Supplementary Material

A new benzoxazole-based fluorescent macrocyclic chemosensor for optical detection of Zn^{2+} and Cd^{2+}

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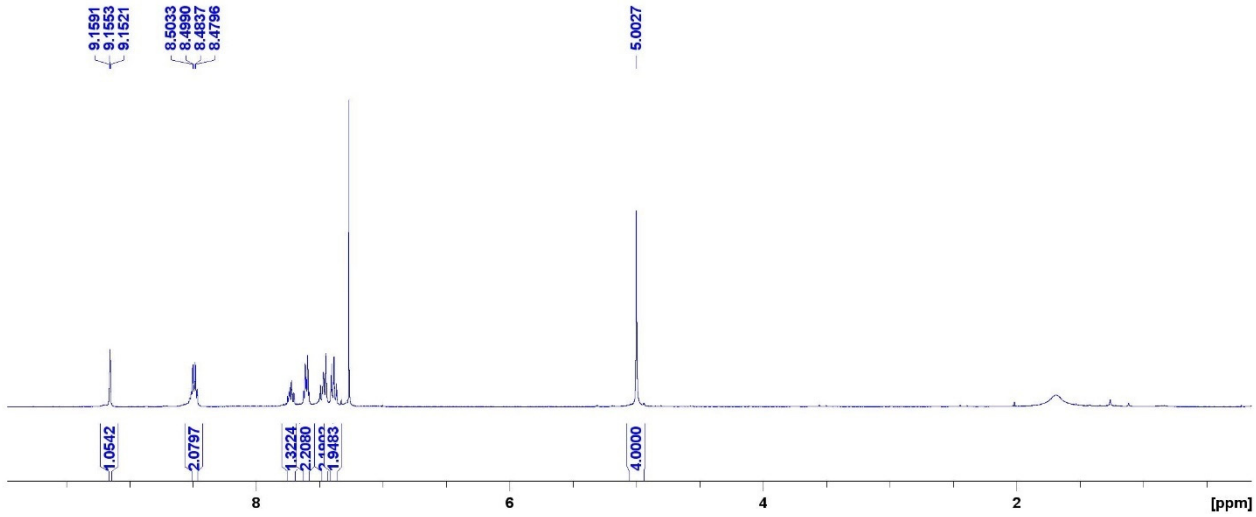

Figure S1. ^{1}H NMR spectrum of **4** in $CDCl_3$.

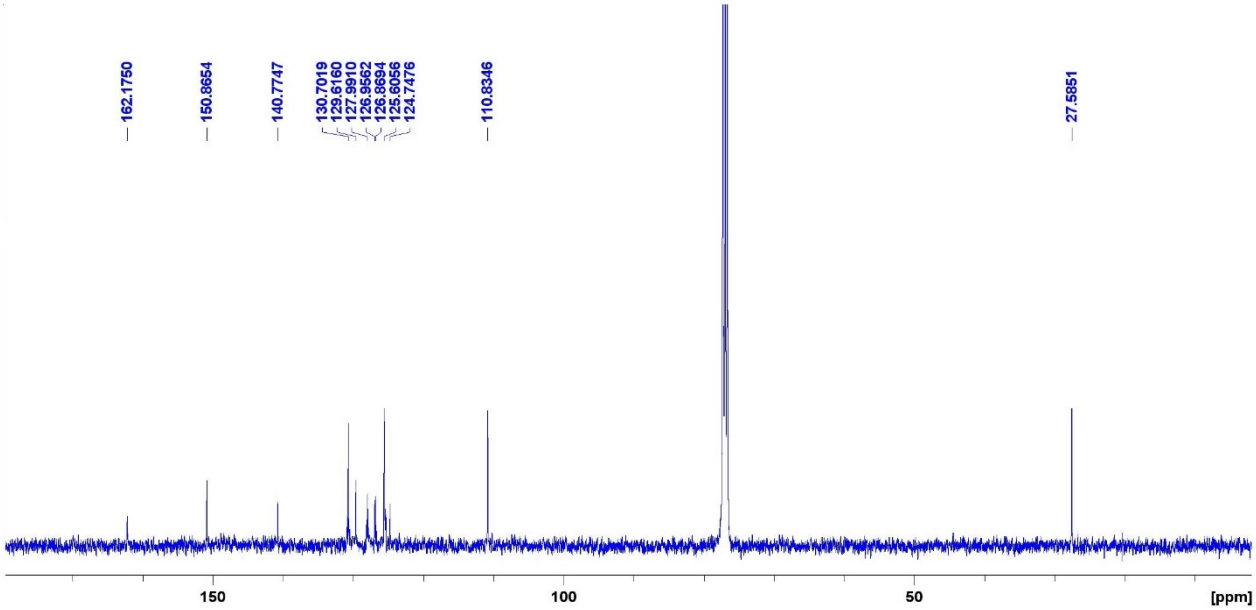

Figure S2. ^{13}C NMR spectrum of compound **4** in $CDCl_3$.

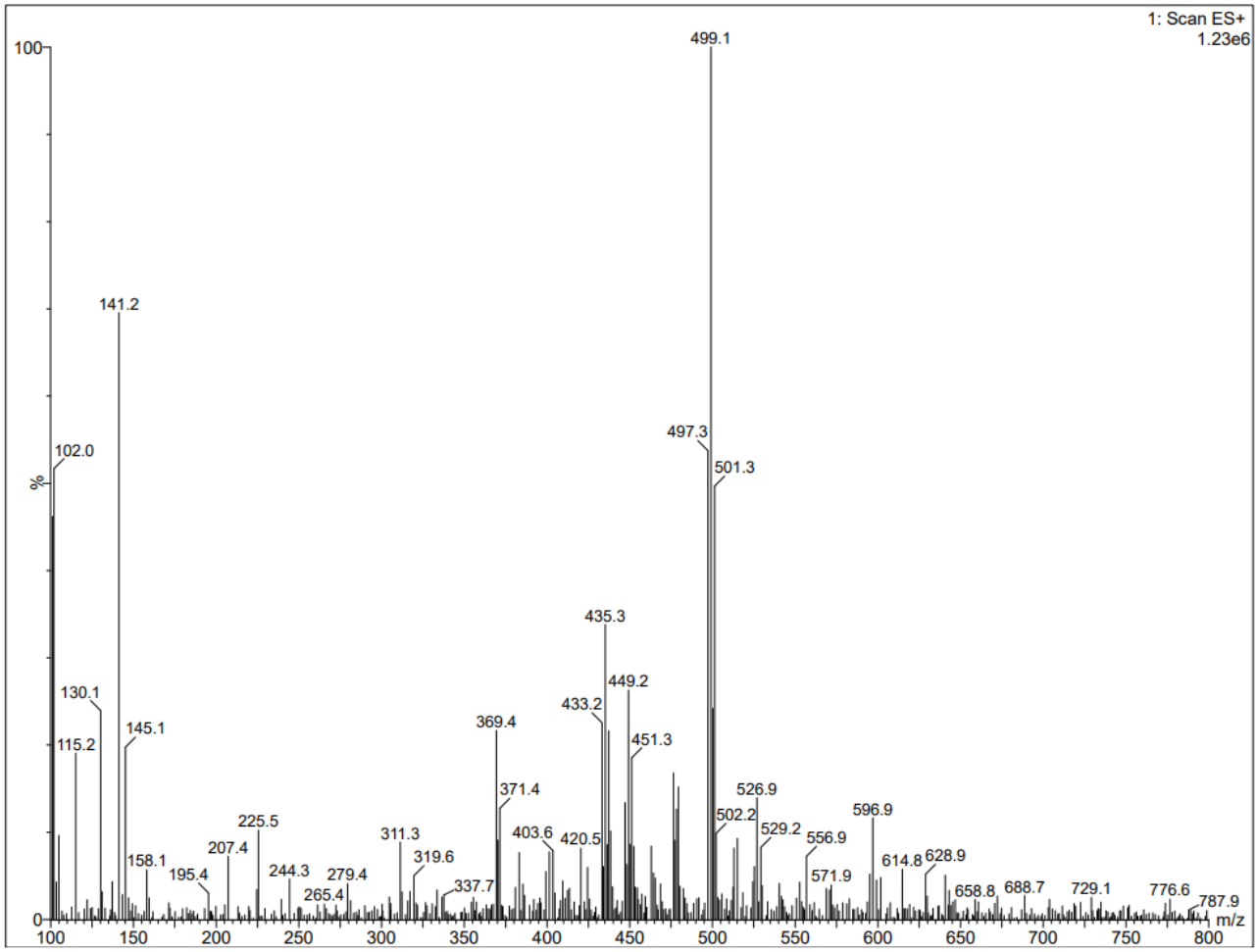

Figure S3. MS-ESI spectrum of compound **4**.

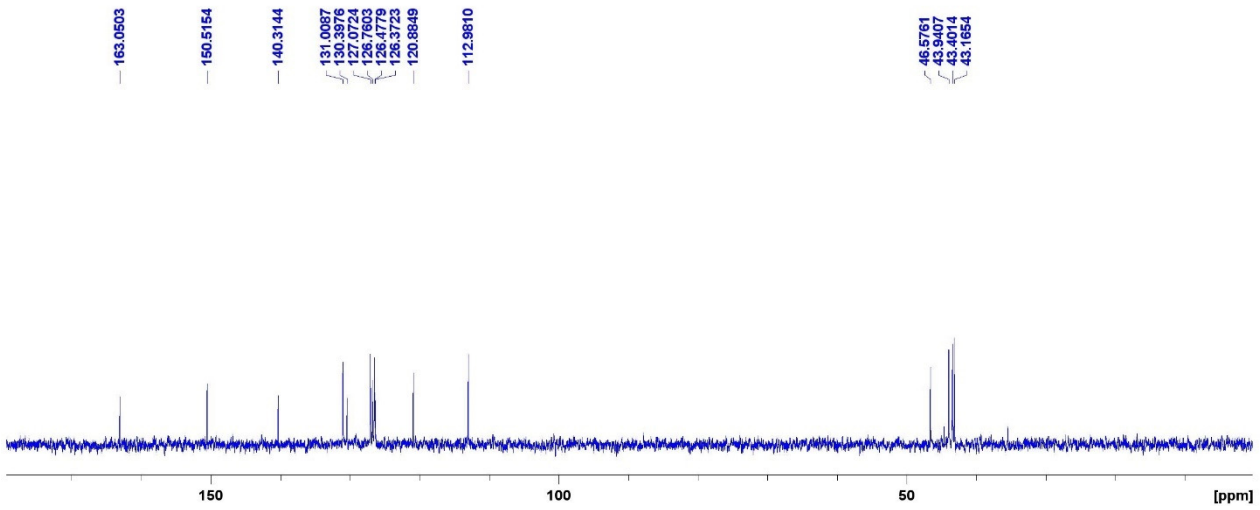

Figure S4. ^{13}C NMR spectrum of ligand **L** in D_2O. [**L**] = 7.7×10^{-3} mol dm^{-3}.

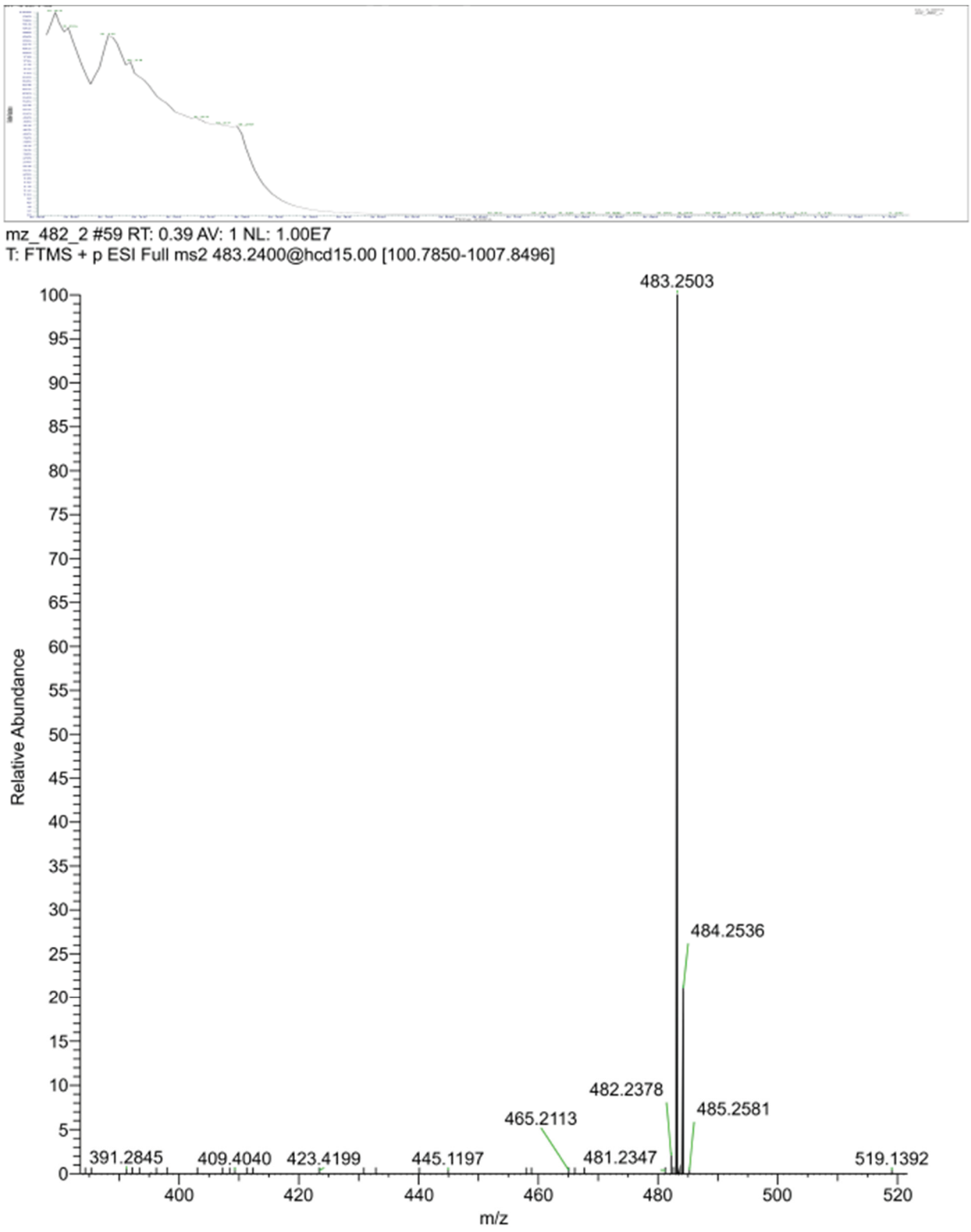

Figure S5. HRMS spectrum of **L**.

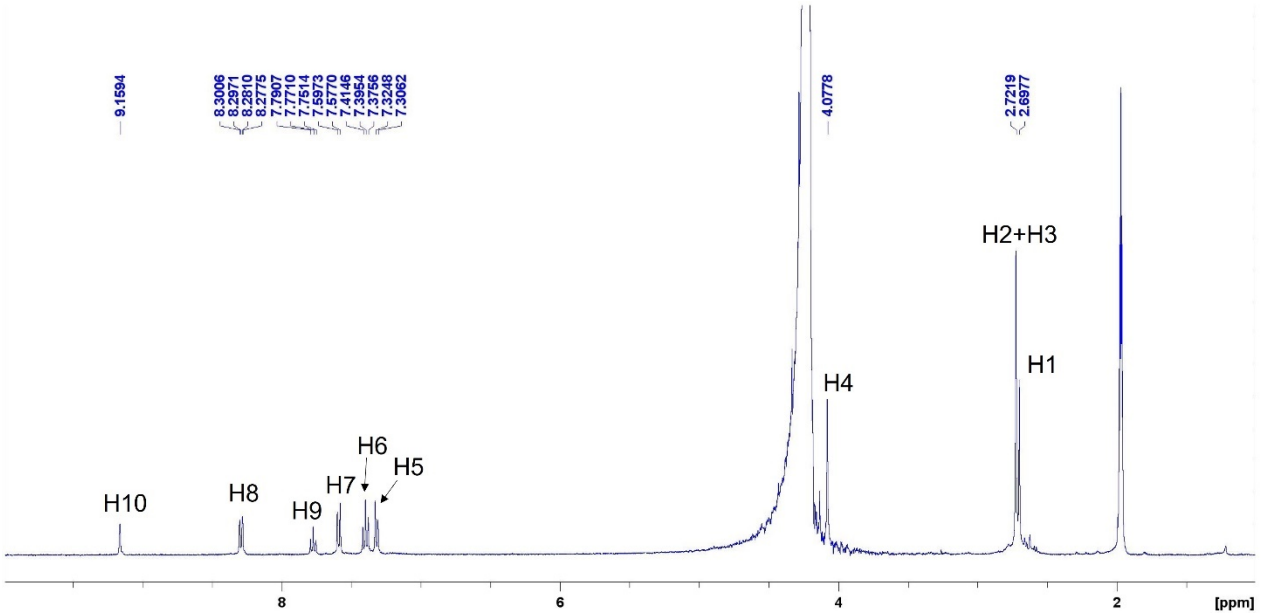

Figure S6. ^{1}H NMR spectrum of **L** at pH 12 in D_2O. [**L**] = 5 × 10^{-3} mol dm^{-3}. See Figure 1 in the main text for protons assignment.

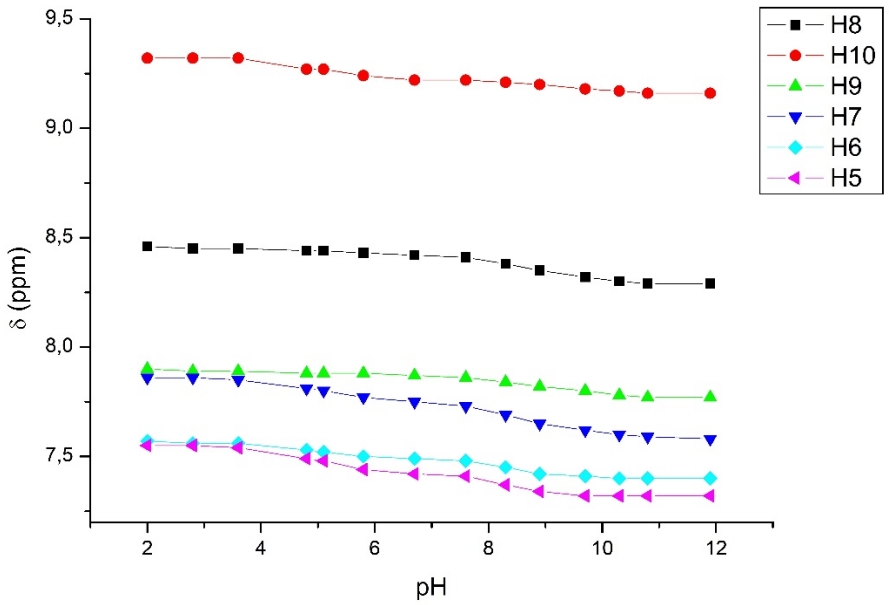

Figure S7. Trend of selected ^{1}H NMR signals of aromatic **L** protons in an acetonitrile-d_3/D_2O 60:40 solution as a function of the pH. [**L**] = 5 × 10^{-3} mol dm^{-3}.

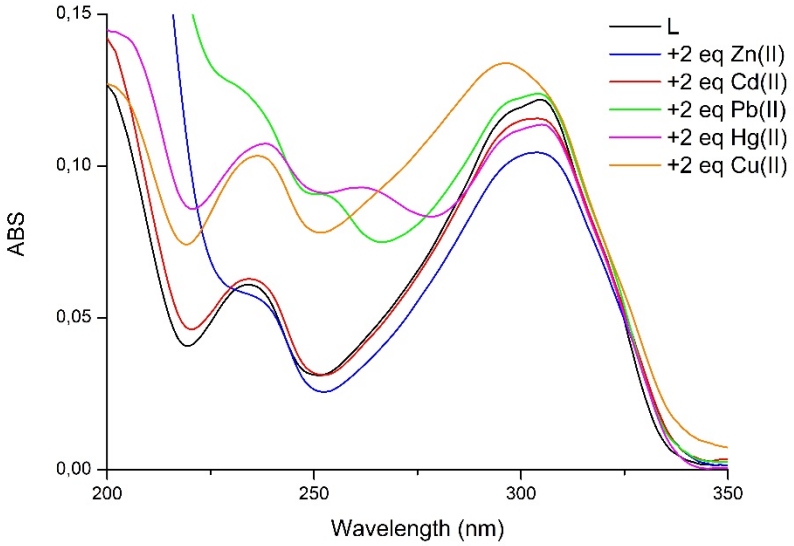

Figure S8. UV-Vis absorption spectra of **L** registered upon addition of 2 equivalents of different metal cations (Zn(II), Cd(II), Pb(II), Hg(II), Cu(II)). [**L**] = 3.2 × 10^{-6} mol dm^{-3} (ACN/aqueous HEPES pH 7.4, 4:1 v/v solvent mixture).

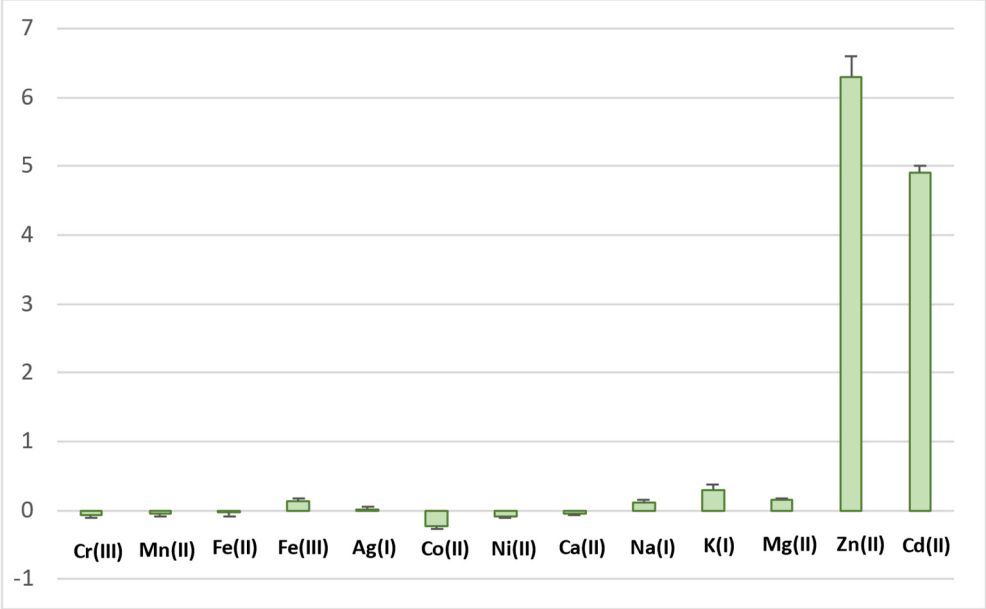

Figure S9. Bar-plot showing the emission of **L** upon addition of 2 equivalents of different metal cations (Fe^{2+}, Fe^{3+}, Co^{2+}, Cr^{3+}, Ni^{2+}, Ag^{+}, Mn^{2+}, Mg^{2+}, Ca^{2+}, Na^{+}, K^{+}). The response to Zn^{2+} and Cd^{2+} has been reported as a reference. I and I_0 are the emission intensities of the ligand in the presence and absence of the metal ions, respectively. [**L**] = 3.2 × 10^{-6} mol dm^{-3} (ACN/aqueous HEPES (pH 7.4) 4:1 v/v solvent mixture). λ_{ex} = 305 nm. λ_{em} = 385 nm (Zn^{2+}), 390 nm (Cd^{2+}), 402 nm for all other tested metal ions.

Determination of LOD, LOQ and LOL [1]

LOD and LOQ were determined using the linear regression method, that consist in calculating a calibration curve measuring the fluorescence response Y of a series of standard solutions of the analyte of concentration X. This method assumes that the instrument response Y is linearly related to the standard concentration X for a limited range of concentration, and it can be expressed using the equation of the line Y=A+BX as a mathematic model. The two parameters A and B, that are the intercept and the slope of the line, respectively, were calculated with the minimum square method together with their respective standard deviations S_A and S_B. In our case the response is the ratio between the emission intensity of each sample and the emission intensity of the blank at 385 nm (Zn^{2+}) and 390 nm (Cd^{2+}) by exciting at 305 nm.

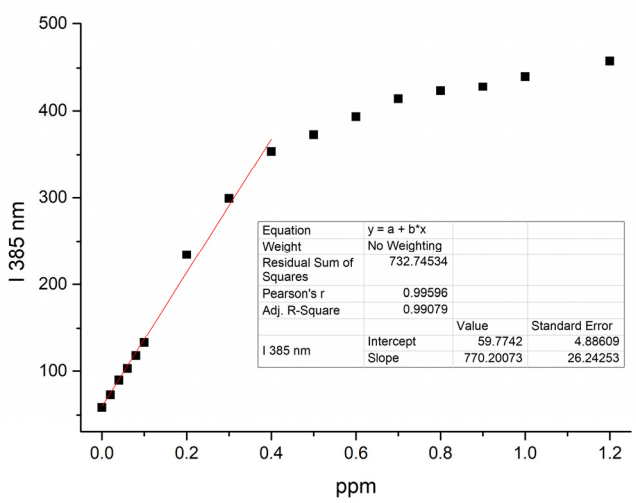

Figure S10. Trend of the emission intensity at 385 nm (λ_{ex}=305 nm) upon increasing amounts of Zn^{2+}, as described in the main text. Inset: linear regression from 0 to 0.4 ppm.

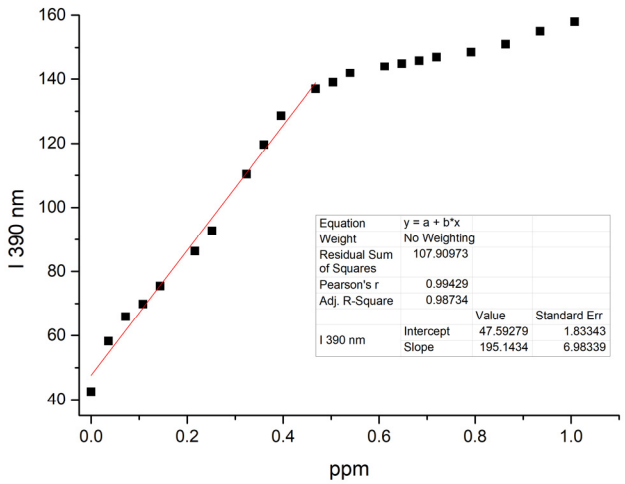

Figure S11. Trend of the emission intensity at 390 nm (λ_{ex}=305 nm) upon increasing amounts of Cd^{2+}, as described in the main text. Inset: linear regression from 0 to 0.45 ppm.

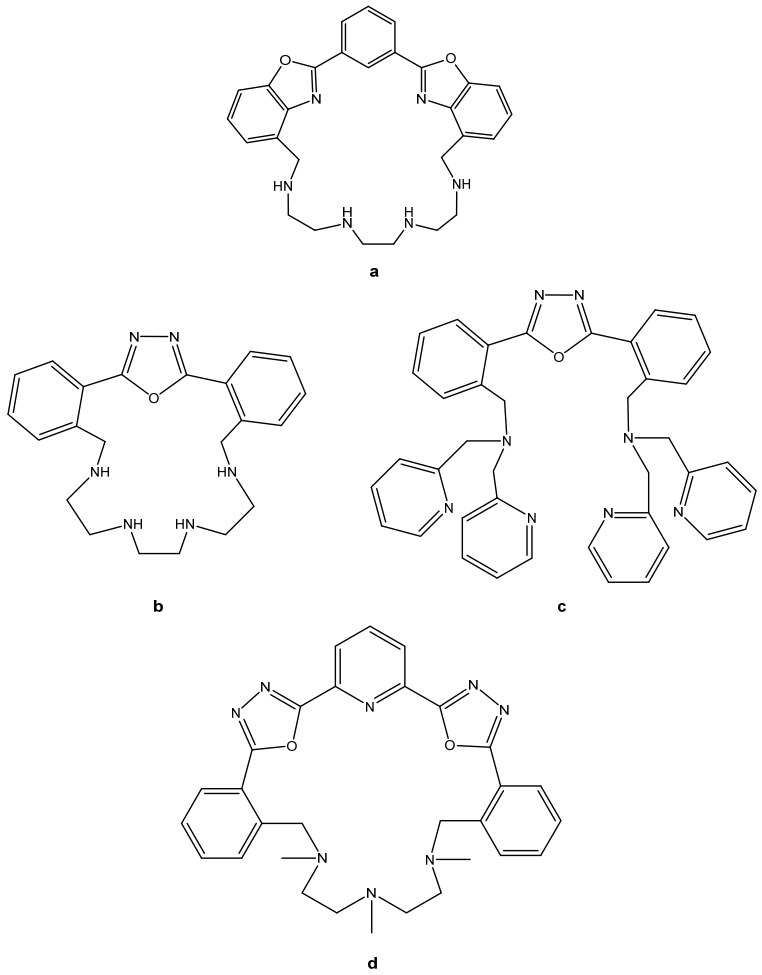

Figure S12. Molecular structures of **L (a)** and the similar systems cited in the main text **(b-d)**.

Table S1. Experimental parameters of **L** and similar systems and their complexes with Zn^{2+} and Cd^{2+}, where applicable.

Compound	Experimental conditions	λ_{ex} (nm)	λ_{em} (nm)	Stokes-shift (cm^{-1})	Φ_{em}	Ref.
a (L)	ACN:HEPES buffer pH 7.4 4:1 v/v, [**L**] = $3.2 \cdot 10^{-6}$	305	402 + Zn^{2+} = 385 + Cd^{2+} = 390	7910 + Zn^{2+} = 6810 + Cd^{2+} = 7150	0.006 + 2 Zn^{2+} = 0.036 + 1 Cd^{2+} = 0.015	This work
b	HEPES buffer pH 7.4 (Zn^{2+}) and pH 8.6 (Cd^{2+}), [**L**] = $1 \cdot 10^{-5}$	280	349 + Zn^{2+} = 361 + Cd^{2+} = 358	5830 + Zn^{2+} = 6780 + Cd^{2+} = 6550		[2,3]
c	EtOH: HEPES buffer pH 7.4 1:1 v/v, [**L**] = $2 \cdot 10^{-5}$	277	355 + Cd^{2+} = 358	7900 + Cd^{2+} = 8200		[4]
d	ACN:HEPES buffer pH 7.0 3:7 v/v, [**L**] = $2 \cdot 10^{-5}$	306	358 + Zn^{2+} = 358 + Cd^{2+} = 358	4750	0.01	[5]

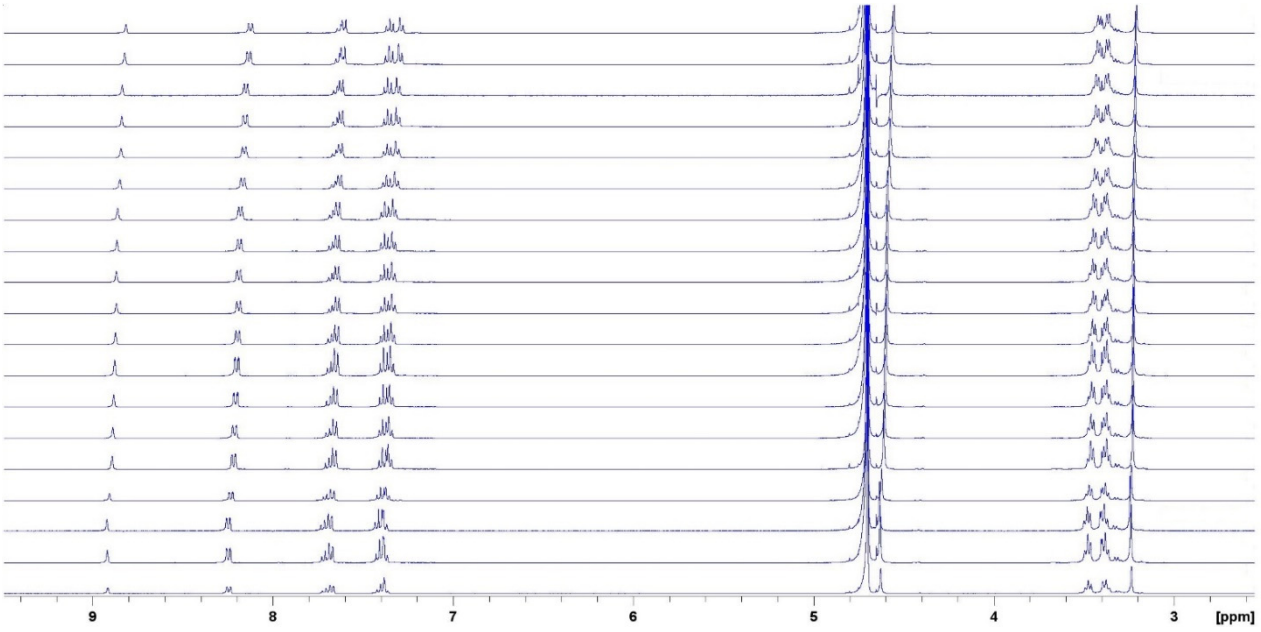

Figure S13. ^{1}H NMR spectra of **L** recorded in D_2O at pH 7.4 upon addition of $Zn(ClO_4)_2$ up to 3 equivalents. [**L**] = 5×10^{-3} mol dm^{-3}.

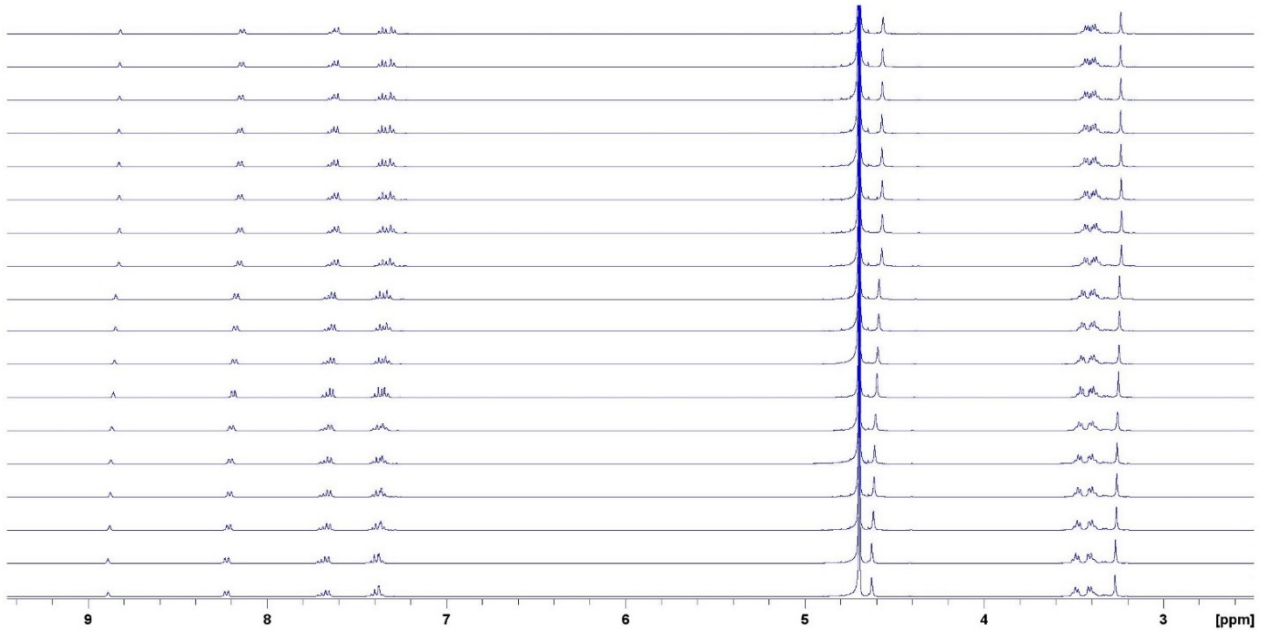

Figure S14. ^{1}H NMR spectra of **L** recorded in D_2O at pH 7.4 upon addition of $Cd(ClO_4)_2$ up to 2 equivalents. [**L**] = 5×10^{-3} mol dm^{-3}.

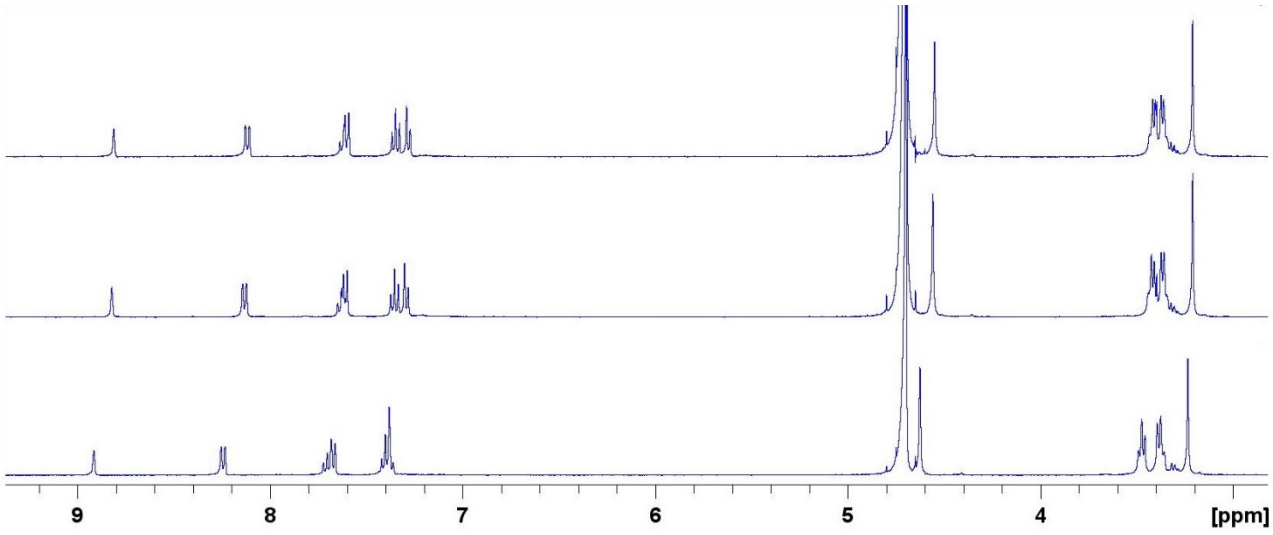

Figure S15. ^{1}H NMR spectra of **L** (bottom), **L** + 2 equivalents of Zn^{2+} (middle),), **L** + 2 equivalents of Zn^{2+} + 2 equivalents Cd^{2+} (top) recorded in D_2O at pH 7.4. [**L**] = 5×10^{-3} mol dm^{-3}.

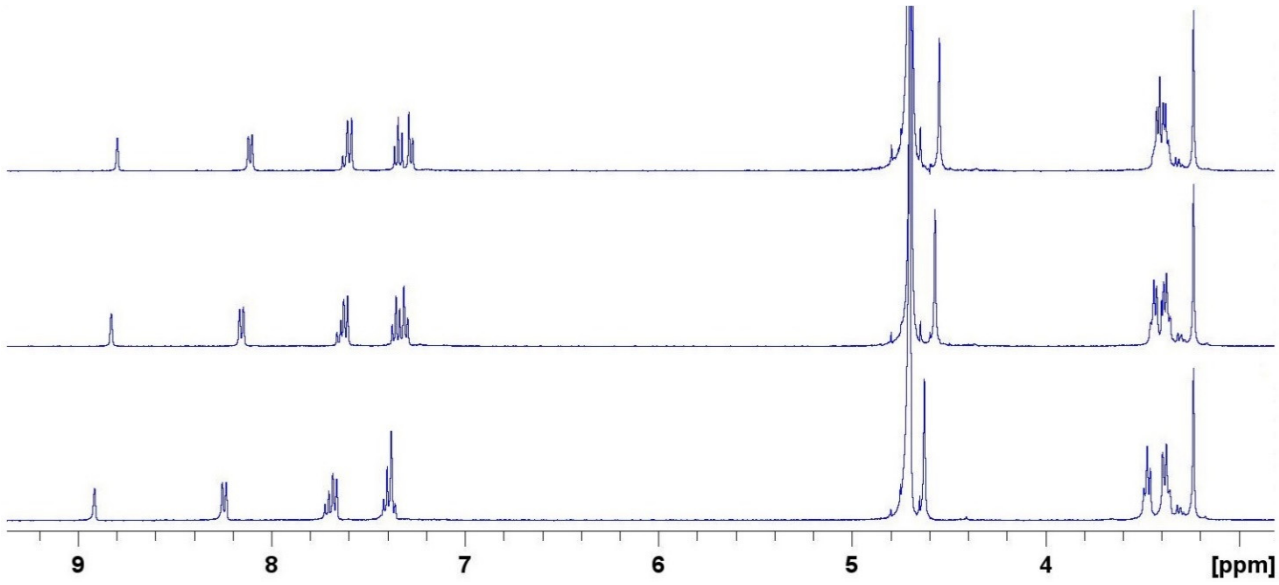

Figure S16. ^{1}H NMR spectra of **L** (bottom), **L** + 1 equivalents of Cd^{2+} (middle),), **L** + 1 equivalents of Cd^{2+} + 1 equivalents of Zn^{2+} (top) recorded in D_2O at pH 7.4. [**L**] = 5×10^{-3} mol dm^{-3}.

Computational details

All the DFT geometry optimizations were performed at the GGA BP86 [6–8] and B3LYP [9–11] level with the Gaussian09 package [12]. The electronic configuration of the systems was described with the standard triple-ζ TZVP basis set with a polarization function of Ahlrichs and co-workers for H, C, N, F, and O while for Zn and Cd the quasi relativistic LANL2DZ ECP effective core potential was adopted [13]. The geometry optimizations were performed without symmetry constraints, and the characterization of the located stationary points was performed by analytical frequency calculations.

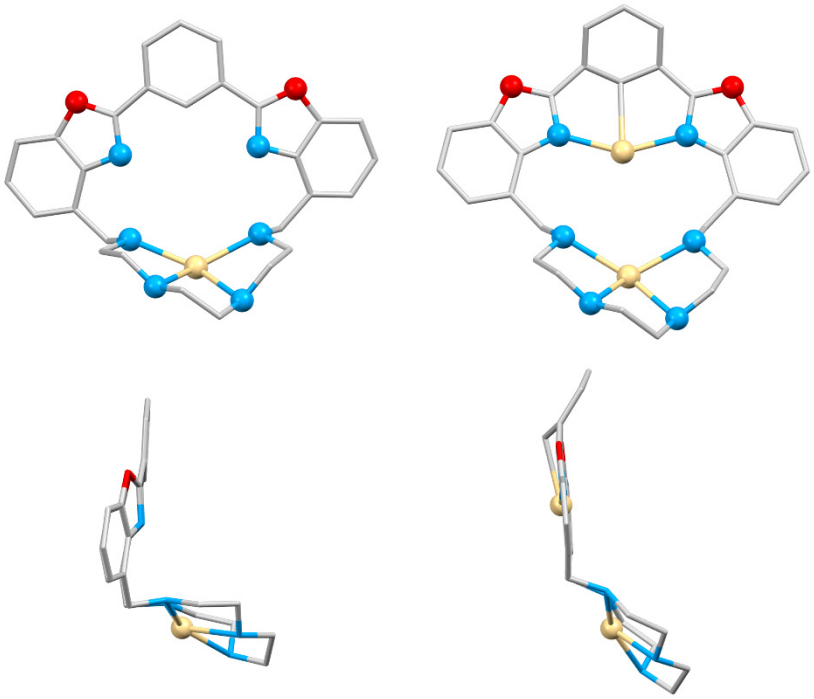

Figure S17. Front view (top) and side view (bottom) of the computed structures of (from left to right) $[Cd\mathbf{L}]^{2+}$ and $[Cd_2\mathbf{L}]^{4+}$.

Cartesian coordinates and energies of calculated structures

L

Zero-point correction = 0.532590 (Hartree/Particle)
Thermal correction to Energy = 0.563661
Thermal correction to Enthalpy = 0.564605
Thermal correction to Gibbs Free Energy = 0.468812
Sum of electronic and zero-point Energies = -1563.478247
Sum of electronic and thermal Energies = -1563.447176
Sum of electronic and thermal Enthalpies = -1563.446232
Sum of electronic and thermal Free Energies = -1563.542024

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N	-3.055301000	2.183971000	0.844898000
C	3.450032000	2.678986000	-0.218723000
H	3.955280000	1.941815000	-0.886996000
H	4.192189000	3.485862000	-0.037490000
C	2.250825000	3.252759000	-0.983463000
H	2.643141000	3.687778000	-1.937876000
H	1.577594000	2.421876000	-1.276212000
C	0.665275000	5.124112000	-0.985927000
H	1.238541000	5.666147000	-1.782700000
H	0.263910000	5.898810000	-0.303550000
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H	-1.065905000	5.219508000	-2.263973000
H	-0.125025000	3.729588000	-2.461153000
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H	-2.313050000	2.249547000	-1.976657000
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H	-4.172079000	3.723385000	-0.021505000
H	-4.416934000	2.167646000	-0.850075000
C	-4.022245000	1.517477000	1.722258000
H	-4.780019000	2.258311000	2.042193000
H	-3.480413000	1.202030000	2.634083000
C	4.140328000	1.445992000	1.795127000
H	3.728666000	1.102634000	2.763474000
H	4.929790000	2.185414000	2.033693000
H	-2.320815000	1.519313000	0.575553000
H	-1.584608000	4.225645000	0.059379000
H	2.130743000	4.753959000	0.399776000
H	2.272550000	1.483230000	0.959010000
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O	3.652559000	-2.776811000	-0.467094000
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C	4.792061000	0.256432000	1.091846000
C	6.184006000	0.128834000	0.938873000
H	6.827044000	0.928420000	1.325185000
C	6.788948000	-0.987817000	0.314166000
H	7.879837000	-1.025195000	0.229436000
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H	6.480535000	-2.914978000	-0.690943000
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C	2.473041000	-2.146359000	-0.076051000
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H	-7.858004000	-1.011945000	0.478456000
C	-6.028311000	-2.055922000	0.000940000
H	-6.506530000	-2.942206000	-0.423225000
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C	-2.470493000	-2.148653000	-0.032672000
H	0.001115000	-1.215399000	0.406987000

Zn^{2+}

Zero-point correction = 0.000000 (Hartree/Particle)
Thermal correction to Energy = 0.001416
Thermal correction to Enthalpy = 0.002360
Thermal correction to Gibbs Free Energy = -0.015877
Sum of electronic and zero-point Energies = -65.017591
Sum of electronic and thermal Energies = -65.016175
Sum of electronic and thermal Enthalpies = -65.015231
Sum of electronic and thermal Free Energies = -65.033468

Zn	0.000000	0.000000	0.000000

$[ZnL]^{2+}$

Zero-point correction =	0.541372 (Hartree/Particle
Thermal correction to Energy =	0.572162
Thermal correction to Enthalpy =	0.573107
Thermal correction to Gibbs Free Energy =	0.480670
Sum of electronic and zero-point Energies =	-1629.043942
Sum of electronic and thermal Energies =	-1629.013151
Sum of electronic and thermal Enthalpies =	-1629.012207
Sum of electronic and thermal Free Energies =	-1629.104644

N	1.911928000	3.996433000	-0.468123000
C	2.696115000	3.022113000	-1.284747000
C	3.179882000	1.875758000	-0.396682000
N	2.053880000	1.242550000	0.379199000
C	2.602141000	0.684905000	1.692125000
C	3.606959000	-0.427921000	1.440161000
C	4.863695000	-0.591380000	2.047274000
C	5.639933000	-1.758632000	1.823087000
C	5.204646000	-2.828360000	1.014094000
C	3.952605000	-2.652920000	0.423004000
C	3.199362000	-1.480940000	0.599319000
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C	2.015332000	-2.818377000	-0.593603000
O	3.179975000	-3.514847000	-0.353063000
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C	-1.641296000	-3.161968000	-1.078187000
C	-1.801883000	-4.398739000	-1.742959000
C	0.649973000	-4.680215000	-1.801937000
C	-0.651558000	-5.128465000	-2.104022000
C	-2.655469000	-2.278355000	-0.495596000
O	-3.952160000	-2.674308000	-0.256296000
C	-4.502219000	-1.644841000	0.504780000
C	-3.493283000	-0.681854000	0.677627000
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C	-3.667396000	0.472081000	1.466501000
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N	-0.817186000	3.910935000	-1.102119000
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H	-1.333175000	2.273568000	-2.334046000
H	-3.176243000	3.119655000	0.005244000
H	-3.361390000	1.648670000	-0.969342000
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H	-6.933932000	-0.180854000	2.309405000
H	-6.561952000	-2.250769000	0.940838000
H	-2.796267000	-4.797415000	-1.963599000
H	-0.773977000	-6.086005000	-2.618365000
H	1.516725000	-5.292448000	-2.067121000
H	-0.223815000	-1.794695000	-0.235549000
H	5.802886000	-3.733104000	0.884090000
H	6.610434000	-1.842919000	2.320150000
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H	1.736453000	0.288781000	2.253206000
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H	3.703805000	1.122937000	-1.008362000
H	3.560863000	3.505320000	-1.776854000
H	2.041357000	2.639940000	-2.090157000
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Zn	0.311041000	2.578581000	0.252791000

$[Zn_2L]^{4+}$

Zero-point correction =	0.540937 (Hartree/Particle)
Thermal correction to Energy =	0.573515
Thermal correction to Enthalpy =	0.574459
Thermal correction to Gibbs Free Energy =	0.478177
Sum of electronic and zero-point Energies =	-1694.132193
Sum of electronic and thermal Energies =	-1694.099615
Sum of electronic and thermal Enthalpies =	-1694.098670
Sum of electronic and thermal Free Energies =	-1694.194953

Zn	3.325951000	-0.203560000	-0.191933000
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C	3.363054000	2.827808000	0.041470000
C	4.623063000	2.251451000	0.695257000
N	5.099981000	1.068237000	-0.090866000
C	6.207550000	0.281289000	0.566546000
C	5.643642000	-0.847225000	1.447117000
N	4.678490000	-1.654005000	0.629631000
C	3.870023000	-2.682551000	1.350010000
C	2.738031000	-3.150440000	0.425366000
N	1.844182000	-1.997306000	0.021394000
C	0.887975000	-2.384399000	-1.104761000
C	-0.175011000	-3.434765000	-0.804622000
C	0.036964000	-4.818609000	-0.978916000
C	-0.983538000	-5.786741000	-0.790044000
C	-2.299417000	-5.436354000	-0.441786000
C	-2.511541000	-4.067118000	-0.295077000
C	-1.504643000	-3.088542000	-0.456803000
O	-3.713001000	-3.408116000	0.000645000
N	-2.123594000	-1.855177000	-0.239312000
C	-3.441017000	-2.101033000	0.001477000
Zn	-1.759659000	0.095519000	-0.229562000
C	-3.964068000	0.242048000	-0.282825000
C	-4.352280000	-0.988483000	0.325127000
C	-5.301523000	-0.940389000	1.370139000
C	-5.755332000	0.321089000	1.822078000
C	-5.143578000	1.529267000	1.411917000
C	-4.193627000	1.491074000	0.367572000
C	-3.144937000	2.486420000	0.080115000

N	-1.872258000	2.075477000	-0.168945000
C	-1.094406000	3.219947000	-0.352851000
C	-1.962545000	4.319345000	-0.165033000
O	-3.241789000	3.818099000	0.115402000
C	-1.567654000	5.650155000	-0.279584000
C	-0.216716000	5.827393000	-0.626501000
C	0.665016000	4.737145000	-0.844301000
C	0.269797000	3.390559000	-0.695649000
C	1.165980000	2.198908000	-1.017232000
H	0.162517000	6.844953000	-0.760847000
H	-2.253830000	6.489574000	-0.136467000
H	-5.372815000	2.463129000	1.935867000
H	-6.516225000	0.356407000	2.609079000
H	-5.649148000	-1.854633000	1.862548000
H	-3.093794000	-6.177812000	-0.318516000
H	-0.743286000	-6.842721000	-0.946455000
H	1.019457000	-5.174260000	-1.307119000
H	1.515414000	-2.722645000	-1.946857000
H	0.405574000	-1.446074000	-1.446395000
H	1.264776000	-1.798823000	0.853137000
H	3.159418000	-3.578909000	-0.501504000
H	5.223793000	-2.138407000	-0.101751000
H	4.483737000	-3.550033000	1.651184000
H	3.473837000	-2.228982000	2.277181000
H	5.100497000	-0.450094000	2.324235000
H	6.473338000	-1.466848000	1.830207000
H	6.856343000	0.941923000	1.167545000
H	6.832975000	-0.141500000	-0.238212000
H	5.459746000	1.415526000	-0.991497000
H	5.398672000	3.037009000	0.747156000
H	4.422357000	1.928028000	1.733443000
H	3.045667000	3.735363000	0.581603000
H	3.584273000	3.116880000	-1.001223000
H	1.688290000	2.366546000	-1.975102000
H	0.540148000	1.295793000	-1.172596000
H	1.682853000	4.970813000	-1.172785000
H	-3.667568000	0.241189000	-1.348801000
H	2.151461000	-3.942258000	0.921372000
H	1.793386000	1.841713000	0.929859000

Cd^{2+}

Zero-point correction =	0.000000 (Hartree/Particle)
Thermal correction to Energy =	0.001416
Thermal correction to Enthalpy =	0.002360
Thermal correction to Gibbs Free Energy =	-0.016695
Sum of electronic and zero-point Energies =	-47.43776
Sum of electronic and thermal Energies =	-47.43635
Sum of electronic and thermal Enthalpies =	-47.435406
Sum of electronic and thermal Free Energies =	-47.454462

Cd	0.000000	0.000000	0.000000

$[CdL]^{2+}$

Zero-point correction =	0.540390 (Hartree/Particle)
Thermal correction to Energy =	0.571603
Thermal correction to Enthalpy =	0.572547
Thermal correction to Gibbs Free Energy =	0.478617
Sum of electronic and zero-point Energies =	-1611.396834
Sum of electronic and thermal Energies =	-1611.365622
Sum of electronic and thermal Enthalpies =	-1611.364678
Sum of electronic and thermal Free Energies =	-1611.458607

N	1.863391000	-3.893645000	0.699396000
C	2.760301000	-2.874159000	1.317529000
C	3.328026000	-1.935870000	0.249420000
N	2.270774000	-1.187561000	-0.507108000
C	2.869007000	-0.575083000	-1.767033000
C	3.834060000	0.546680000	-1.425492000
C	5.136016000	0.726004000	-1.922844000
C	5.885566000	1.890892000	-1.614940000
C	5.380982000	2.938763000	-0.818488000
C	4.086214000	2.746120000	-0.335038000
C	3.347737000	1.581568000	-0.602524000
N	2.103149000	1.673373000	0.000502000
C	2.083953000	2.880431000	0.548009000
O	3.261986000	3.583227000	0.411396000
C	0.866360000	3.494795000	1.079893000
C	-0.296656000	2.792827000	0.731192000
C	-1.579847000	3.272943000	1.029519000
C	-1.707415000	4.497378000	1.723991000
C	0.743482000	4.719395000	1.774776000
C	-0.542297000	5.194826000	2.095074000
C	-2.646854000	2.444966000	0.466095000
O	-3.933517000	2.909641000	0.306924000
C	-4.580190000	1.917241000	-0.424535000
C	-3.635101000	0.905128000	-0.663983000
N	-2.432791000	1.248714000	-0.062988000
C	-5.889209000	1.850574000	-0.902360000
C	-6.193203000	0.698519000	-1.654768000
C	-5.243704000	-0.321970000	-1.919229000
C	-3.927804000	-0.238752000	-1.433204000
C	-2.792904000	-1.206979000	-1.733882000
N	-1.995101000	-1.530566000	-0.480247000
C	-2.850505000	-2.289891000	0.490554000
C	-2.070492000	-2.784623000	1.711590000
N	-0.981190000	-3.697245000	1.271501000
C	-0.031893000	-4.132682000	2.327056000
C	1.199042000	-4.795168000	1.685925000
H	1.901323000	-5.106753000	2.482070000
H	0.893276000	-5.708729000	1.146639000
H	0.256903000	-3.240786000	2.911879000
H	-0.496736000	-4.841401000	3.037522000
H	-2.767146000	-3.280305000	2.413645000

H	-1.415938000	-4.537481000	0.863116000
H	-1.609962000	-1.937804000	2.253926000
H	-3.288072000	-3.150084000	-0.048982000
H	-3.692285000	-1.658690000	0.825305000
H	-1.823236000	-0.578318000	-0.070235000
H	-2.087151000	-0.751158000	-2.451576000
H	-3.161444000	-2.147957000	-2.175113000
H	-5.547013000	-1.176689000	-2.533230000
H	-7.202844000	0.591135000	-2.061170000
H	-6.628418000	2.634042000	-0.720581000
H	-2.693196000	4.908321000	1.960085000
H	-0.639466000	6.142777000	2.631987000
H	1.628780000	5.300250000	2.049068000
H	-0.200463000	1.882325000	0.142933000
H	5.963322000	3.840215000	-0.614429000
H	6.892985000	1.988853000	-2.029181000
H	5.580054000	-0.027077000	-2.582556000
H	2.025712000	-0.174226000	-2.357010000
H	3.346614000	-1.375474000	-2.355653000
H	1.991907000	-0.343316000	0.043162000
H	3.903465000	-2.526133000	-0.486551000
H	4.036728000	-1.231808000	0.719345000
H	3.598586000	-3.352591000	1.859586000
H	2.180428000	-2.304119000	2.066952000
H	2.431562000	-4.473197000	0.068001000
Cd	0.229173000	-2.442948000	-0.401182000

$[Cd_2L]^{4+}$

Zero-point correction =	0.538929 (Hartree/Particle)
Thermal correction to Energy =	0.572261
Thermal correction to Enthalpy =	0.573206
Thermal correction to Gibbs Free Energy =	0.473778
Sum of electronic and zero-point Energies =	-1658.827655
Sum of electronic and thermal Energies =	-1658.794323
Sum of electronic and thermal Enthalpies =	-1658.793379
Sum of electronic and thermal Free Energies =	-1658.892807

Cd	3.123218000	-0.245333000	-0.323499000
N	2.097965000	2.028352000	-0.076522000
C	3.299181000	2.931195000	0.113710000
C	4.433084000	2.267141000	0.912302000
N	5.004572000	1.103994000	0.162161000
C	5.990260000	0.263338000	0.932432000
C	5.328543000	-0.903744000	1.692322000
N	4.543431000	-1.771048000	0.754923000
C	3.681197000	-2.815898000	1.384954000
C	2.641069000	-3.340570000	0.379954000
N	1.652974000	-2.274297000	-0.042071000
C	0.726871000	-2.754952000	-1.159288000
C	-0.386385000	-3.715482000	-0.773025000
C	-0.269406000	-5.119074000	-0.849901000
C	-1.348341000	-5.995654000	-0.563800000
C	-2.624622000	-5.530002000	-0.200000000
C	-2.741868000	-4.141866000	-0.146111000
C	-1.678999000	-3.253377000	-0.416159000
O	-3.873327000	-3.376700000	0.163773000
N	-2.192393000	-1.967450000	-0.254956000
C	-3.504789000	-2.091367000	0.067144000
Cd	-1.544522000	0.106356000	-0.488557000
C	-3.965897000	0.296897000	-0.201099000
C	-4.328179000	-0.926148000	0.431988000
C	-5.199233000	-0.864832000	1.544209000
C	-5.599827000	0.397452000	2.034668000
C	-5.003769000	1.593053000	1.576502000
C	-4.131736000	1.545005000	0.464613000
C	-3.134386000	2.574201000	0.126310000
N	-1.861052000	2.250040000	-0.209328000
C	-1.148891000	3.440181000	-0.344477000
C	-2.054246000	4.480804000	-0.044389000
O	-3.292491000	3.899348000	0.257006000
C	-1.715981000	5.832694000	-0.069740000
C	-0.384484000	6.095784000	-0.439420000
C	0.536786000	5.065233000	-0.760121000
C	0.197245000	3.696858000	-0.708340000
C	1.132965000	2.574345000	-1.128706000
H	-0.052182000	7.136425000	-0.501627000
H	-2.428884000	6.628619000	0.163174000
H	-5.185083000	2.533816000	2.106617000
H	-6.302477000	0.442213000	2.873212000
H	-5.528094000	-1.778720000	2.049775000
H	-3.458473000	-6.205606000	0.010367000
H	-1.185722000	-7.074550000	-0.646183000
H	0.678889000	-5.563453000	-1.170838000
H	1.369277000	-3.206612000	-1.933692000
H	0.290647000	-1.846983000	-1.628989000
H	1.059781000	-2.108503000	0.786929000
H	3.142858000	-3.704586000	-0.534174000
H	5.208256000	-2.241285000	0.121757000
H	4.282545000	-3.667775000	1.750974000
H	3.188463000	-2.371653000	2.269622000
H	4.635525000	-0.535040000	2.471514000
H	6.117999000	-1.478030000	2.210251000
H	6.553944000	0.885311000	1.650680000
H	6.723210000	-0.127750000	0.206128000
H	5.494959000	1.474378000	-0.663754000
H	5.210775000	3.027592000	1.112245000
H	4.074194000	1.912539000	1.896176000
H	2.998900000	3.862744000	0.624400000
H	3.664133000	3.207177000	-0.891558000
H	1.746597000	2.889102000	-1.989866000
H	0.534273000	1.712402000	-1.496802000
H	1.539266000	5.361108000	-1.087305000
H	-3.722714000	0.291779000	-1.279735000
H	2.108391000	-4.196847000	0.829651000
H	1.594405000	2.037475000	0.824906000

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