Mn^{2+}$, $Cr^{3+}$, $Fe^{3+}$, $Co^{2+}$, $Zn^{2+}$, $Mg^{2+}$, $Li^{+}$, $Ni^{2+}$, $Cd^{2+}$, $K^{+}$, $Ca^{2+}$, $Pb^{2+}$) and tetrafluoroborate ($Ag^{+}$) salts were used as the metal cation source. Water was purified by the Milli-Q system. **1** was synthesized according to literature procedure.[1]




### Synthesis of L.

**1** (86.0 mg, 0.30 mmol), 1-aza-18-crown 6-ether (92.2 mg, 0.35 mmol), KI (30 mg), and DIPEA (500 μL) were added to MeCN (40 mL), and the solution was refluxed for 12 h under $N_2$. The resultant was concentrated by evaporation and purified by silica gel column chromatography ($CH_2Cl_2$/MeOH, 11/1 v/v), affording **L** as a yellow solid (80.0 mg, 52%). $^1$H NMR (400 MHz, $CD_3OD$, TMS): δ = 2.88–2.91 (m, 4H), 3.54–3.71 (m, 22H), 7.31 (t, $J$ = 7.10 Hz, 1H), 7.44–7.47 (m, 2H), 7.56–7.60 (m, 1H), 7.69–7.71 (m, 1H), 7.83–7.85 (m, 1H), 8.25 (dd, $J$ = 1.37, 7.79 Hz, 1H), 8.70 (d, $J$ = 8.24 Hz, 1H). $^{13}$C NMR (100 MHz, $CD_3OD$, TMS): δ = 173.13, 163.15, 150.82, 142.14, 139.45, 133.75, 129.80, 127.30, 126.37, 125.08, 122.21, 120.88, 115.29, 111.85, 71.19, 71.08, 71.04, 71.02, 69.38, 59.74, 57.83. FAB–MS: m/z calcd for $C_{27}H_{35}N_3O_7$: 513.25; found: 536.4 [M + $Na^{+}$]. HR–MS (FAB): m/z calcd for [M + $Na^{+}$], 536.2373; Found, 536.2377.

### Measurements.

UV–vis absorption spectra were measured at 298 K on an UV–visible photodiode–array spectrophotometer (Shimadzu; Multispec–1500) equipped with a temperature controller.[2] Fluorescence spectra were measured at 298 K on a JASCO FP–6500 fluorescence spectrophotometer equipped with a temperature controller. FT-IR spectra were recorded at room temperature using a JASCO FTIR–610 spectrometer with a liquid sample cell with a $CaF_2$ window.[3] $^1$H and $^{13}$C NMR spectra were obtained by a JEOL JNM–AL400 spectrometer using TMS as standard. FAB and ESI–MS analysis was performed by a JEOL–JMS 700 Mass Spectrometer.

### Potentiometric titration.

The titrations were performed on a COMTITE–550 potentiometric automatic titrator (Hiranuma Co., Ltd.) with a glass electrode GE–101.[4,5] Aqueous solution (water/MeCN, 1/1 v/v) containing

**L** in the absence or presence of $Pb(ClO_4)_2$ (1 equiv) was kept under dry $N_2$ at 298 K. The titration was done at 298 ± 1 K in the presence of 0.15 M NaCl. The program HYPERQUAD was used for determination of protonation and stability constants.[6] $K_w$ (= $[H^+]\cdot[OH^-]$) value used was $10^{-14.00}$ (298 K). The stability constants used for $Pb^{2+}$ hydrolysis (298 K) were log K $(Pb(OH)/Pb\cdot OH) = -8.00$, $(Pb(OH)_2/Pb\cdot 2OH) = -17.41$, $(Pb(OH)_3/Pb\cdot 3OH) = -28.06$, $(Pb_2(OH)/2Pb\cdot OH) = -6.07$, $(Pb_3(OH)_4/3Pb\cdot 4OH) = -24.45$, $(Pb_4(OH)_4/4Pb\cdot 4OH) = -20.31$, and $(Pb_6(OH)_8/6Pb\cdot 8OH) = -43.61$, respectively.[7]

**Computational details.**

Ab initio calculations were carried out with the Gaussian 03 program.[8] Geometry optimization was performed with the density functional theory (DFT) using the B3LYP function within the Gaussian 03 program. Calculations were carried out using the 6–31G* basis set for all atoms except for $Pb^{2+}$, for which Stuttgart/Dresden (SDD)[9] basis set with effective core potential was used. Electronic excitation energies and oscillator strengths were calculated with the time–dependent density functional theory (TDDFT) at the same level of optimization using the polarizable continuum model (PCM)[10] with water as a solvent. Cartesian coordinates for respective compounds are summarized in the end of this ESI.

**References**

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**Table S1.** Calculated excitation energy (*E*), wavelength (λ), and oscillator strength (*f*) for low-laying singlet state ($S_n$) of **L** and **L**–$Pb^{2+}$.

| Species | | Main orbital transition (CIC[a]) | *E* / eV | λ / nm | *f* |
|---|---|---|---|---|---|
| **L** | $S_0 \rightarrow S_1$ | HOMO→LUMO (0.70109) | 3.1850 | 389.28 | 0.0007 |
| | $S_0 \rightarrow S_2$ | HOMO−1→LUMO (0.64740) | 3.8267 | 323.99 | 0.4833 |
| **L**–$Pb^{2+}$ | $S_0 \rightarrow S_1$ | HOMO→LUMO (0.66580) | 3.8539 | 321.71 | 0.6499 |
| | $S_0 \rightarrow S_2$ | HOMO−1→LUMO (0.42379) | 4.2011 | 295.13 | 0.0732 |

[a] CI expansion coefficients for the main orbital transitions.

**Table S2.** Protonation/stability constants of **L**.[a]

| Reaction | log K |
|---|---|
| **L** + $H^+$ = **L**H | 6.04 ± 0.19 |
| **L** + $Pb^{2+}$ = **L**–$Pb^{2+}$ | 6.20 ± 0.25 |

[a] Measurements were carried out in an aqueous solution (water/MeCN; 1/1 v/v) at 298 K in the presence of 0.15 M NaCl.

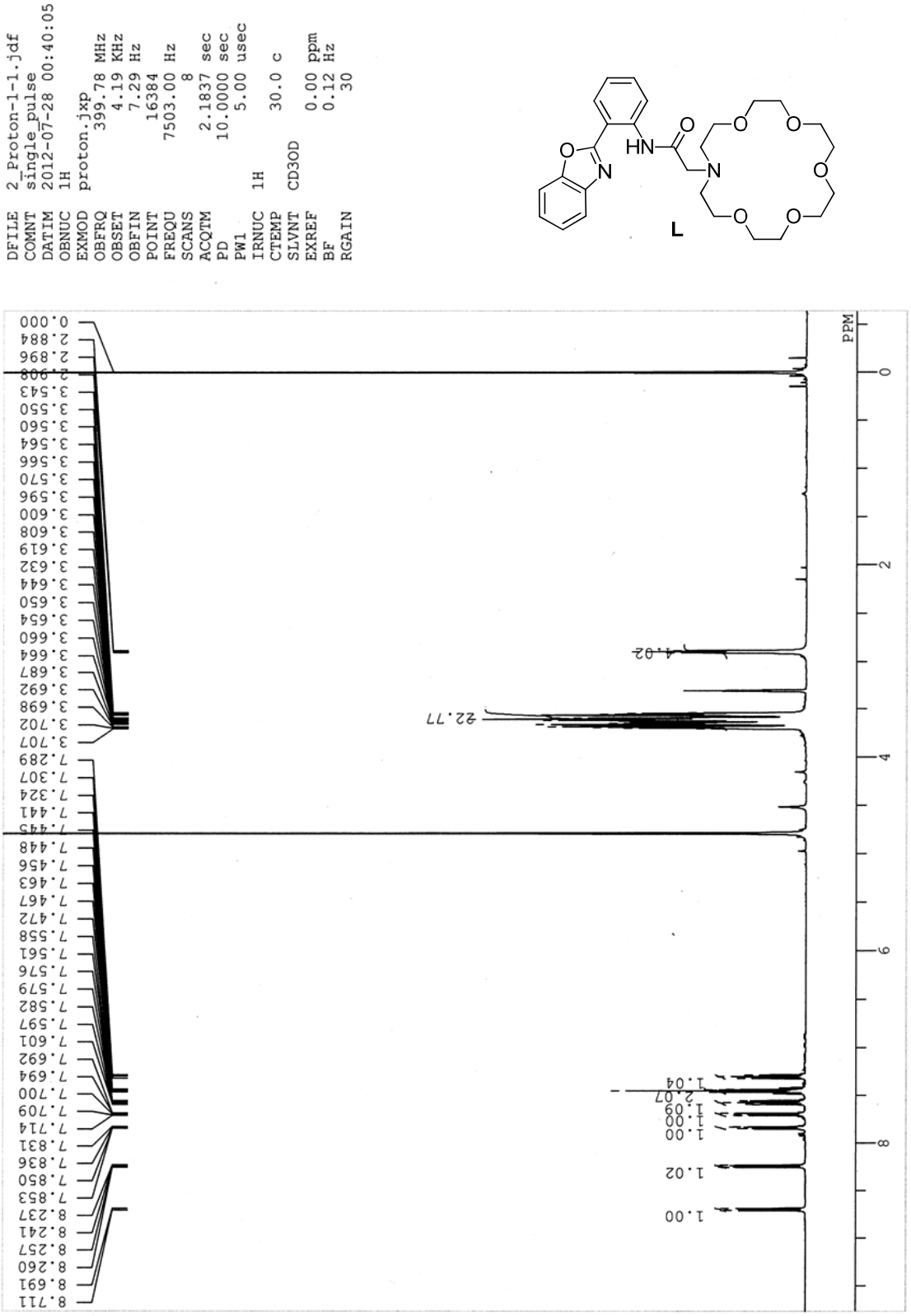



**Fig. S1** $^{1}$H NMR chart of **L** in $CD_3OD$ (400 MHz).

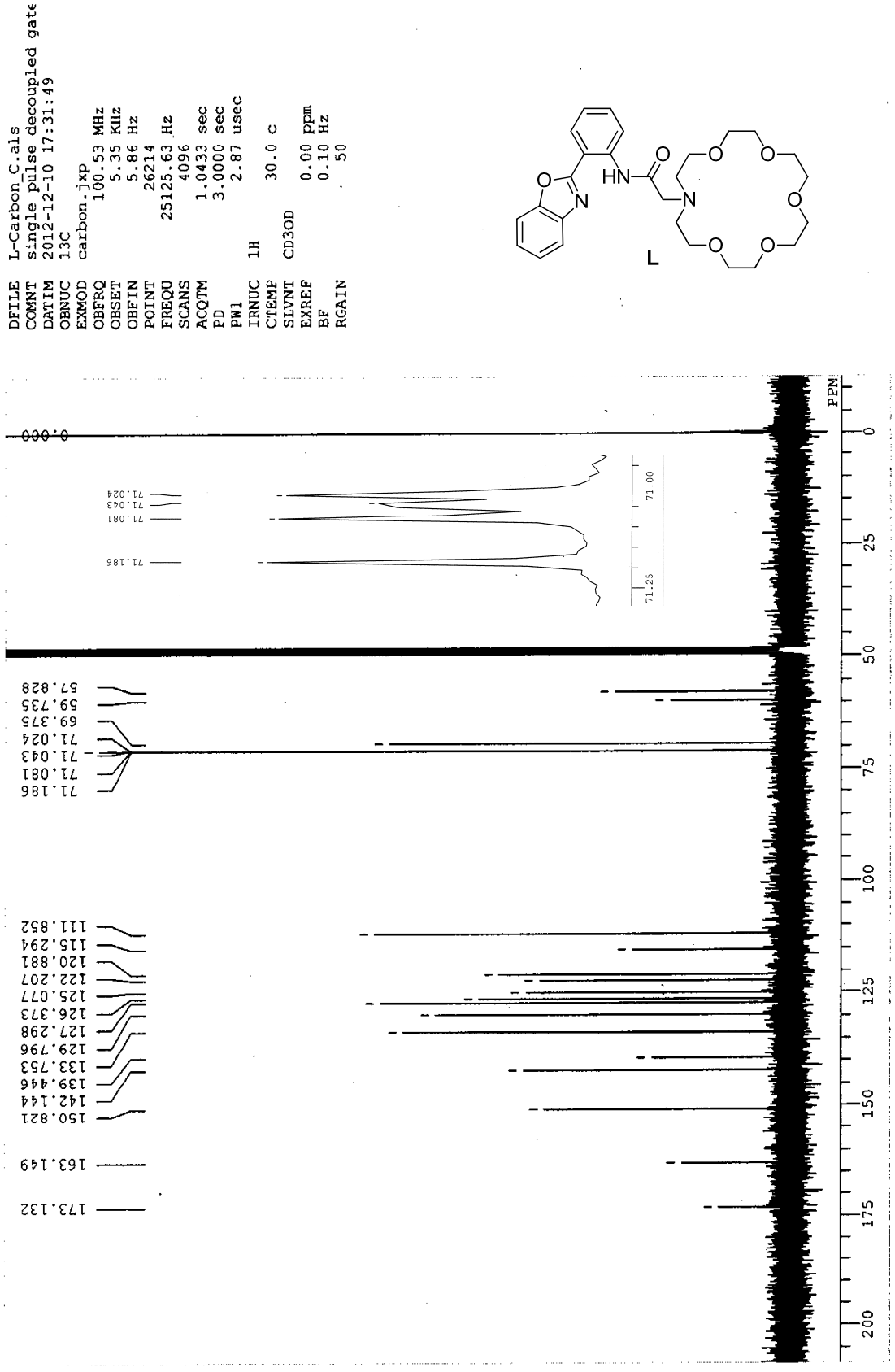



**Fig. S2** $^{13}$C NMR chart of **L** in $CD_3OD$ (100 MHz).

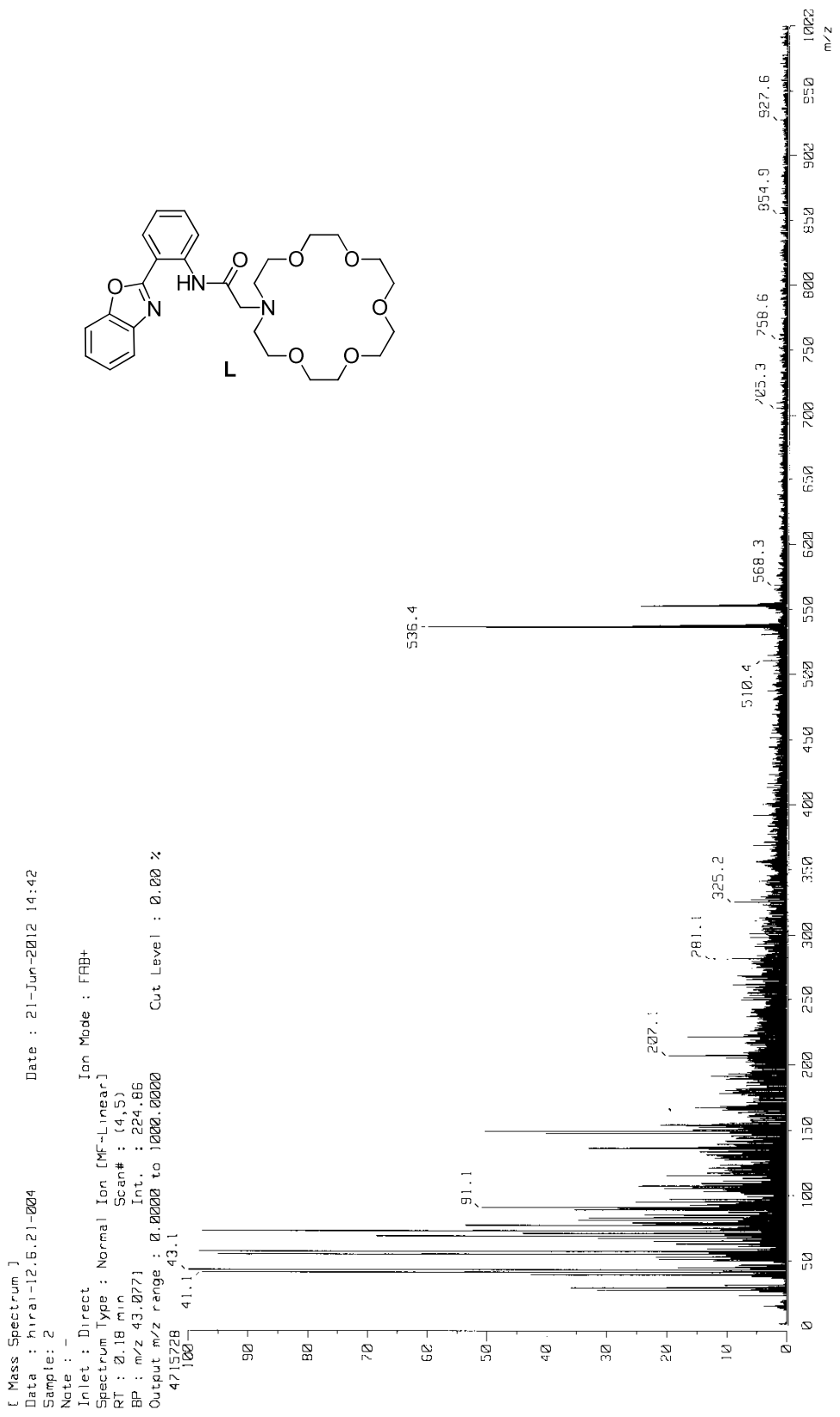



**Fig. S3** FAB–MS chart of **L**.

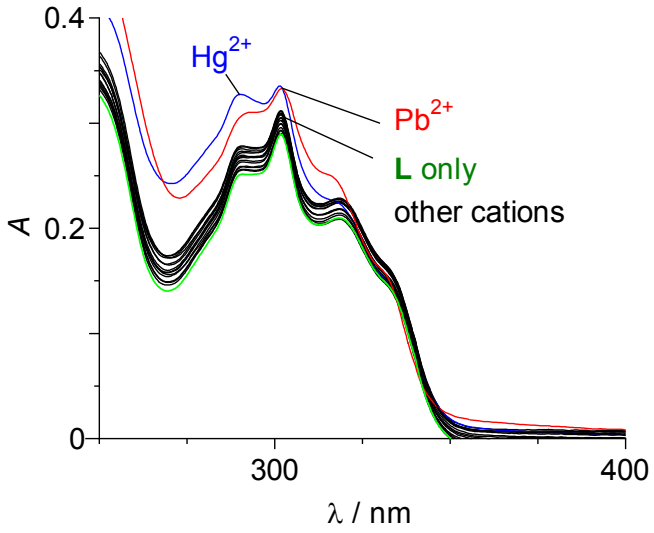



**Fig. S4** Absorption spectra of **L** (20 μM) measured in a buffered water/MeCN mixture (1/1 v/v; HEPES 100 mM; pH 7.0) with each respective metal cation (1 equiv).

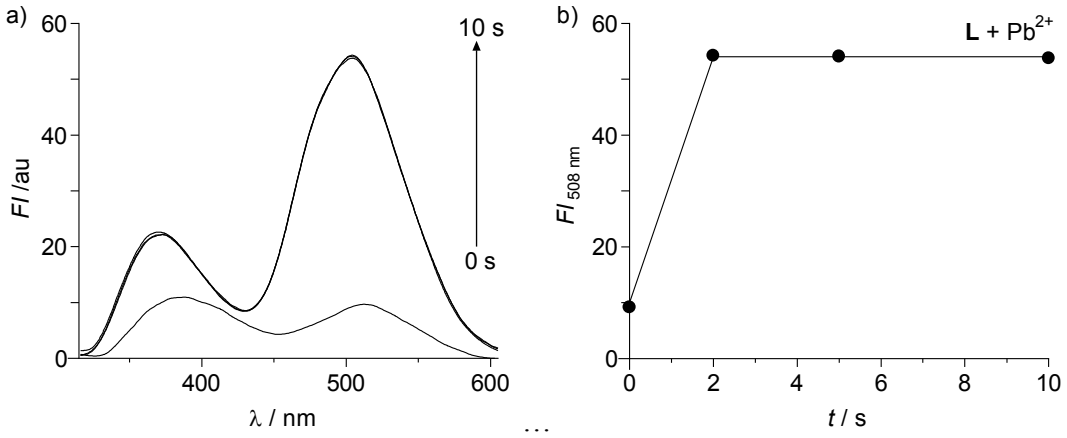



**Fig. S5** (a) Time-dependent change in fluorescence spectra ($\lambda_{ex}$ = 311 nm) of **L** (20 μM) measured in a buffered water/MeCN mixture (1/1 v/v; HEPES 100 mM; pH 7.0), after addition of 1 equiv of $Pb^{2+}$. (b) Change in fluorescence intensity at 508 nm.

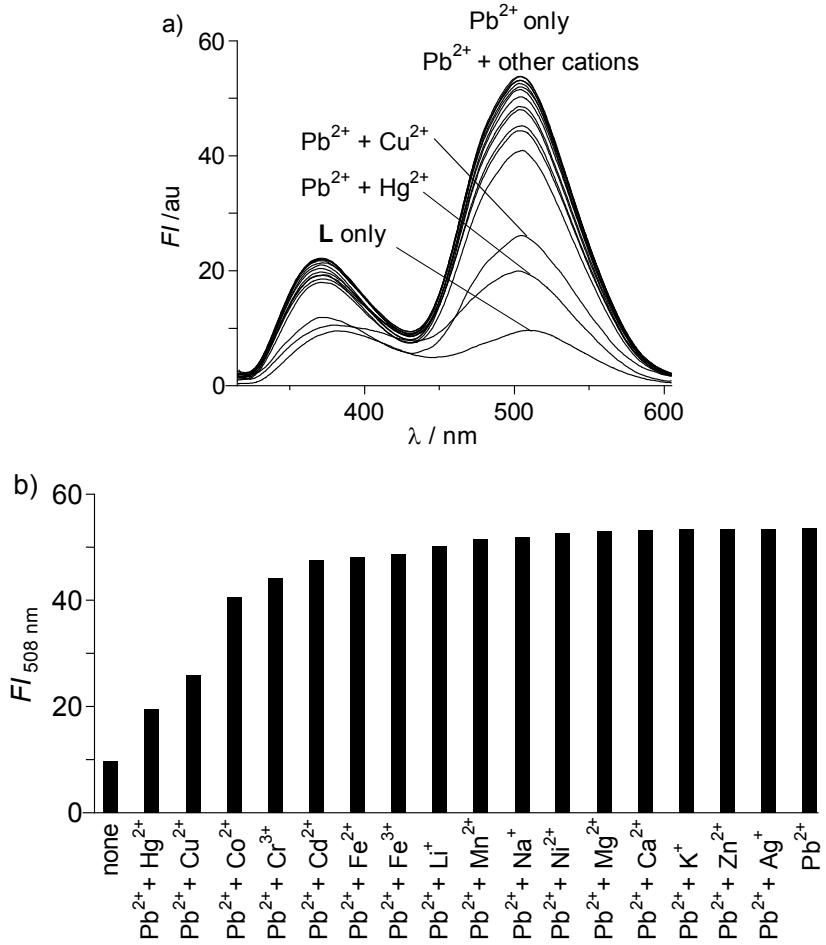



**Fig. S6** (a) Fluorescence spectra ($\lambda_{ex}$ = 311 nm) of **L** (20 μM) measured in a buffered water/MeCN mixture (1/1 v/v; HEPES 100 mM; pH 7.0) with 1 equiv of $Pb^{2+}$ together with 1 equiv of other respective metal cation. (b) Fluorescence intensity at 508 nm.

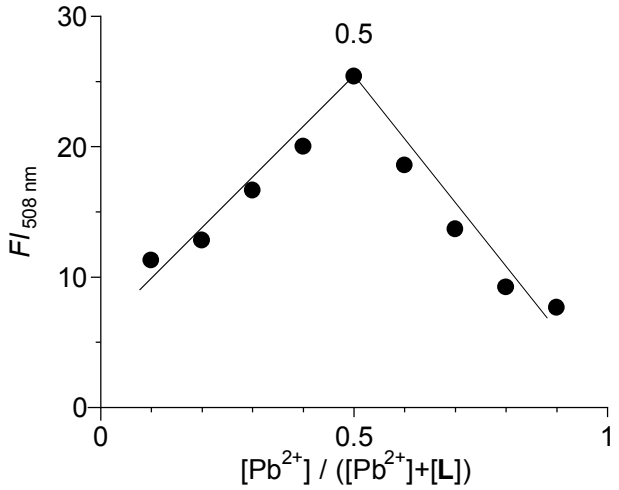



**Fig. S7** Job's plot of **L** with $Pb^{2+}$ obtained by fluorescence measurements ($\lambda_{ex}$ = 311 nm). Total concentration of **L** and $Pb^{2+}$ is 20 μM.

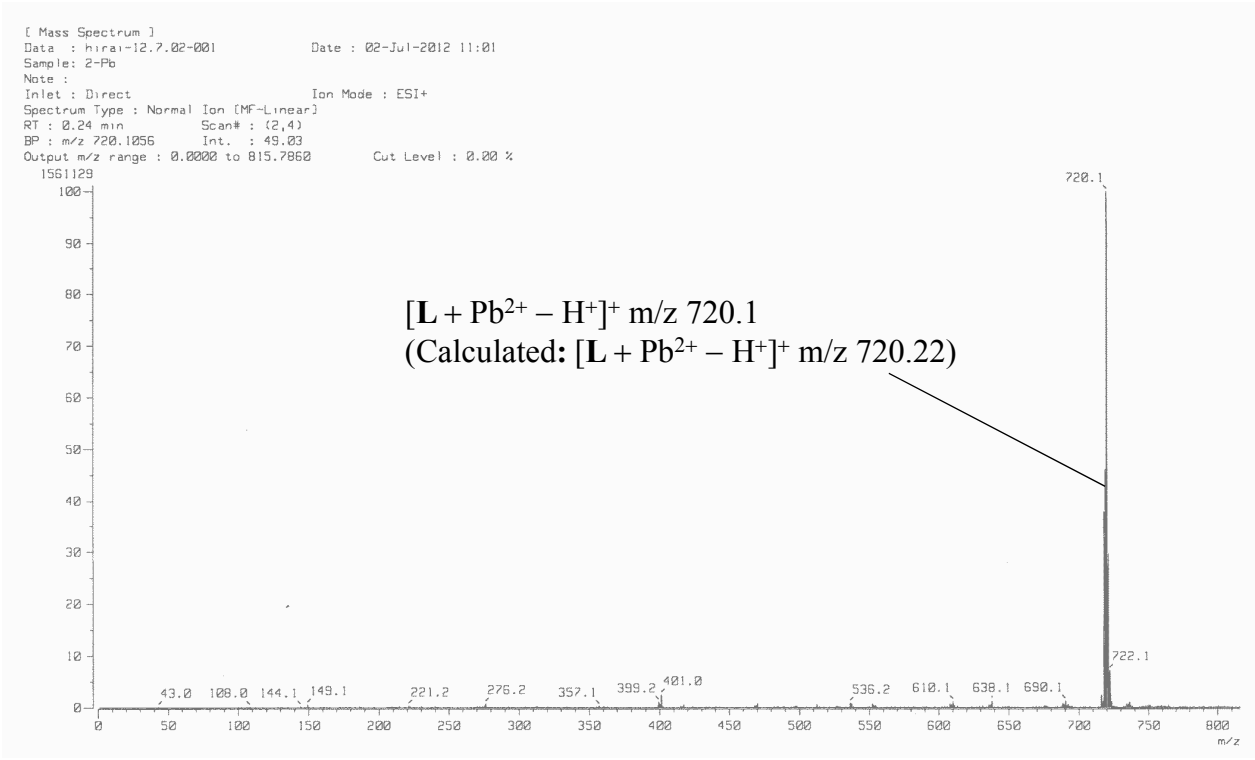



**Fig. S8** ESI–MS chart of a water/MeCN (1/1 v/v) mixture containing of **L** and 1 equiv of $Pb(ClO_4)_2$.

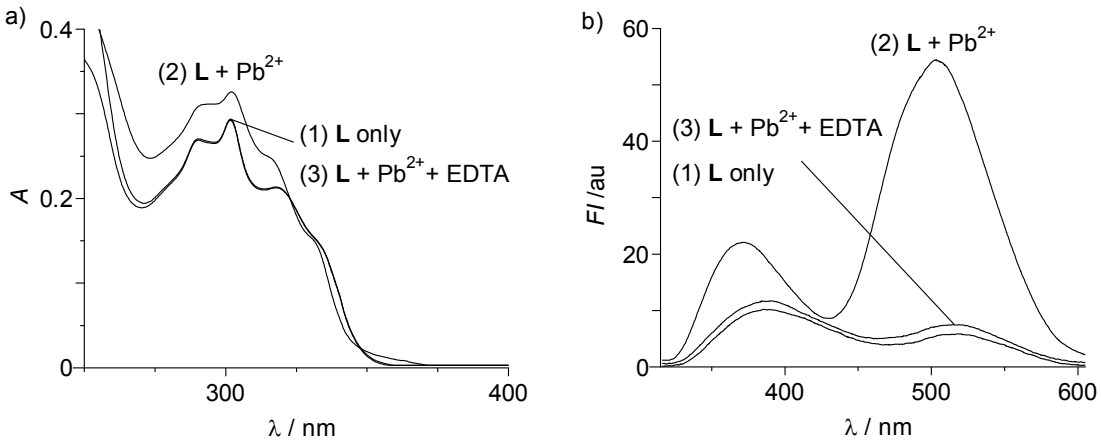



**Fig. S9** (a) Absorption and (b) fluorescence spectra ($\lambda_{ex}$ = 311 nm) of **L** (20 μM) in a buffered water/MeCN mixture (1/1 v/v; HEPES 100 mM; pH 7.0) measured (1) without cations, (2) with $Pb^{2+}$ (1 equiv), and (3) after addition of EDTA (20 equiv) to the sample (2).

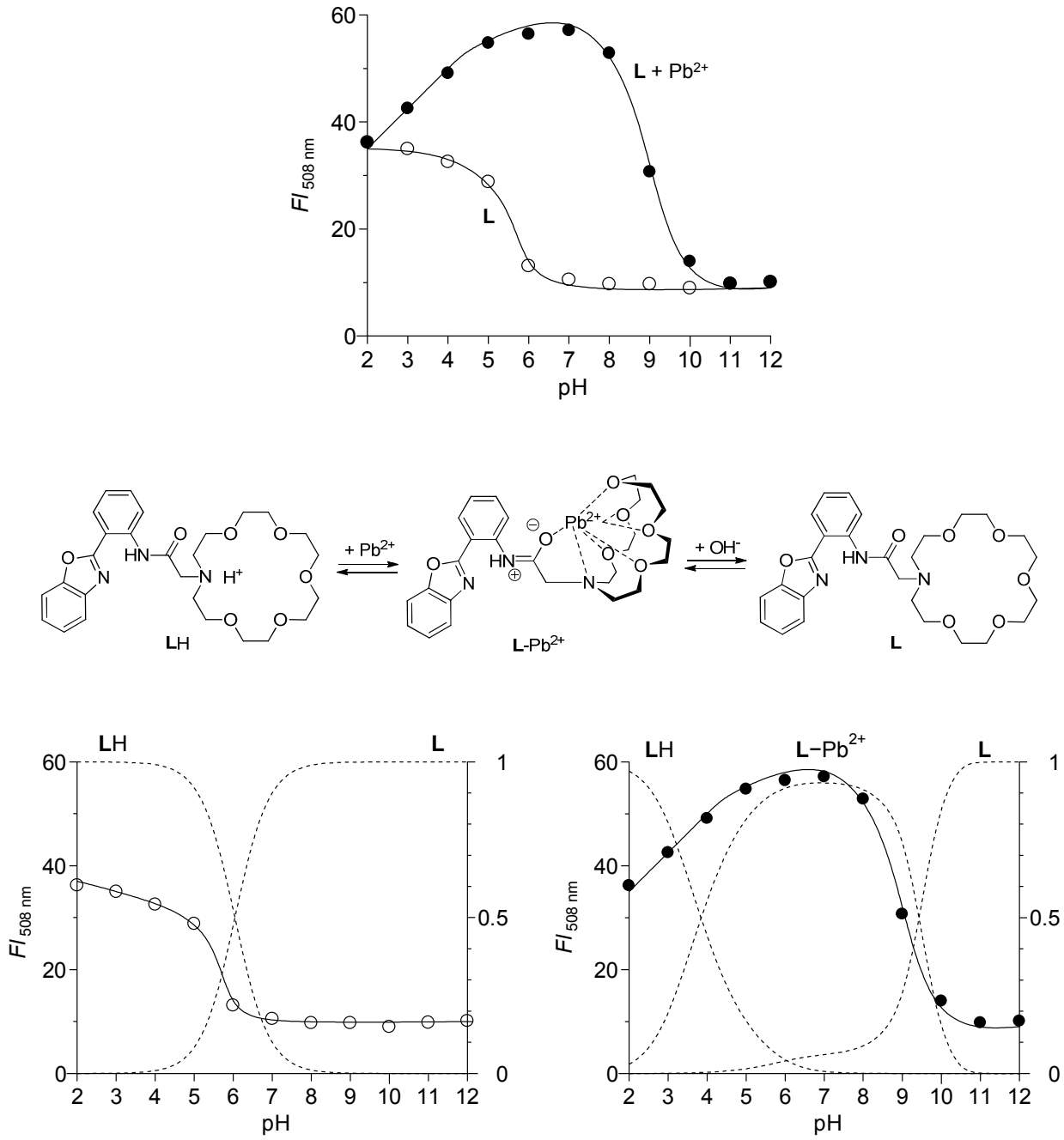



**Fig. S10** (Top) Effect of pH on the fluorescence spectra of **L** measured in a water/MeCN (1/1 v/v) mixture with or without 1 equiv of $Pb^{2+}$. (Bottom) Relationship between the fluorescence intensity and the mole fraction distribution of species determined by potentiometric titration (Table S2).

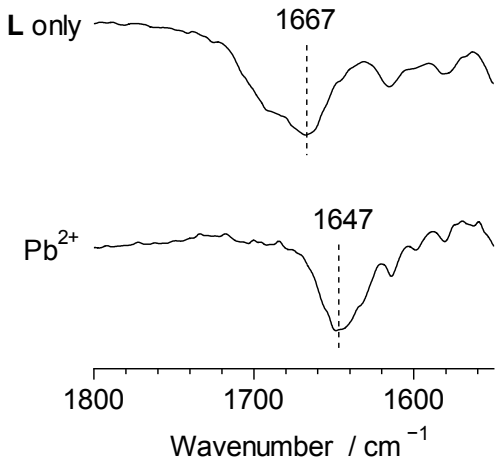



**Fig. S11** IR spectra of **L** (2 mM) measured at 298 K in a $D_2O$/MeCN (1/1 v/v, pH 7.0) mixture with and without $Pb^{2+}$ (1 equiv).

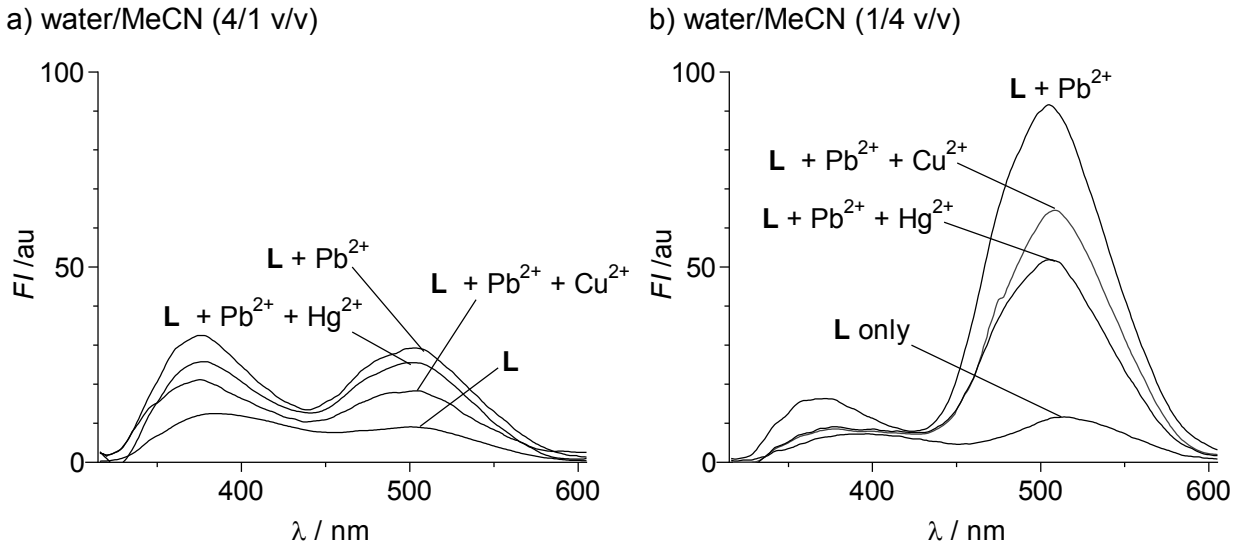
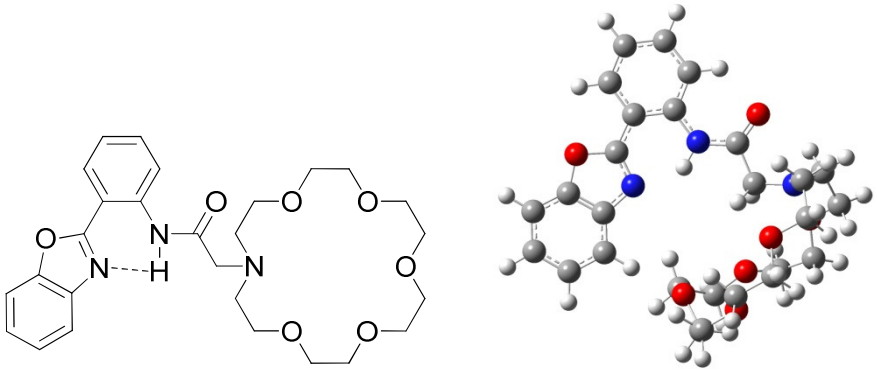



**Fig. S12** Fluorescence spectra ($\lambda_{ex}$ = 311 nm) of **L** (20 μM) in a buffered water/MeCN mixture (HEPES 100 mM; pH 7.0) with solvent composition, measured with 1 equiv of $Pb^{2+}$ together with 1 equiv of $Cu^{2+}$ or $Hg^{2+}$.

## Cartesian coordinates (in Å) of L



| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
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| C | 4.760101 | -3.903607 | -0.318499 | C | -3.354039 | -1.112962 | -3.267125 | H | -3.249275 | 3.250518 | -2.229155 |
| C | 3.362796 | -4.066715 | -0.299934 | O | -0.742721 | -2.6374 | 0.699994 | H | -3.581498 | 1.532926 | -3.903183 |
| C | 2.496086 | -2.977409 | -0.202716 | C | -1.693877 | -3.640406 | 0.395243 | H | -4.421559 | 1.04706 | -2.405854 |
| C | 3.077476 | -1.709386 | -0.123784 | C | -1.859235 | -3.693373 | -1.11298 | H | -3.010385 | -3.222513 | -3.449633 |
| C | 4.471047 | -1.571987 | -0.144403 | C | -3.247746 | 2.921744 | 0.292715 | H | -1.522895 | -2.249144 | -3.312603 |
| N | 2.513762 | -0.439585 | -0.021174 | C | -4.210697 | 2.197354 | 1.230018 | H | -3.510951 | -1.063747 | -4.359641 |
| C | 3.526235 | 0.385884 | 0.008721 | O | -3.461573 | 1.390397 | 2.127584 | H | -4.34472 | -1.187509 | -2.789984 |
| O | 4.758413 | -0.232653 | -0.058687 | C | -4.174775 | 0.296965 | 2.657203 | H | -2.666436 | -3.41508 | 0.853562 |
| C | 3.515527 | 1.838298 | 0.089075 | C | -3.217765 | -0.600733 | 3.417617 | H | -1.356086 | -4.626636 | 0.759943 |
| C | 2.306177 | 2.59476 | 0.048394 | O | -2.252438 | -1.106517 | 2.515464 | H | -0.864973 | -3.747716 | -1.58555 |
| C | 2.395619 | 3.998816 | 0.11291 | C | -1.521245 | -2.200193 | 3.020149 | H | -2.411312 | -4.610148 | -1.388864 |
| C | 3.629701 | 4.629276 | 0.216927 | C | -0.376433 | -2.519271 | 2.062303 | H | -3.825621 | 3.668753 | -0.264497 |
| C | 4.81644 | 3.892074 | 0.259648 | H | 6.426055 | -2.49906 | -0.253603 | H | -2.5146 | 3.479789 | 0.890378 |
| C | 4.749205 | 2.509407 | 0.194756 | H | 5.397411 | -4.779809 | -0.396195 | H | -4.891775 | 1.570661 | 0.634541 |
| N | 1.075105 | 1.934846 | -0.043245 | H | 2.950507 | -5.069999 | -0.363869 | H | -4.819568 | 2.925904 | 1.795117 |
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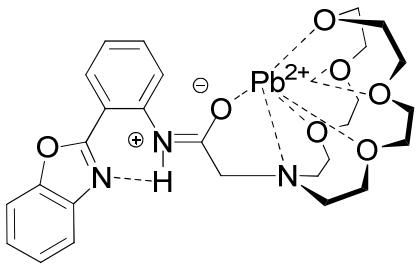
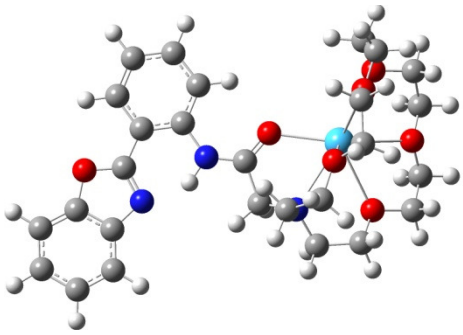
| O | -0.378005 | 3.683765 | -0.433033 | H | 1.482187 | 4.572631 | 0.06808 | H | -4.974452 | 0.630942 | 3.34291 |
| C | -1.329724 | 1.460866 | -0.232752 | H | 3.661023 | 5.714641 | 0.265836 | H | -3.797578 | -1.421445 | 3.8738 |
| C | -2.701171 | 2.312438 | -2.077415 | H | 5.778174 | 4.38942 | 0.341334 | H | -2.729209 | -0.04023 | 4.231131 |
| N | -2.596763 | 2.018668 | -0.652821 | H | 5.657064 | 1.917628 | 0.22364 | H | -2.184189 | -3.072273 | 3.15742 |
| O | -2.663279 | 0.025895 | -2.803712 | H | 1.133086 | 0.915191 | -0.009766 | H | -1.080431 | -1.975646 | 4.007471 |
| C | -3.429064 | 1.216958 | -2.854365 | H | -1.432072 | 1.065467 | 0.78427 | H | 0.353635 | -1.705364 | 2.082241 |
| O | -2.556151 | -2.542204 | -1.535746 | H | -1.087305 | 0.599411 | -0.865455 | H | 0.122153 | -3.438469 | 2.418925 |

## Cartesian coordinates (in Å) of L–$Pb^{2+}$ complex



| | | | | | | | | | | | |
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| C | -7.791185 | -2.817527 | -0.047571 | C | 5.119608 | 1.722346 | -1.424298 | H | 2.518771 | -3.610151 | 0.761909 |
| C | -6.442882 | -2.468266 | -0.058699 | C | 5.005347 | 0.550252 | -2.375959 | H | 5.454274 | -2.043457 | -2.761456 |
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| C | -4.352779 | 2.001922 | -0.269577 | O | 3.416706 | 1.426294 | 1.70165 | H | 4.341661 | 0.794644 | -3.21684 |
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| C | -2.686377 | 4.256486 | -0.400605 | H | -9.297856 | 0.276515 | -0.193468 | H | -0.670825 | -1.024023 | 2.063039 |
| C | -4.072716 | 4.415125 | -0.399516 | H | -9.847085 | -2.16456 | -0.084687 | H | 1.79795 | -2.76869 | 2.575813 |
| C | -4.895051 | 3.295118 | -0.333982 | H | -8.069083 | -3.865825 | -0.001981 | H | 0.859693 | -1.834221 | 3.754503 |
| N | -2.427818 | 0.527651 | -0.217928 | H | -5.660798 | -3.219629 | -0.023817 | H | 3.879014 | -0.993415 | 2.916347 |
| C | -1.178408 | 0.079714 | -0.230047 | H | -1.044174 | 2.864557 | -0.338084 | H | 2.763252 | -0.620069 | 4.256107 |
| O | -0.146814 | 0.812147 | -0.226709 | H | -2.038761 | 5.126212 | -0.453481 | H | 4.260815 | 1.307737 | 3.606372 |
| C | -1.042229 | -1.443363 | -0.336516 | H | -4.512786 | 5.405648 | -0.45055 | H | 2.521011 | 1.698714 | 3.552242 |
| C | 0.52922 | -3.307929 | -0.136906 | H | -5.972949 | 3.408485 | -0.334304 | H | 5.213505 | 2.4386 | 1.508697 |
| N | 0.153602 | -1.955059 | 0.371741 | H | -3.192528 | -0.181254 | -0.192454 | H | 3.868332 | 3.419389 | 2.133217 |
| O | 2.631574 | -2.57107 | -1.037088 | H | -0.934138 | -1.670208 | -1.403348 | H | 2.716354 | 3.456491 | 0.011014 |
| C | 2.028443 | -3.580911 | -0.220124 | H | -1.961561 | -1.939204 | 0.005674 | H | 4.395573 | 3.948646 | -0.281679 |
| O | 4.489524 | -0.57193 | -1.647507 | H | 0.130774 | -3.409385 | -1.149422 | Pb | 2.120923 | -0.065601 | -0.141364 |
| C | 4.449939 | -1.787074 | -2.397731 | | | | | | | | |