Electronic Supplementary Information

The ability of the NiSOD binding loop to chelate zinc(II): the role of the terminal amino group in the enzymatic functions

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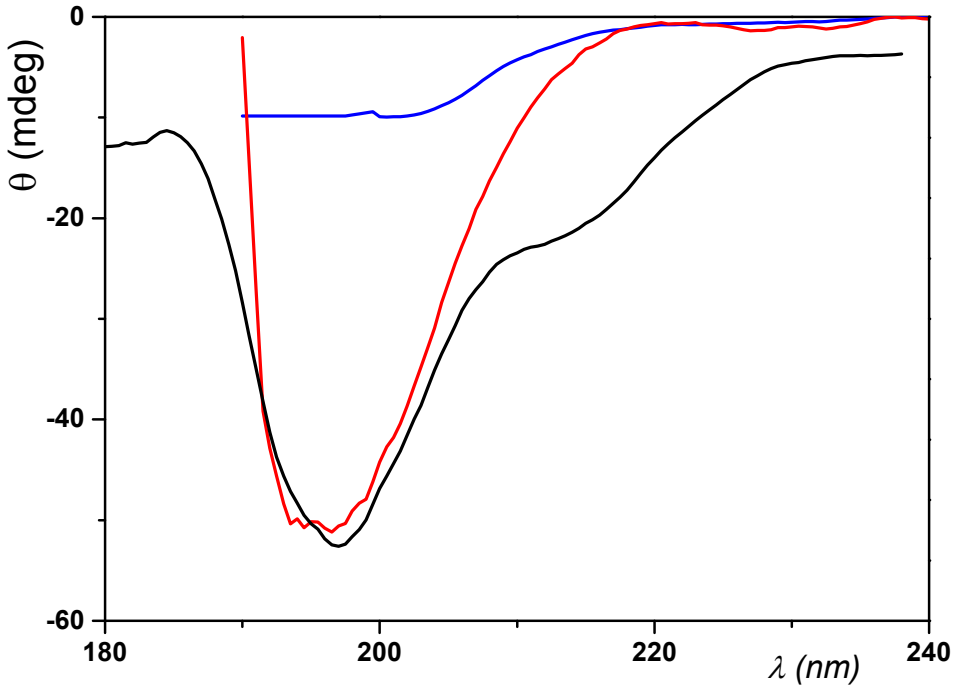

Figure S1. UV-CD spectra registered in the **L3** system at pH 10. 24 (black), after oxidation (blue) and after in situ reduction by dithiothreitol of the oxidized sample (red).

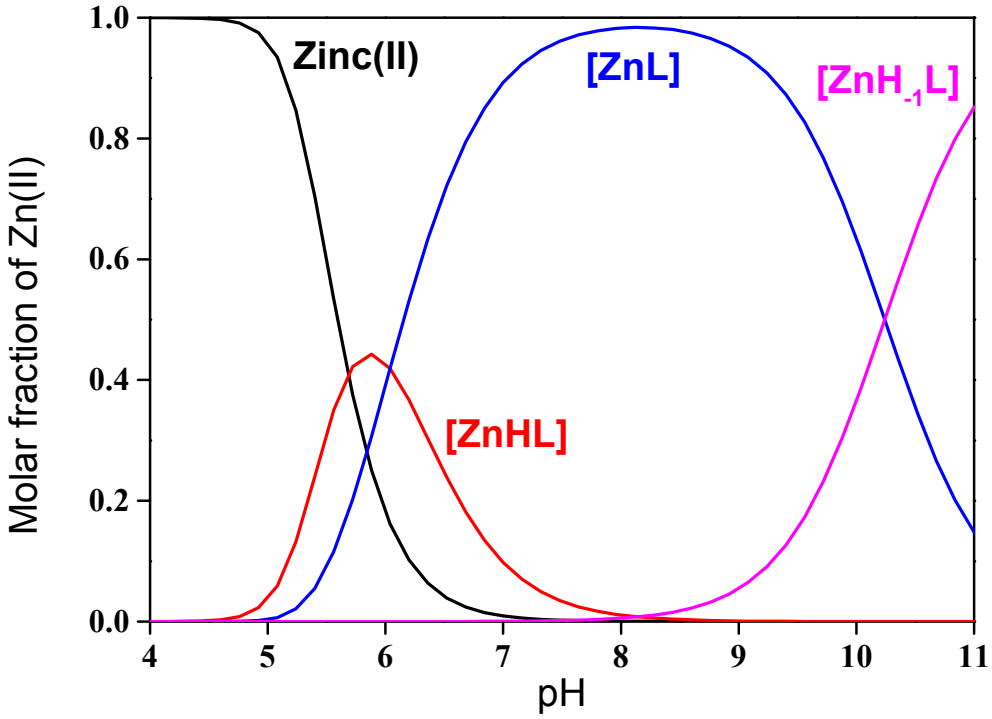

Figure S2. Species distribution of the complexes formed in the Zn(II):**L4** 1:1 system as a function of pH. c_L = 1.5 mM

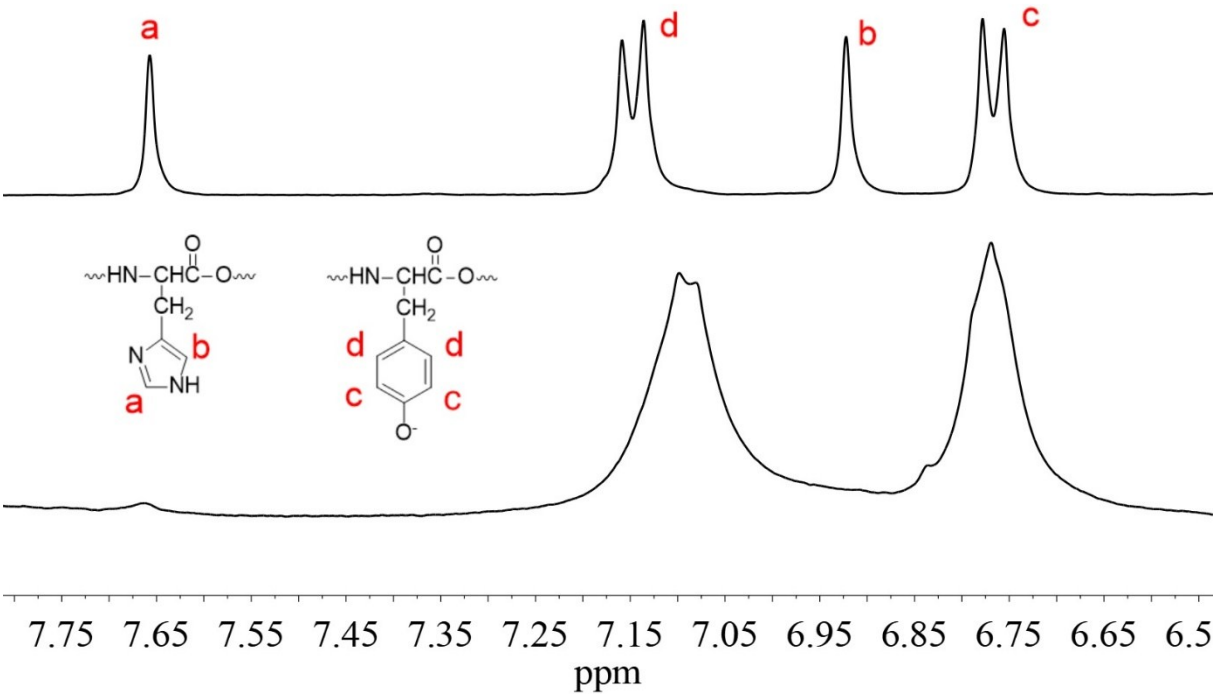

Figure S3. Downfield region of the ^{1}H NMR spectra of the **L2** systems in the absence (top) and presence (bottom) of zinc(II) at pD 9.3

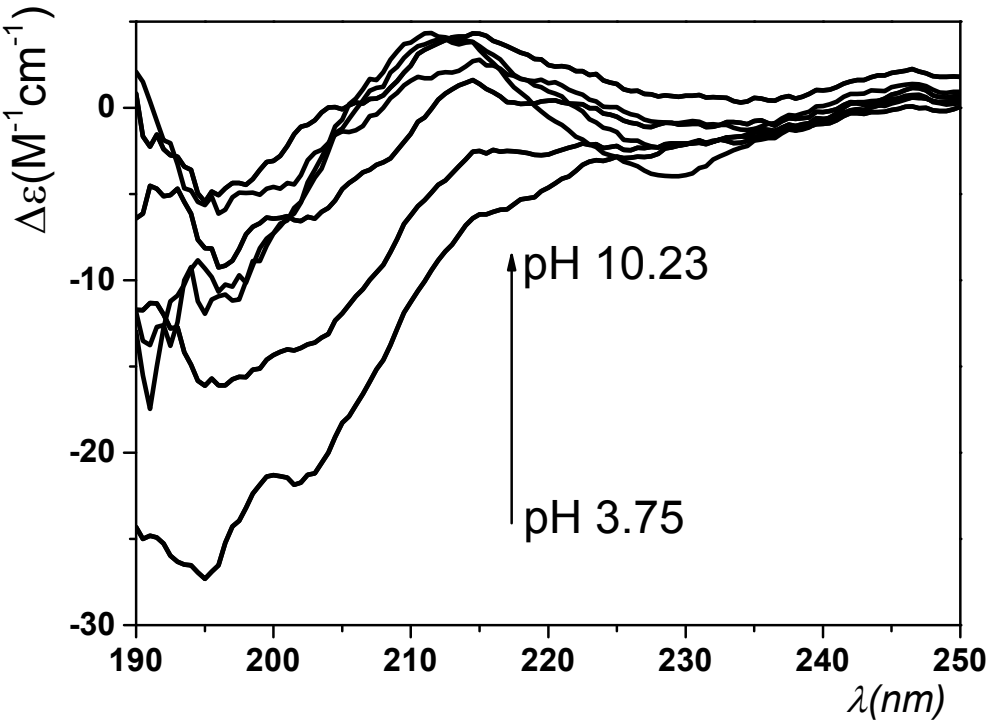

Figure S4. pH dependent CD spectra for the Zn(II):**L1** 1:1 system as a function of pH. c_L = 0.1 mM

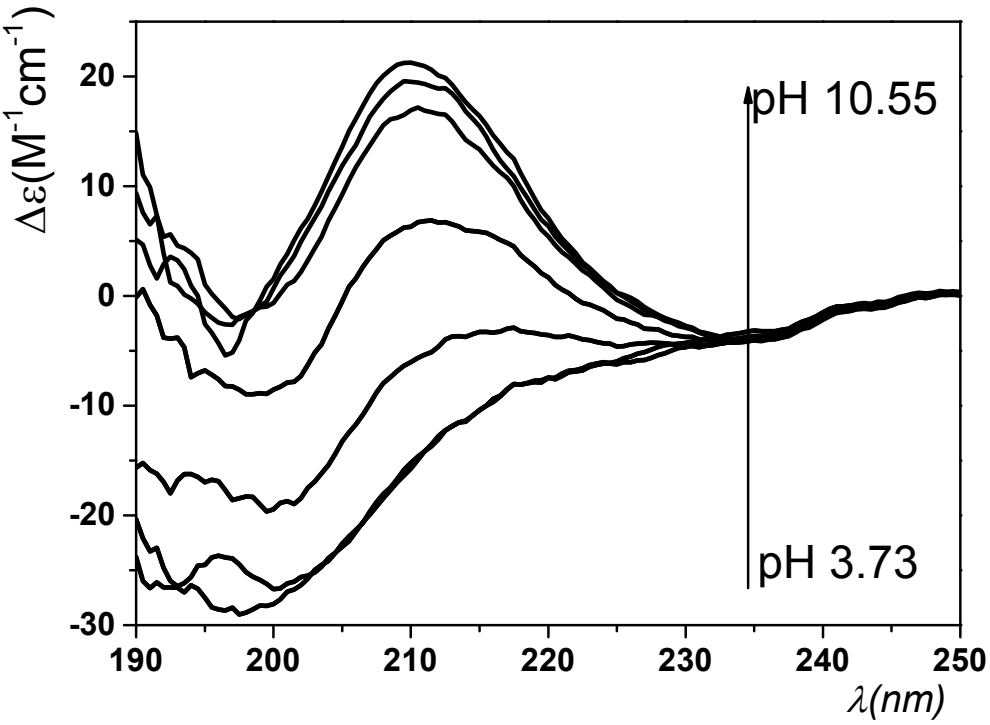

Figure S5. pH dependent CD spectra for the Zn(II):**L2** 1:1 system as a function of pH. c_L = 0.1 mM

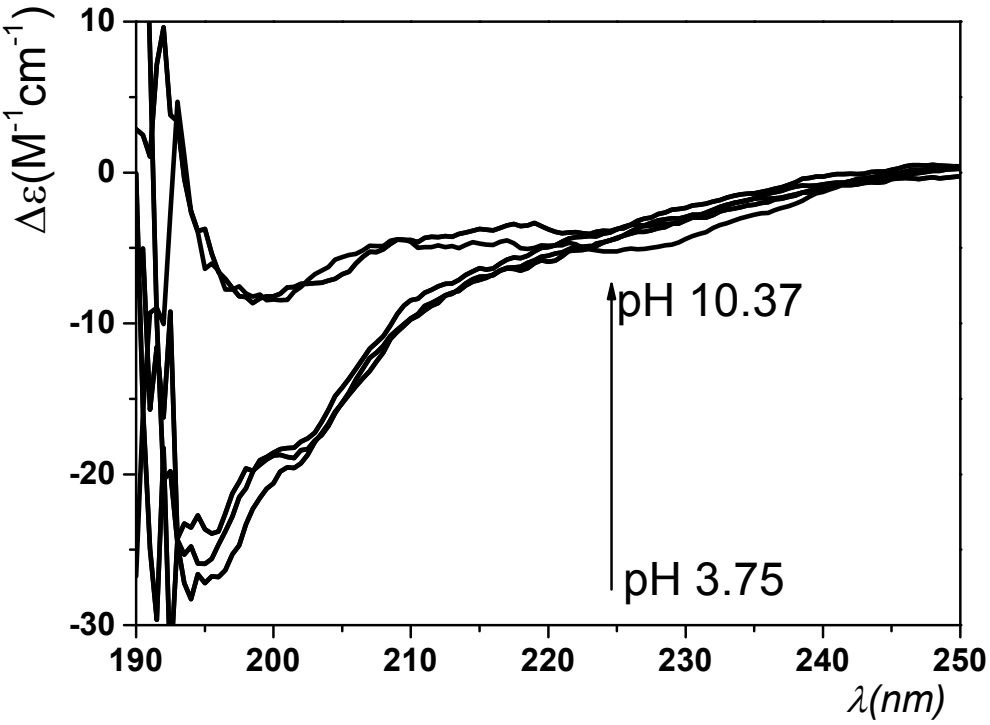

Figure S6. pH dependent CD spectra for the Zn(II):**L3** 1:1 system as a function of pH. c_L = 0.1 mM

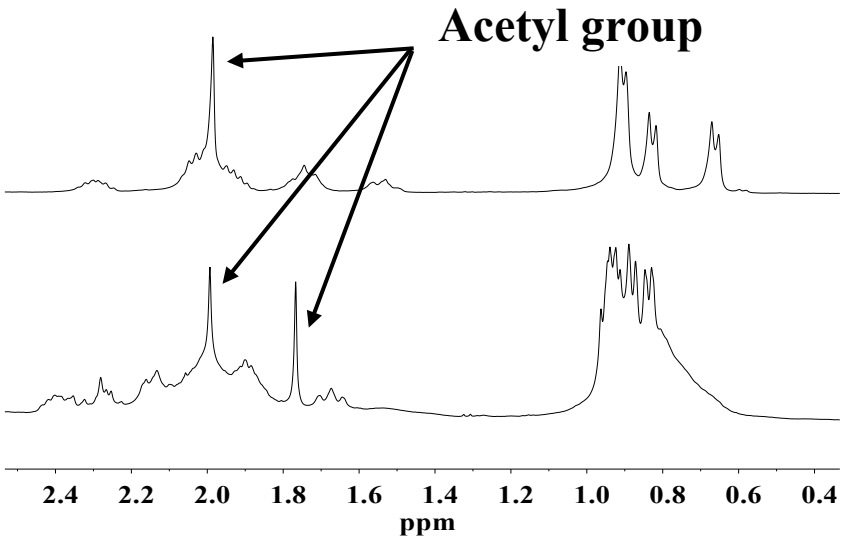

Figure S7. The aliphatic region of the ^{1}H NMR spectra of the **L2** system in the absence (top) and presence (bottom) of zinc(II) at pD 11.2.

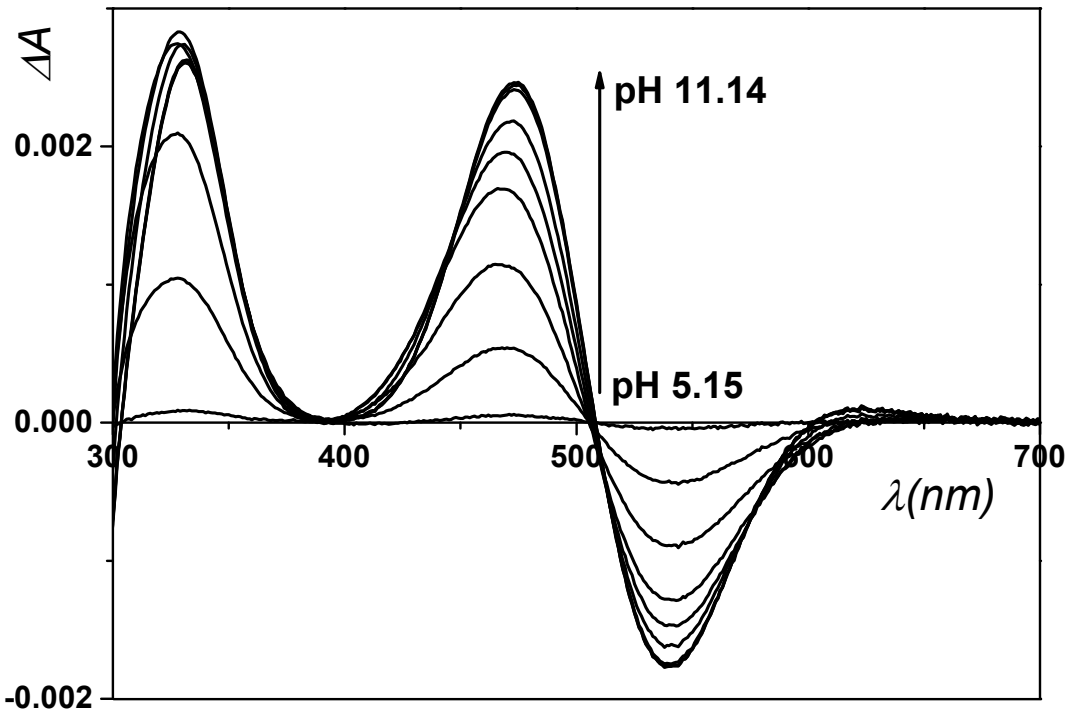

Figure S8. pH dependent CD spectra for the Ni(II):**L4** 1:1 system as a function of pH. c_L = 1.0 mM

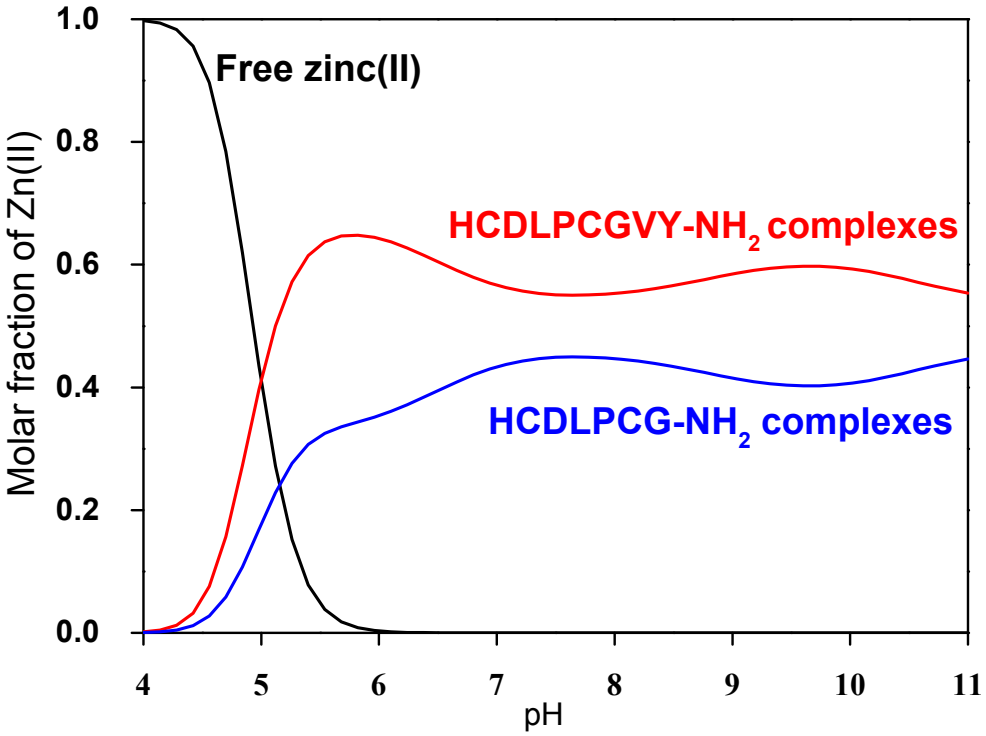

Figure S9. Distribution curves as a function of pH calculated in the Zn(II):**L1**:**L4** 1:1:1 system. c_L = 1.5 mM†

†The stepwise protonation constants of **L4** used in this calculation were as follows: H_5L = 3.40(5); H_4L = 5.12; H_3L = 7.00(6); H_2L = 8.20(6); HL = 8.78(6).

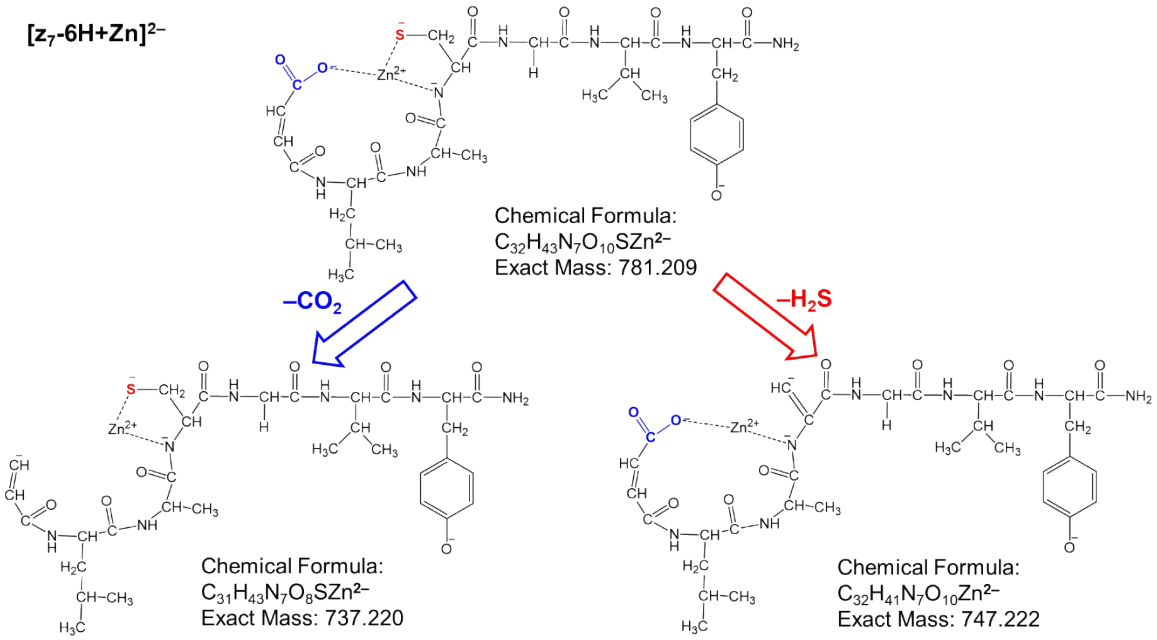

Figure S10. Fragmentation pathway of $[Zn(II)+z_7]^-$ fragment.

[DLACGV-3H-H_2S+Zn]$^{2-}$

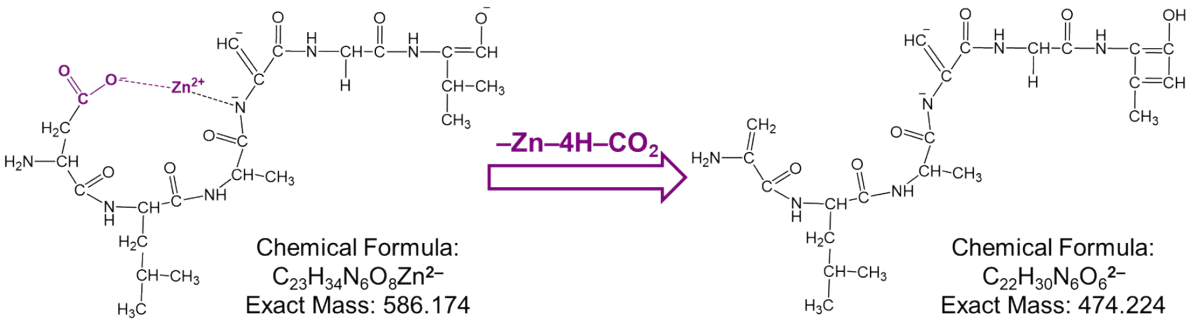

Figure S11. Fragmentation pathway of [Zn(II)+DLACGV]$^{2-}$ fragment.

Table S1. The results of ESI-TOF-MS experiments: measured and calculated *m/z* values obtained for the [$ZnH_{-1}L$] complexes.

Ligand	Stoichiometry	m/z (observed)	m/z (calculated)
L1	$[C_{43}H_{59}N_{12}O_{12}S_2Zn]^{3-}$	354.434	354.436
	$H[C_{43}H_{59}N_{12}O_{12}S_2Zn]^{2-}$	532.153	532.159
L2	$[C_{45}H_{61}N_{12}O_{13}S_2Zn]^{3-}$	368.439	368.440
	$H[C_{45}H_{61}N_{12}O_{13}S_2Zn]^{2-}$	553.161	553.164
L3	$[C_{41}H_{57}N_{12}O_{12}S_2Zn]^{3-}$	345.764	345.765
L4	$[C_{29}H_{42}N_{10}O_9S_2Zn]^{2-}$	401.091	401.094

Table S2. MS/MS fragmentation of **L1**.

Fragment	***m/z* (calculated)**	***m/z* (observed)**	**Stoichiometry**	**Charge**
c_1-2H	153.078	153.077	$C_6H_9N_4O$	1-
c_2-2H	256.087	256.086	$C_9H_{14}N_5O_2S$	1-
c_2-2H-H_2S	222.100	222.098	$C_9H_{12}N_5O_2$	1-
c_2-2H-H_2S-CHNO	179.094	179.093	$C_8H_{10}N_4O$	1-
c_2-2H-H_2S-NH_3	205.073	205.072	$C_9H_9N_4O_2$	1-
c_5-2H	581.251	581.249	$C_{24}H_{37}N_8O_7S$	1-
c_5-2H-H_2S	547.263	547.261	$C_{24}H_{35}N_8O_7$	1-
CDLP-2H-CO-CH_2N	371.152	371.150	$C_{16}H_{25}N_3O_5S$	1-
CDLP-2H-CO-CH_2N-O_2	339.162	339.160	$C_{16}H_{25}N_3O_3S$	1-
CDLP-2H-CO-CH_2N-O_2-HS	306.182	306.181	$C_{16}H_{24}N_3O_3$	1-
$H_{-2}L$	501.203	501.200	$C_{43}H_{62}N_{12}O_{12}S_2$	2-
$H_{-2}L$-2H_2S	467.215	467.213	$C_{43}H_{58}N_{12}O_{12}$	2-
$H_{-2}L$-2H_2S-C	461.215	461.213	$C_{42}H_{58}N_{12}O_{12}$	2-
$H_{-2}L$-2H_2S-H_2O	458.210	458.208	$C_{43}H_{56}N_{12}O_{11}$	2-
$H_{-2}L$-H_2S	484.209	484.207	$C_{43}H_{60}N_{12}O_{12}S$	2-
$H_{-2}L$-H_2S-H_2O	475.204	475.202	$C_{43}H_{58}N_{12}O_{11}S$	2-
Tyr-NH_3	162.056	162.055	$C_9H_8NO_2$	1-
x_2-2H	304.130	304.129	$C_{15}H_{18}N_3O_4$	1-
x_4-1H-H_2S	431.181	431.179	$C_{20}H_{25}N_5O_6$	1-
y_2-2H	278.151	278.150	$C_{14}H_{20}N_3O_3$	1-
y_3-2H	335.172	335.171	$C_{16}H_{23}N_4O_4$	1-
y_4-2H-H_2S	404.194	404.192	$C_{19}H_{26}N_5O_5$	1-
y_7-2H	763.345	763.342	$C_{34}H_{51}N_8O_{10}S$	1-
y_7-2H-H_2S	729.358	729.355	$C_{34}H_{49}N_8O_{10}$	1-
z_4-3H	421.155	421.153	$C_{19}H_{25}N_4O_5S$	1-
z_4-3H-CH_2S-CO	347.172	347.171	$C_{17}H_{23}N_4O_4$	1-
z_4-3H-H_2S	387.167	387.166	$C_{19}H_{23}N_4O_5$	1-
z_4-3H-H_2S-C_2H_2	361.152	361.150	$C_{17}H_{21}N_4O_5$	1-
z_7-3H	746.319	746.316	$C_{34}H_{48}N_7O_{10}S$	1-
z_7-3H-H_2S	712.331	712.328	$C_{34}H_{46}N_7O_{10}$	1-
z_7-3H-H_2S	355.662	355.660	$C_{34}H_{45}N_7O_{10}$	2-
z_7-3H-H_2S-H_2O	694.321	694.318	$C_{34}H_{44}N_7O_9$	1-

Table S3. MS/MS fragmentation of [$ZnH_{-1}L$] complex formed between Zn(II) and **L1**.

Fragment	***m/z* (calculated)**	***m/z* (observed)**	**Stoichiometry**	**Charge**
c_1-2H	153.078	153.077	$C_6H_9N_4O$	1-
c_2-2H-H_2S	222.100	222.098	$C_9H_{12}N_5O_2$	1-
c_2-2H-H_2S-CHNO	179.094	179.093	$C_8H_{10}N_4O$	1-
c_2-2H-H_2S-NH_3	205.073	205.072	$C_9H_9N_4O_2$	1-
c_2-4H+Zn	318.001	318.000	$C_9H_{12}N_5O_2SZn$	1-
c_5-4H+Zn	643.165	643.165	$C_{24}H_{35}N_8O_7SZn$	1-
c_5-4H+Zn-H_2S	609.177	609.179	$C_{24}H_{33}N_8O_7Zn$	1-
Tyr side chain	106.042	106.042	C_7H_6O	1-
Tyr-NH_3	162.056	162.055	$C_9H_8NO_2$	1-
x_4-1H-H_2S	431.181	431.179	$C_{20}H_{25}N_5O_6$	1-
x_4-1H-H_2S	431.181	431.181	$C_{20}H_{25}N_5O_6$	1-
x_4-2H-H_2S	215.087	215.087	$C_{20}H_{24}N_5O_6$	2-
x_8-1H+Zn-CH_2S	303.761	303.760	$C_{37}H_{53}N_9O_{12}SZn$	3-
x_8-1H+Zn-H_2S	307.761	307.761	$C_{38}H_{53}N_9O_{12}SZn$	3-
y_2-2H	278.151	278.150	$C_{14}H_{20}N_3O_3$	1-
y_4-2H-H_2S	201.593	201.593	$C_{19}H_{25}N_5O_5$	2-
y_5-3H-CH_2S	244.120	244.119	$C_{23}H_{32}N_6O_6$	2-
y_5-3H-H_2S	250.120	250.119	$C_{24}H_{32}N_6O_6$	2-
y_5-4H+Zn	597.148	597.149	$C_{24}H_{33}N_6O_6SZn$	1-
y_5-5H+Zn	298.070	298.070	$C_{24}H_{32}N_6O_6SZn$	2-
y_7-5H+Zn	412.126	412.125	$C_{34}H_{48}N_8O_{10}SZn$	2-
z_4-3H	421.155	421.153	$C_{19}H_{25}N_4O_5S$	1-
z_4-3H-H_2S	387.167	387.166	$C_{19}H_{23}N_4O_5$	1-
z_4-4H	210.074	210.074	$C_{19}H_{24}N_4O_5S$	2-
z_7-5H+Zn	808.232	808.231	$C_{34}H_{46}N_7O_{10}SZn$	1-
z_7-5H+Zn-CO_2	764.243	764.241	$C_{33}H_{46}N_7O_8SZn$	1-
z_7-6H+Zn	403.613	403.611	$C_{34}H_{45}N_7O_{10}SZn$	2-
z_7-6H+Zn-CO_2	381.618	381.617	$C_{33}H_{45}N_7O_8SZn$	2-
$ZnH_{-1}L$-2H_2S	498.172	498.174	$C_{43}H_{56}N_{12}O_{12}Zn$	2-
$ZnH_{-1}L$-2H_2S-CHNO	476.669	476.666	$C_{43}H_{56}N_{12}O_{12}Zn$	2-
$ZnH_{-1}L$-CH_2S	339.108	339.107	$C_{42}H_{57}N_{12}O_{12}SZn$	3-
$ZnH_{-1}L$-H_2S	343.108	343.108	$C_{43}H_{57}N_{12}O_{12}SZn$	3-
$ZnH_{-1}L$-H_2S	515.166	515.166	$C_{43}H_{58}N_{12}O_{12}SZn$	2-
$ZnH_{-1}L$-Tyr side chain	319.090	319.089	$C_{36}H_{53}N_{12}O_{11}S_2Zn$	3-

Table S4. MS/MS fragmentation of **L2**.

Fragment	***m/z* (calculated)**	***m/z* (observed)**	**Stoichiometry**	**Charge**
c_1-2H	195.089	195.088	$C_8H_{11}N_4O_2$	1-
c_1-2H-C_2H_2O	153.078	153.077	$C_6H_9N_4O$	1-
c_1-2H-NH_3	178.062	178.061	$C_8H_8N_3O_2$	1-
c_2-2H	298.098	298.096	$C_{11}H_{16}N_5O_3S$	1-
c_2-2H-H_2S	264.110	264.109	$C_{11}H_{14}N_5O_3$	1-
c_2-2H-H_2S-C_2H_2O	222.100	222.099	$C_9H_{12}N_5O_2$	1-
c_2-2H-H_2S-C_2H_2O-NH_3	205.073	205.072	$C_9H_9N_4O_2$	1-
c_2-2H-H_2S-H_2O	246.100	246.098	$C_{11}H_{12}N_5O_2$	1-
c_5-2H	623.262	623.258	$C_{26}H_{39}N_8O_8S$	1-
c_5-2H-H_2S	589.274	589.271	$C_{26}H_{37}N_8O_8$	1-
CDLP-2H-CH_2NO	383.152	383.150	$C_{17}H_{25}N_3O_5S$	1-
CDLP-2H-CO-C_2H_5N-O_2	324.139	324.137	$C_{15}H_{22}N_3O_3S$	1-
CDLP-2H-CO-CH_2N	371.152	371.150	$C_{16}H_{25}N_3O_5S$	1-
CDLP-2H-CO-CH_2N-O_2	339.162	339.160	$C_{16}H_{25}N_3O_3S$	1-
CDLP-2H-CO-CH_2N-O_2-HS	306.182	306.181	$C_{16}H_{24}N_3O_3$	1-
$H_{-2}L$	522.208	522.205	$C_{45}H_{64}N_{12}O_{13}S_2$	2-
$H_{-2}L$-$2H_2S$	488.221	488.218	$C_{45}H_{60}N_{12}O_{13}$	2-
$H_{-2}L$-$2H_2S$-C	482.221	482.218	$C_{44}H_{60}N_{12}O_{13}$	2-
$H_{-2}L$-$2H_2S$-CO_2	466.226	466.223	$C_{44}H_{60}N_{12}O_{11}$	2-
$H_{-2}L$-$2H_2S$-H_2O	479.215	479.212	$C_{45}H_{58}N_{12}O_{12}$	2-
$H_{-2}L$-H_2S	505.215	505.211	$C_{45}H_{62}N_{12}O_{13}S$	2-
$H_{-2}L$-H_2S-H_2O	496.209	496.206	$C_{45}H_{60}N_{12}O_{12}S$	2-
Tyr-NH_3	162.056	162.055	$C_9H_8NO_2$	1-
x_2-2H	304.130	304.129	$C_{15}H_{18}N_3O_4$	1-
x_4-1H-H_2S	431.181	431.179	$C_{20}H_{25}N_5O_6$	1-
y_2-2H	278.151	278.150	$C_{14}H_{20}N_3O_3$	1-
y_3-2H	335.172	335.171	$C_{16}H_{23}N_4O_4$	1-
y_4-2H-H_2S	404.194	404.192	$C_{19}H_{26}N_5O_5$	1-
y_7-2H	763.345	763.342	$C_{34}H_{51}N_8O_{10}S$	1-
y_7-2H-H_2S	729.358	729.355	$C_{34}H_{49}N_8O_{10}$	1-
y_8-2H-$2H_2S$	398.686	398.684	$C_{37}H_{51}N_9O_{11}$	2-
y_8-2H-$2H_2S$	798.379	798.375	$C_{37}H_{52}N_9O_{11}$	1-
y_8-2H-H_2S	832.367	832.363	$C_{37}H_{54}N_9O_{11}S$	1-
y_8-2H-H_2S-NH_3	815.340	815.335	$C_{37}H_{51}N_8O_{11}S$	1-
z_4-3H	421.155	421.153	$C_{19}H_{25}N_4O_5S$	1-
z_4-3H-CH_2S-CO	347.172	347.171	$C_{17}H_{23}N_4O_4$	1-

z_4-3H-H_2S	387.167	387.166	$C_{19}H_{23}N_4O_5$	1-
z_4-3H-H_2S-C_2H_2	361.152	361.150	$C_{17}H_{21}N_4O_5$	1-
z_7-3H	746.319	746.316	$C_{34}H_{48}N_7O_{10}S$	1-
z_7-3H-H_2S	355.662	355.660	$C_{34}H_{45}N_7O_{10}$	2-
z_7-3H-H_2S	712.331	712.328	$C_{34}H_{46}N_7O_{10}$	1-
z_7-3H-H_2S-H_2O	694.321	694.318	$C_{34}H_{44}N_7O_9$	1-

Table S5. MS/MS fragmentation of [$ZnH_{-1}L$] complex formed between Zn(II) and **L2**.

Fragment	***m/z* (calculated)**	***m/z* (observed)**	**Stoichiometry**	**Charge**
a_5-4H+Zn	640.154	640.150	$C_{25}H_{34}N_7O_7SZn$	1-
b_3-4H+Zn	458.012	458.009	$C_{25}H_{41}N_6O_8SZn$	1-
b_4-4H+Zn	571.096	571.092	$C_{21}H_{27}N_6O_7SZn$	1-
c_1-2H	195.089	195.088	$C_8H_{11}N_4O_2$	1-
c_1-2H-NH_3	178.062	178.061	$C_8H_8N_3O_2$	1-
c_2-2H	298.098	298.096	$C_{11}H_{16}N_5O_3S$	1-
c_2-2H-H_2S	264.110	264.108	$C_{11}H_{14}N_5O_3$	1-
c_2-2H-H_2S-C_2H_2O	222.100	222.098	$C_9H_{12}N_5O_2$	1-
c_2-2H-H_2S-C_2H_2O-NH_3	205.073	205.072	$C_9H_9N_4O_2$	1-
c_2-2H-H_2S-H_2O	246.100	246.098	$C_{11}H_{12}N_5O_2$	1-
c_2-4H+Zn	360.011	360.009	$C_{11}H_{14}N_5O_3S$	1-
c_5-4H+Zn	685.175	685.171	$C_{26}H_{39}N_8O_8S$	1-
DLPCGV-6H-H_2S-CO_2	501.247	501.244	$C_{24}H_{33}N_6O_6$	1-
DLPCGV-6H-H_2S-CO_2-H_2O	483.236	483.233	$C_{24}H_{31}N_6O_5$	1-
Tyr-NH_3	162.056	162.055	$C_9H_8NO_2$	1-
x_2-2H	304.130	304.128	$C_{15}H_{18}N_3O_4$	1-
x_4-1H-H_2S	431.181	431.178	$C_{20}H_{25}N_5O_6$	1-
y_2-2H	278.151	278.149	$C_{14}H_{20}N_3O_3$	1-
y_3-2H	335.172	335.170	$C_{16}H_{23}N_4O_4$	1-
y_4-2H-H_2S	404.194	404.191	$C_{19}H_{26}N_5O_5$	1-
y_5-4H+Zn	597.148	597.144	$C_{24}H_{33}N_6O_6SZn$	1-
y_6-2H-H_2S	614.331	614.327	$C_{30}H_{44}N_7O_7$	1-
y_7-4H+Zn	825.259	825.253	$C_{34}H_{49}N_8O_{10}SZn$	1-
y_7-5H+Zn	412.126	412.125	$C_{34}H_{48}N_8O_{10}SZn$	2-
y_8-4H-H_2S+Zn	894.280	894.276	$C_{37}H_{52}N_9O_{11}SZn$	1-
y_8-5H-H_2S+Zn	446.637	446.633	$C_{37}H_{51}N_9O_{11}SZn$	2-
z_4-3H	421.155	421.153	$C_{19}H_{25}N_4O_5S$	1-
z_4-3H-CH_2S-CO	347.172	347.170	$C_{17}H_{23}N_4O_4$	1-
z_4-3H-H_2S	387.167	387.165	$C_{19}H_{23}N_4O_5$	1-
z_7-5H+Zn	808.233	808.228	$C_{34}H_{46}N_7O_{10}SZn$	1-
z_7-5H-CO_2+Zn	764.243	764.238	$C_{33}H_{46}N_7O_8SZn$	1-
z_7-5H-H_2O+Zn	790.222	790.217	$C_{34}H_{44}N_7O_9SZn$	1-
z_7-6H+Zn	403.613	403.611	$C_{34}H_{45}N_7O_{10}SZn$	2-
$ZnH_{-1}L$-2H_2S	519.177	519.174	$C_{45}H_{58}N_{12}O_{13}Zn$	2-
$ZnH_{-1}L$-2H_2S-CO_2	497.179	497.183	$C_{44}H_{58}N_{12}O_{11}Zn$	2-
$ZnH_{-1}L$-2H_2S-H_2O	510.172	510.169	$C_{45}H_{56}N_{12}O_{12}Zn$	2-

$ZnH_{-1}L\text{-}H_2S$	536.171	536.167	$C_{45}H_{60}N_{12}O_{13}SZn$	2-
$ZnH_{-1}L\text{-}H_2S\text{-}CO_2$	514.176	514.173	$C_{44}H_{60}N_{12}O_{11}SZn$	2-
$ZnH_{-1}L\text{-}H_2S\text{-}H_2O$	527.166	527.162	$C_{45}H_{58}N_{12}O_{12}SZn$	2-

Table S6. MS/MS fragmentation of **L3**.

Fragment	*m/z* (calculated)	*m/z* (observed)	Stoichiometry	Charge
c_1-2H	153.078	153.077	$C_6H_9N_4O$	1-
c_2-2H	256.087	256.086	$C_9H_{14}N_5O_2S$	1-
c_2-2H-H_2S	222.100	222.098	$C_9H_{12}N_5O_2$	1-
c_2-2H-H_2S-CHNO	179.094	179.093	$C_8H_{10}N_4O$	1-
c_2-2H-H_2S-NH_3	205.073	205.072	$C_9H_9N_4O_2$	1-
c_5-2H	555.235	555.232	$C_{22}H_{35}N_8O_7S$	1-
c_5-2H-NH_3	538.209	538.207	$C_{22}H_{32}N_7O_7S$	1-
c_5-2H-NH_3-H_2S	504.221	504.219	$C_{22}H_{30}N_7O_7$	1-
$H_{-2}L$	488.195	488.195	$C_{41}H_{60}N_{12}O_{12}S_2$	2-
$H_{-2}L$-2H_2S	454.208	454.205	$C_{41}H_{56}N_{12}O_{12}$	2-
$H_{-2}L$-2H_2S-C	448.208	448.205	$C_{40}H_{56}N_{12}O_{12}$	2-
$H_{-2}L$-2H_2S-H_2O	445.202	445.200	$C_{41}H_{54}N_{12}O_{11}$	2-
$H_{-2}L$-2H_2S-H_2O-NHCO	423.699	423.697	$C_{40}H_{53}N_{11}O_{10}$	2-
$H_{-2}L$-H_2S	471.201	471.199	$C_{41}H_{58}N_{12}O_{12}S$	2-
$H_{-2}L$-H_2S-H_2O	462.196	462.194	$C_{41}H_{56}N_{12}O_{11}S$	2-
Tyr-NH_3	162.056	162.055	$C_9H_8NO_2$	1-
x_2-2H	304.130	304.129	$C_{15}H_{18}N_3O_4$	1-
x_4-1H-H_2S	431.181	431.179	$C_{20}H_{25}N_5O_6$	1-
y_2-2H	278.151	278.150	$C_{14}H_{20}N_3O_3$	1-
y_3-2H	335.172	335.171	$C_{16}H_{23}N_4O_4$	1-
y_4-2H-H_2S	404.194	404.192	$C_{19}H_{26}N_5O_5$	1-
y_5-2H-H_2S	475.231	475.229	$C_{22}H_{31}N_6O_6$	1-
y_5-2H-H_2S-H_2O	457.220	457.218	$C_{22}H_{29}N_6O_5$	1-
y_6-2H-H_2S	588.315	588.312	$C_{28}H_{42}N_7O_7$	1-
y_6-2H-H_2S-H_2O	570.305	570.302	$C_{28}H_{40}N_7O_6$	1-
y_7-2H	737.330	737.324	$C_{32}H_{49}N_8O_{10}S$	1-
y_7-2H-H_2S	703.342	703.339	$C_{32}H_{47}N_8O_{10}$	1-
y_7-2H-H_2S	351.167	351.166	$C_{32}H_{46}N_8O_{10}$	2-
y_7-2H-H_2S-2H_2O	333.157	333.155	$C_{32}H_{42}N_8O_8$	2-
y_7-2H-H_2S-NH_3	342.654	342.653	$C_{32}H_{43}N_7O_{10}$	2-
z_4-3H	421.155	421.153	$C_{19}H_{25}N_4O_5S$	1-
z_4-3H-CH_2S-CO	347.172	347.171	$C_{17}H_{23}N_4O_4$	1-
z_4-3H-H_2S	387.167	387.166	$C_{19}H_{23}N_4O_5$	1-
z_4-3H-H_2S-C_2H_2	361.152	361.150	$C_{17}H_{21}N_4O_5$	1-
z_5-2H-H_2S-CH_3CO	416.194	416.192	$C_{20}H_{26}N_5O_5$	1-
z_5-3H-H_2S-H_2O	440.194	440.192	$C_{22}H_{26}N_5O_5$	1-

z_7-3H	720.303	720.300	$C_{32}H_{46}N_7O_{10}S$	1-
z_7-3H-H_2O	702.293	702.288	$C_{32}H_{44}N_7O_9S$	1-
z_7-3H-H_2S	686.316	686.312	$C_{32}H_{44}N_7O_{10}$	1-
z_7-3H-H_2S-2H_2O	650.294	650.291	$C_{32}H_{40}N_7O_8$	1-
z_7-3H-H_2S-CO_2	642.326	642.322	$C_{31}H_{44}N_7O_8$	1-
z_7-3H-H_2S-CO_2-H_2O	624.315	624.312	$C_{31}H_{42}N_7O_7$	1-
z_7-3H-H_2S-H_2O	668.305	668.302	$C_{32}H_{42}N_7O_9$	1-

Table S7. MS/MS fragmentation of [$ZnH_{-1}L$] complex formed between Zn(II) and **L3**.

Fragment	***m/z* (calculated)**	***m/z* (observed)**	**Stoichiometry**	**Charge**
b_4-4H+Zn	529.085	529.083	$C_{19}H_{25}N_6O_6SZn$	1-
b_4-H_2O-4H+Zn	511.075	511.074	$C_{19}H_{23}N_6O_5SZn$	1-
b_4-H_2O-4H-$C_4H_6N_3$+Zn	415.019	415.016	$C_{15}H_{17}N_3O_5SZn$	1-
c_1-2H	153.078	153.077	$C_6H_9N_4O$	1-
c_2-2H-H_2S	222.100	222.100	$C_9H_{12}N_5O_2$	1-
c_2-2H-H_2S-CHNO	179.094	179.093	$C_8H_{10}N_4O$	1-
c_2-4H+Zn	318.001	318.000	$C_9H_{12}N_5O_2SZn$	1-
c_2-5H+Zn	158.497	158.496	$C_9H_{11}N_5O_2SZn$	2-
c_5-4H+Zn	617.148	617.148	$C_{22}H_{33}N_8O_7SZn$	1-
c_5-4H+Zn-NH_3	600.122	600.122	$C_{22}H_{30}N_7O_7SZn$	1-
c_5-4H+Zn-NH_3-H_2O	582.112	582.111	$C_{22}H_{28}N_7O_6SZn$	1-
DLACGV-3H-H_2S+Zn	293.087	293.085	$C_{23}H_{34}N_6O_8Zn$	2-
DLACGV-7H-H_2S-CO_2	237.112	237.111	$C_{22}H_{30}N_6O_6$	2-
L-H-H_2S-2NH_3	454.175	454.173	$C_{41}H_{63}N_{12}O_{12}S_2$	2-
Tyr-NH_3	162.056	162.056	$C_9H_8NO_2$	1-
x_2-2H	304.130	304.129	$C_{15}H_{18}N_3O_4$	1-
x_4-1H-H_2S	431.181	431.180	$C_{20}H_{25}N_5O_6$	1-
z_4-3H-H_2S-C_2H_2	361.152	361.150	$C_{17}H_{21}N_4O_5$	1-
x_4-2H-H_2S	215.087	215.087	$C_{20}H_{24}N_5O_6$	2-
y_4-2H-H_2S	201.593	201.593	$C_{19}H_{25}N_5O_5$	2-
y_4-2H-H_2S	404.194	404.193	$C_{19}H_{26}N_5O_5$	1-
y_4-3H	218.587	218.587	$C_{19}H_{27}N_5O_5S$	2-
z_4-3H	421.155	421.155	$C_{19}H_{25}N_4O_5S$	1-
z_4-3H-H_2S	387.167	387.166	$C_{19}H_{23}N_4O_5$	1-
z_4-4H	210.074	210.073	$C_{19}H_{24}N_4O_5S$	2-
z_5-5H+Zn	554.106	554.105	$C_{22}H_{28}N_5O_6SZn$	1-
z_5-5H+Zn-$C_2H_2NO_3$	466.102	466.101	$C_{20}H_{26}N_4O_3SZn$	1-
z_7-5H+Zn	782.217	782.215	$C_{32}H_{44}N_7O_{10}SZn$	1-
z_7-5H-CO_2+Zn	738.227	738.227	$C_{31}H_{44}N_7O_8SZn$	1-
z_7-5H-H_2O+Zn	764.206	764.206	$C_{32}H_{42}N_7O_9SZn$	1-
z_7-5H-H_2O-H_2S+Zn	730.218	730.217	$C_{32}H_{40}N_7O_9Zn$	1-
z_7-5H-H_2S+Zn	748.229	748.228	$C_{32}H_{42}N_7O_{10}Zn$	1-
z_7-6H+Zn	390.605	390.603	$C_{32}H_{43}N_7O_{10}SZn$	2-
z_7-6H-CO_2+Zn	368.610	368.608	$C_{31}H_{43}N_7O_8SZn$	2-
z_7-6H-CO_2-H_2O+Zn	359.604	359.602	$C_{31}H_{41}N_7O_7SZn$	2-
z_7-6H-H_2O+Zn	381.599	381.598	$C_{32}H_{41}N_7O_9SZn$	2-

z_7-6H-H_2O-H_2S+Zn	364.606	364.604	$C_{32}H_{39}N_7O_9Zn$	2-
z_7-6H-H_2S+Zn	373.611	373.610	$C_{32}H_{41}N_7O_{10}Zn$	2-
$ZnH_{-1}L$-2H_2S-$C_4H_{10}O_2$	440.130	440.130	$C_{37}H_{44}N_{12}O_{10}Zn$	2-
$ZnH_{-1}L$-2H_2S-H_2O	476.159	476.157	$C_{41}H_{52}N_{12}O_{11}Zn$	2-
$ZnH_{-1}L$-H_2S	334.436	334.435	$C_{41}H_{55}N_{12}O_{12}SZn$	3-
$ZnH_{-1}L$-H_2S	502.158	502.157	$C_{41}H_{56}N_{12}O_{12}SZn$	2-
$ZnH_{-1}L$-H_2S-2H_2O	484.148	484.147	$C_{41}H_{52}N_{12}O_{10}SZn$	2-
$ZnH_{-1}L$-H_2S-H_2O	328.433	328.431	$C_{41}H_{53}N_{12}O_{11}SZn$	3-
$ZnH_{-1}L$-H_2S-H_2O	493.153	493.152	$C_{41}H_{54}N_{12}O_{11}SZn$	2-

Table S8. MS/MS fragmentation of **L4**.

Fragment	***m/z* (calculated)**	***m/z* (observed)**	**Stoichiometry**	**Charge**
c_1-2H	153.078	153.077	$C_6H_9N_4O$	1-
c_2-2H	256.087	256.086	$C_9H_{14}N_5O_2S$	1-
c_2-2H-H_2S	222.100	222.098	$C_9H_{12}N_5O_2$	1-
c_2-2H-H_2S-CHNO	179.094	179.093	$C_8H_{10}N_4O$	1-
c_2-2H-H_2S-NH_3	205.073	205.072	$C_9H_9N_4O_2$	1-
c_5-2H	581.251	581.249	$C_{24}H_{37}N_8O_7S$	1-
c_5-2H-H_2S	547.263	547.261	$C_{24}H_{35}N_8O_7$	1-
c_5-2H-H_2S-H_2O	529.253	529.249	$C_{24}H_{33}N_8O_6$	1-
DLP-2H	324.156	324.154	$C_{15}H_{22}N_3O_5$	1-
$H_{-2}L$	370.137	370.135	$C_{29}H_{44}N_{10}O_9S_2$	2-
$H_{-2}L$-2H_2S	336.150	336.147	$C_{29}H_{40}N_{10}O_9$	2-
$H_{-2}L$-2H_2S	673.306	673.302	$C_{29}H_{41}N_{10}O_9$	1-
$H_{-2}L$-2H_2S-C	330.150	330.147	$C_{28}H_{40}N_{10}O_9$	2-
$H_{-2}L$-2H_2S-C	661.306	661.302	$C_{28}H_{41}N_{10}O_9$	1-
$H_{-2}L$-2H_2S-C_2ONH_2	308.647	308.645	$C_{27}H_{39}N_9O_8$	2-
$H_{-2}L$-2H_2S-C_2ONH_2	618.300	618.296	$C_{27}H_{40}N_9O_8$	1-
$H_{-2}L$-2H_2S-C-H_2O	321.144	321.142	$C_{28}H_{38}N_{10}O_8$	2-
$H_{-2}L$-2H_2S-CHNO	630.300	630.296	$C_{28}H_{40}N_9O_8$	1-
$H_{-2}L$-2H_2S-$CONH_2$	314.647	314.645	$C_{28}H_{39}N_9O_8$	2-
$H_{-2}L$-2H_2S-H_2O	327.144	327.142	$C_{29}H_{40}N_{10}O_9$	2-
$H_{-2}L$-2H_2S-H_2O	655.296	655.291	$C_{29}H_{39}N_{10}O_8$	1-
$H_{-2}L$-CH_2S	347.143	347.141	$C_{28}H_{42}N_{10}O_9S$	1-
$H_{-2}L$-H_2S	353.143	353.141	$C_{29}H_{42}N_{10}O_9S$	2-
$H_{-2}L$-H_2S	707.294	707.289	$C_{29}H_{43}N_{10}O_9S$	1-
$H_{-2}L$-H_2S-CHNO	664.288	664.283	$C_{28}H_{42}N_9O_8S$	1-
$H_{-2}L$-H_2S-H_2O	344.138	344.136	$C_{29}H_{40}N_{10}O_8S$	2-
y_3-2H	273.103	273.101	$C_{10}H_{17}N_4O_3S$	1-
y_3-2H-H_2S	239.115	239.113	$C_{10}H_{15}N_4O_3$	1-
y_5-2H	501.214	501.211	$C_{20}H_{33}N_6O_7S$	1-
y_6-3H	301.608	301.606	$C_{23}H_{37}N_7O_8S_2$	2-
y_6-3H-H_2S	284.614	284.612	$C_{23}H_{35}N_7O_8S$	2-
z_2-3H	159.023	159.022	$C_5H_7N_2O_2S$	1-
z_2-3H-H_2S	125.036	125.035	$C_5H_5N_2O_2$	1-
z_5-3H	484.187	484.184	$C_{20}H_{30}N_5O_7S$	1-
z_5-3H-CH_2S-CO_2	394.210	394.207	$C_{18}H_{28}N_5O_5$	1-
z_5-3H-CH_2S-CO_2-NH_3	377.183	377.181	$C_{18}H_{25}N_4O_5$	1-

z_5-3H-CH_2S-H_2O	420.189	420.186	$C_{19}H_{26}N_5O_6$	1-
z_5-3H-CO_2	440.197	440.195	$C_{19}H_{30}N_5O_5S$	1-
z_5-3H-H_2O	466.177	466.174	$C_{20}H_{28}N_5O_6S$	1-
z_5-3H-H_2S	450.199	450.197	$C_{20}H_{28}N_5O_7$	1-
z_5-3H-H_2S-CO_2	406.210	406.207	$C_{19}H_{28}N_5O_5$	1-
z_5-3H-H_2S-CO_2-H_2O	388.199	388.196	$C_{19}H_{26}N_5O_4$	1-
z_5-3H-H_2S-H_2O	432.189	432.186	$C_{20}H_{26}N_5O_6$	1-

Table S9. MS/MS fragmentation of [$ZnH_{-1}L$] complex formed between Zn(II) and **L4**.

Fragment	***m/z* (calculated)**	***m/z* (observed)**	**Stoichiometry**	**Charge**
b_3-4H+Zn	416.001	415.999	$C_{13}H_{14}N_5O_5SZn$	1-
b_3-4H-H_2S+Zn	382.014	382.011	$C_{13}H_{12}N_5O_5Zn$	1-
b_4-4H-CO_2+Zn	485.095	485.092	$C_{18}H_{25}N_6O_4SZn$	1-
b_4-4H-H_2O+Zn	511.075	511.071	$C_{19}H_{23}N_6O_5SZn$	1-
c_1-2H	153.078	153.077	$C_6H_9N_4O$	1-
c_2-2H	256.087	256.086	$C_9H_{14}N_5O_2S$	1-
c_2-2H-H_2S	222.100	222.098	$C_9H_{12}N_5O_2$	1-
c_2-2H-H_2S-CHNO	179.094	179.093	$C_8H_{10}N_4O$	1-
c_2-2H-H_2S-NH_3	205.073	205.072	$C_9H_9N_4O_2$	1-
c_2-4H+Zn	318.000	317.999	$C_9H_{12}N_5O_2SZn$	1-
c_2-4H-NH_3+Zn	300.974	300.972	$C_9H_9N_4O_2SZn$	1-
c_5-4H+Zn	643.165	643.160	$C_{24}H_{35}N_8O_7SZn$	1-
c_5-4H+Zn-H_2O	625.154	625.150	$C_{24}H_{33}N_8O_6SZn$	1-
y_3-2H-H_2S	239.115	239.113	$C_{10}H_{15}N_4O_3$	1-
y_3-4H+Zn	335.016	335.014	$C_{10}H_{15}N_4O_3SZn$	1-
y_4-4H+Zn	448.100	448.098	$C_{16}H_{26}N_5O_4SZn$	1-
y_5-4H+Zn	563.127	563.124	$C_{20}H_{31}N_6O_7SZn$	1-
y_5-5H+Zn	281.060	281.058	$C_{20}H_{30}N_6O_7SZn$	1-
z_2-3H	159.023	159.022	$C_5H_7N_2O_2S$	1-
z_2-3H-H_2S	125.036	125.035	$C_5H_5N_2O_2$	1-
z_5-3H-H_2O	528.090	528.087	$C_{20}H_{26}N_5O_6S$	1-
z_5-5H+Zn	546.100	546.097	$C_{20}H_{28}N_5O_7SZn$	1-
z_5-5H-CO_2+Zn	502.111	502.108	$C_{19}H_{28}N_5O_5SZn$	1-
z_5-6H+Zn	272.547	272.545	$C_{20}H_{27}N_5O_7SZn$	1-
$ZnH_{-1}L$-CH_2S	378.100	378.098	$C_{28}H_{40}N_{10}O_9SZn$	2-
$ZnH_{-1}L$-H_2S	384.100	384.097	$C_{29}H_{40}N_{10}O_9SZn$	2-
$ZnH_{-1}L$-H_2S	769.208	769.203	$C_{29}H_{41}N_{10}O_9SZn$	1-
$ZnH_{-1}L$-H_2S-CHNO	362.597	362.595	$C_{29}H_{40}N_{10}O_9SZn$	2-
$ZnH_{-1}L$-H_2S-CHNO	726.202	726.198	$C_{28}H_{40}N_9O_8SZn$	1-
$ZnH_{-1}L$-H_2S-H_2O	375.095	375.093	$C_{29}H_{38}N_{10}O_8SZn$	2-