

Ferrocene-based Compartmental Ligand for the Assembly of Neutral Zn^{II}/Ln^{III}Heterometallic Complexes

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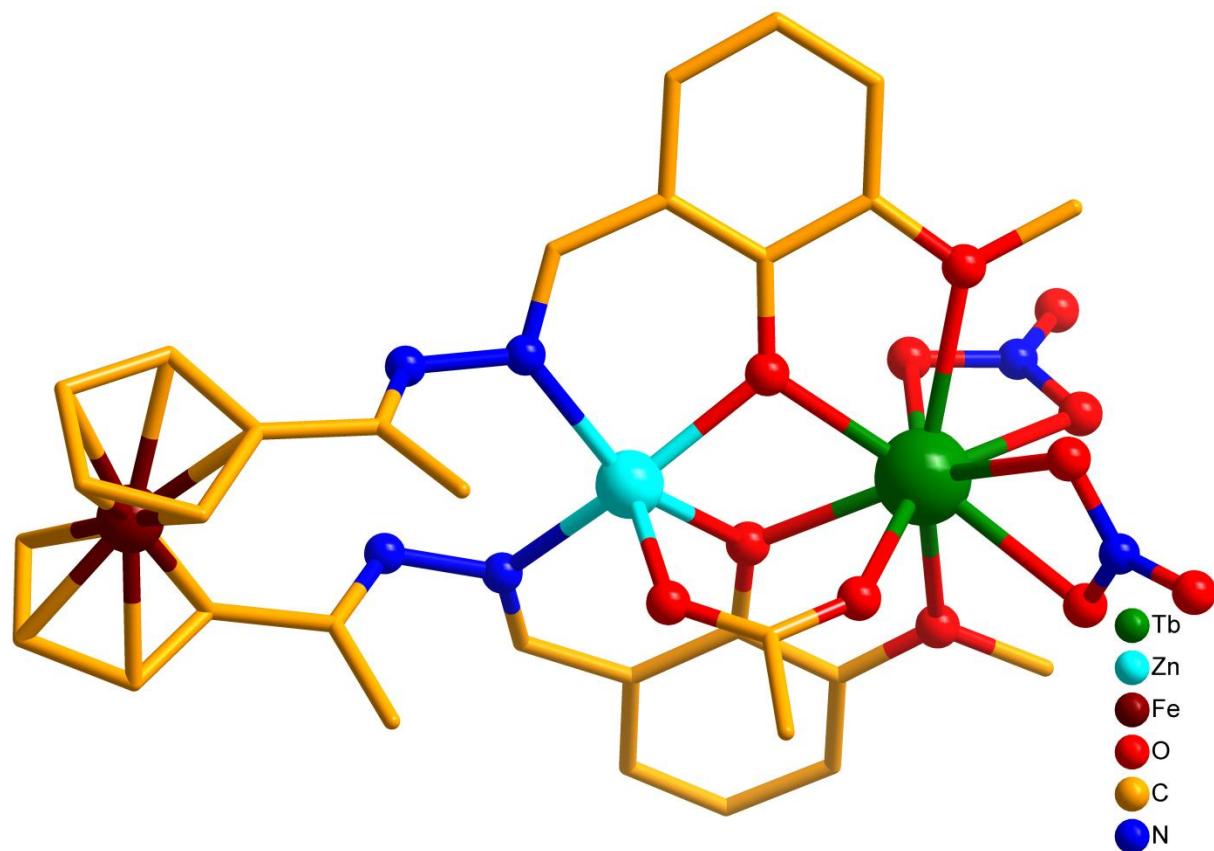


Figure S1.Molecular structure of **3**. Hydrogen atoms are omitted for clarity.

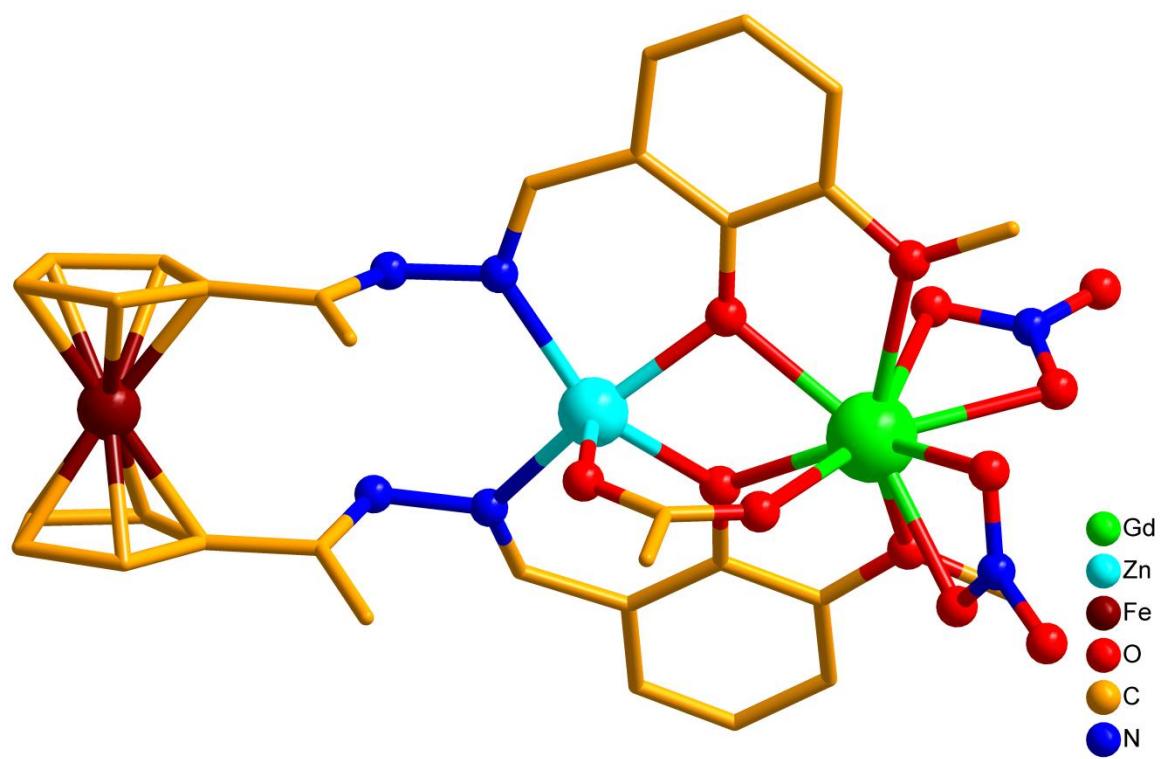


Figure S2. Molecular structure of $[\text{LZn}(\mu\text{-OAc})\text{Gd}(\text{NO}_3)_2, 2\text{CHCl}_3](\mathbf{4})$. Hydrogen atoms and solvent molecules are omitted for clarity.

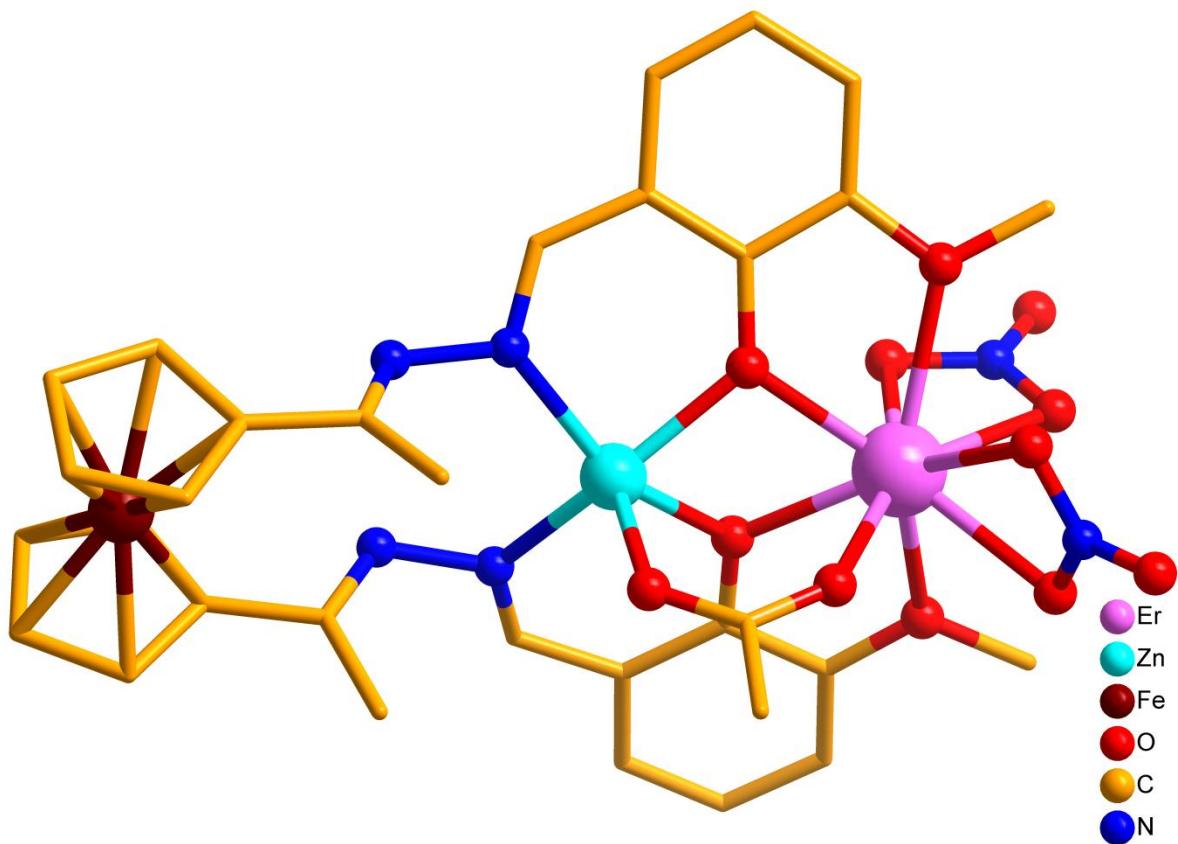


Figure S3. Molecular structure of $\text{LZn}(\mu\text{-OAc})\text{Er}(\text{NO}_3)_2$ (**5**). Hydrogen atoms are omitted for clarity.

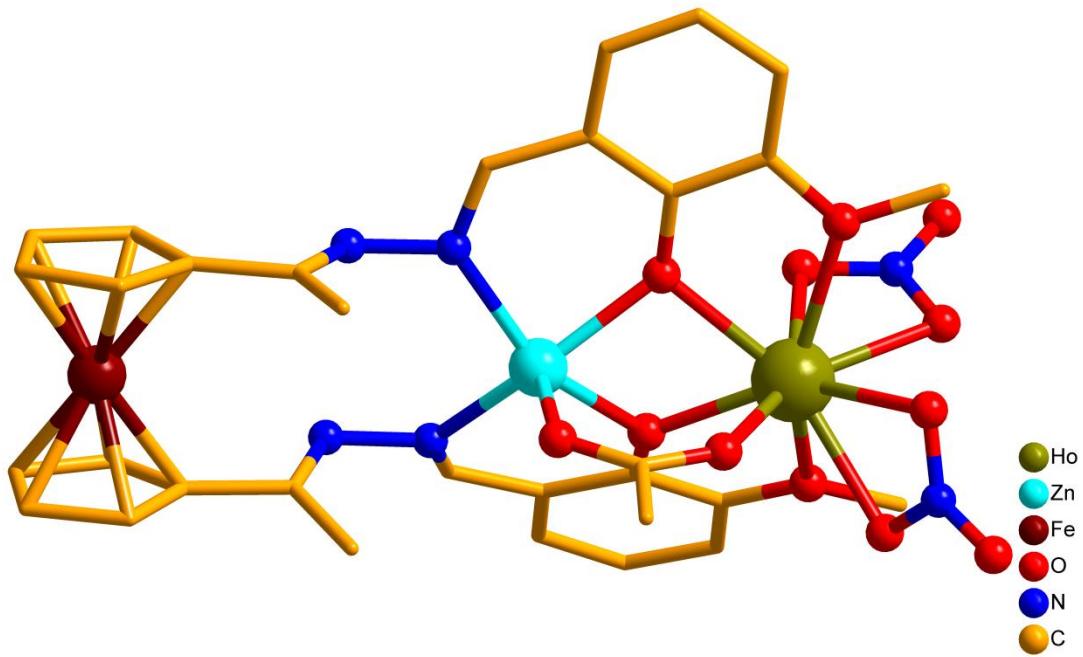


Figure S4. Molecular structure of $\text{LZn}(\mu\text{-OAc})\text{Ho}(\text{NO}_3)_2$ (6). Hydrogen atoms are omitted for clarity.

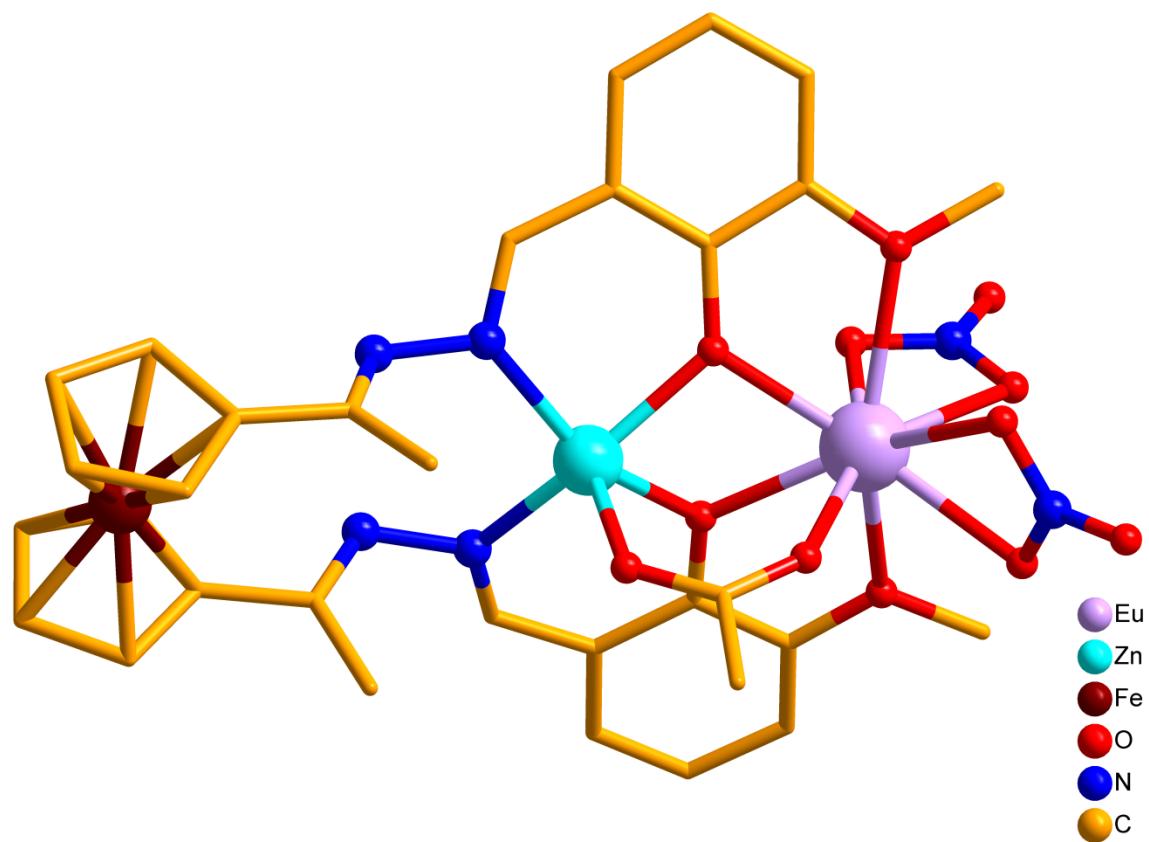


Figure S5.Molecular structure of $\text{LZn}(\mu\text{-OAc})\text{Eu}(\text{NO}_3)_2$ (**7**). Hydrogen atoms are omitted for clarity

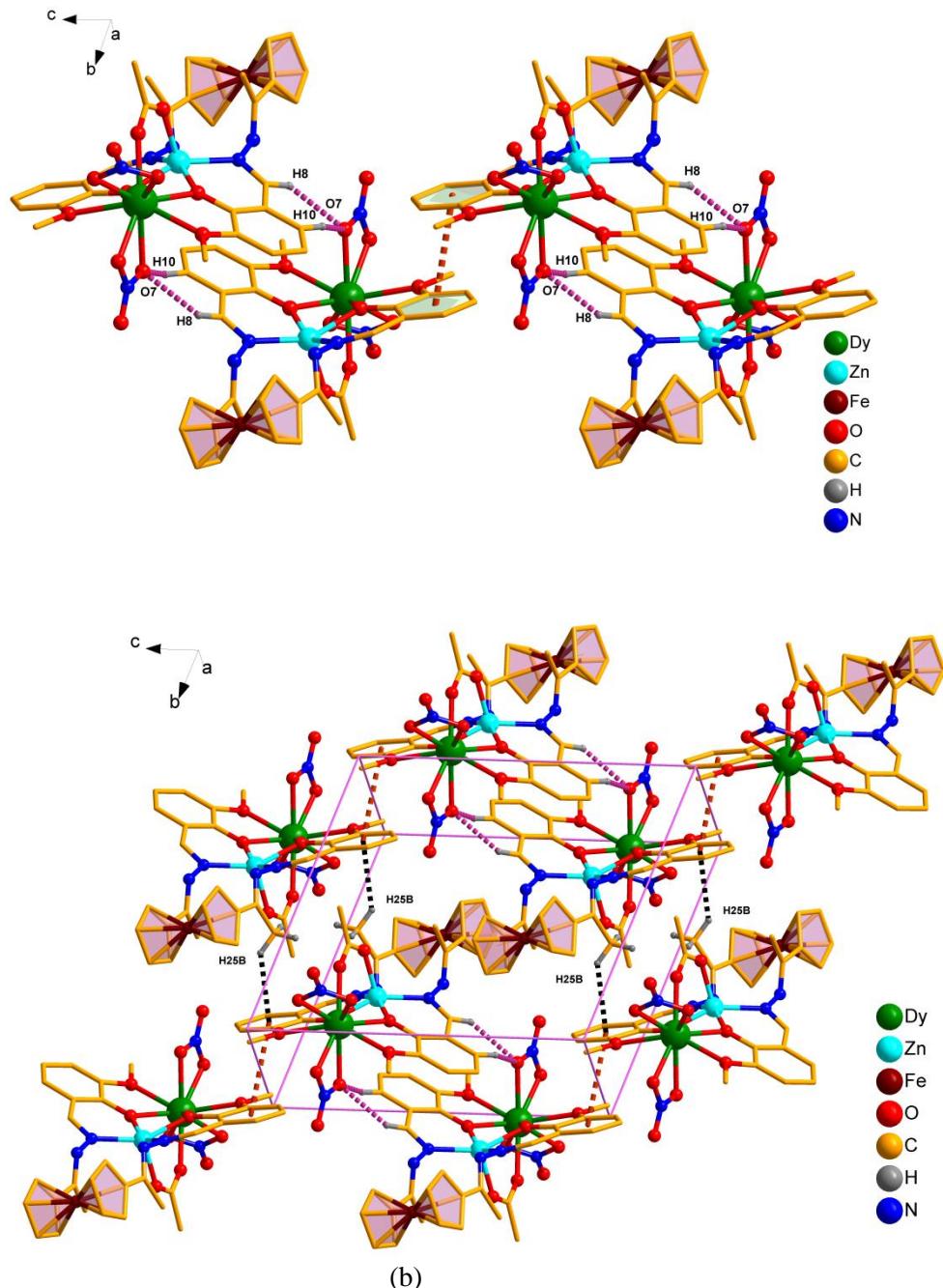


Figure S6. Views showing supramolecular interactions in 2 (a) hydrogen bonding and $\pi\cdots\pi$ stacking (b) molecular packing diagram. Some hydrogen atoms have been omitted for the sake of

clarity. The metric parameters involved are: C8-H8···O7, 2.5552(61) Å; C8-H8···O7, 148.108(57)°; C10-H10···O7, 2.7501 (10) Å; C10-H10···O7, 146.154(68)°; π···π, 3.6928(15) Å; C25-H25B···π, 2.7501(10) Å; C25-H25B···π, 137.102(65)°; Symmetry transformations used to generate equivalent atoms: #1 -x+1, -y, -z + 1; #2 -x+1, -y, -z+1; #3 -x+1, -y, -z, #4 x, 1+y, z.

Mass spectroscopy

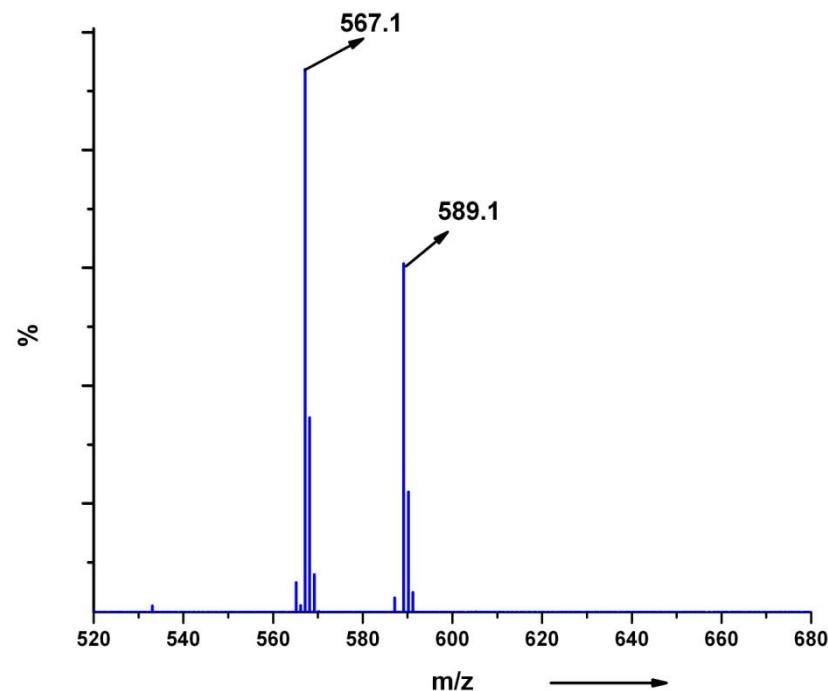


Figure S7.ESI-MS mass spectrum of H_2L showing the parent ion at m/z 589.1

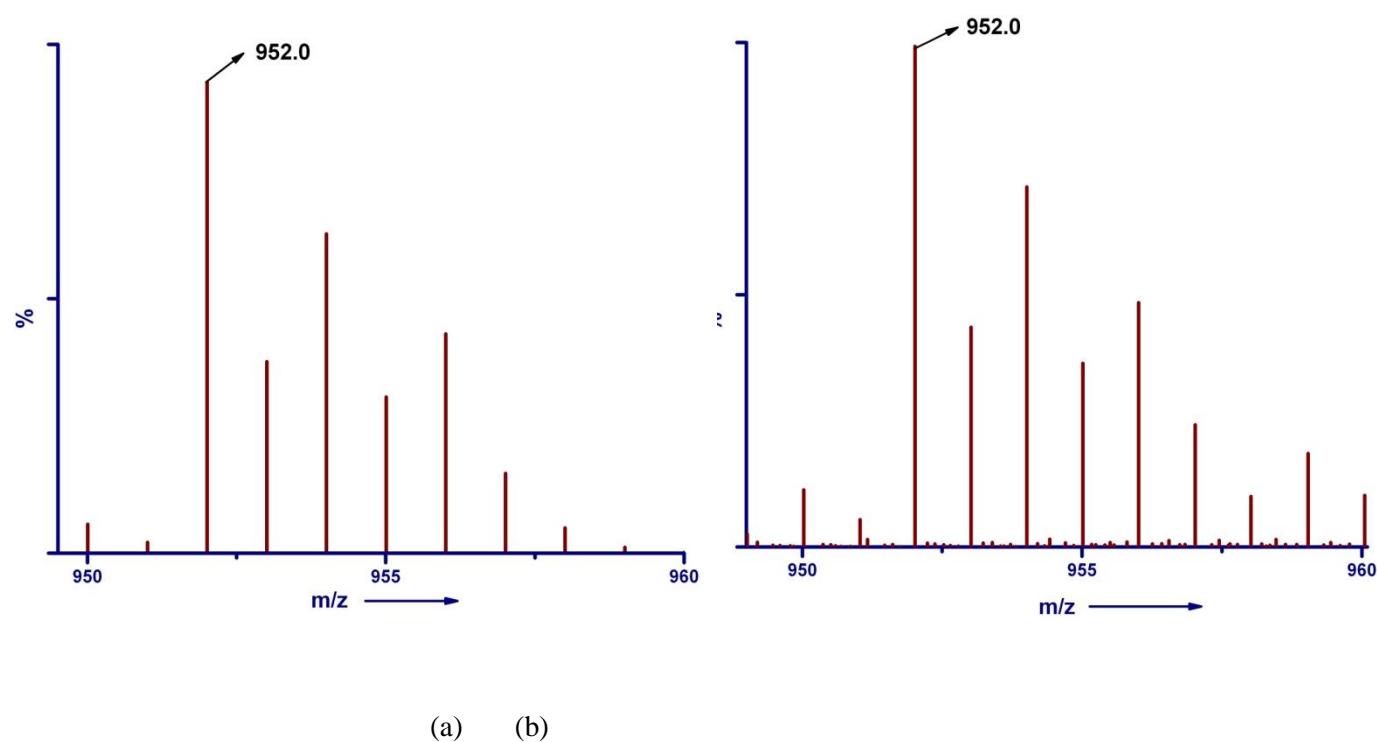


Figure S8.ESI-MS mass spectrum of **3**showing the species $[L\text{ZnTb}(\text{NO}_3)_2 + \text{CH}_3\text{CN}]^+$ (a) theoretical simulation (b) experimental spectrum.

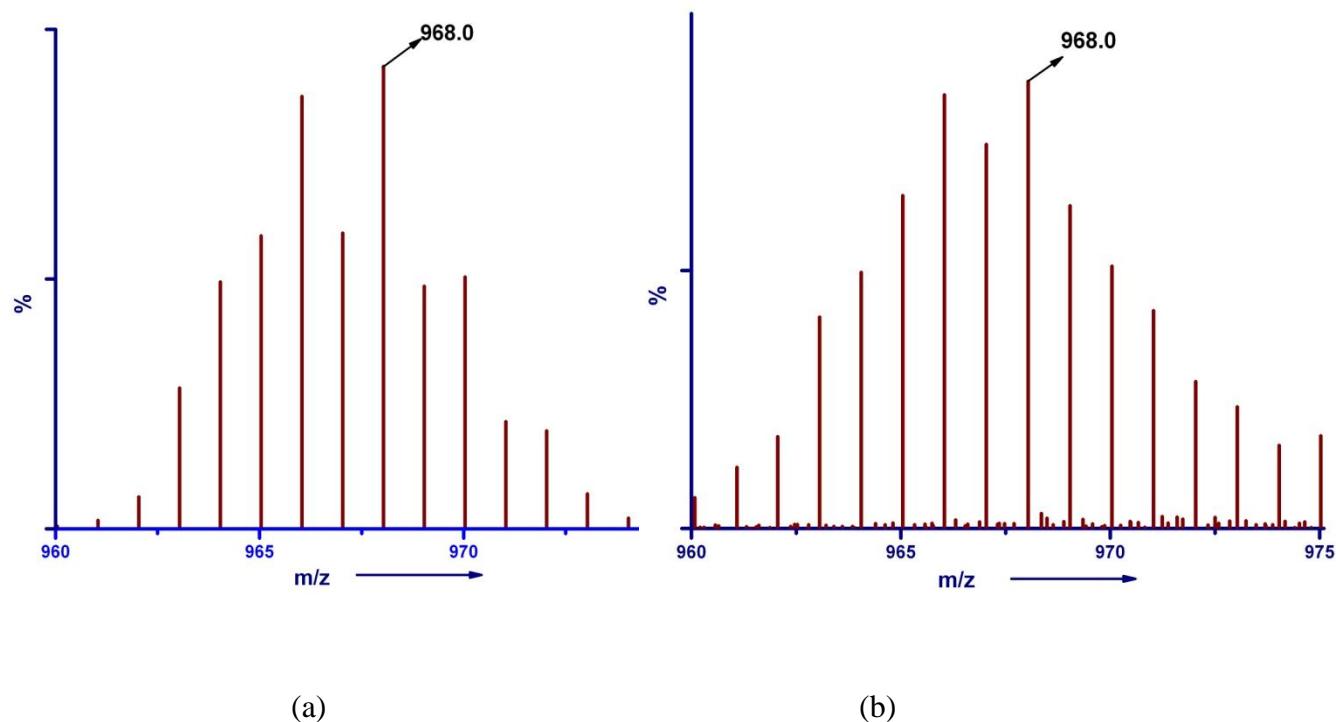


Figure S9.ESI-MS mass spectrum of **4**showing the species $[L\text{ZnGd}(\text{OAc})(\text{NO}_3) + \text{CH}_3\text{CN} + \text{H}_2\text{O}]^+$ (a) theoretical simulation (b) experimental spectrum.

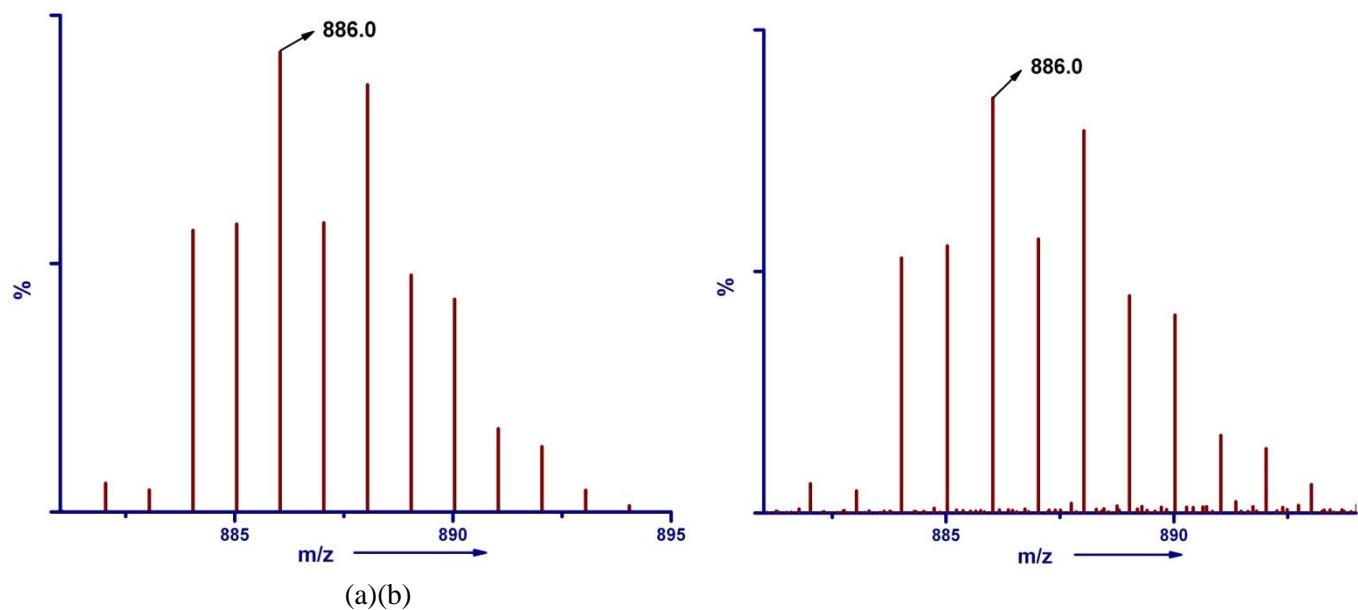


Figure S10. ESI-MS mass spectrum of **5** showing the species $[L\text{ZnEr}(\text{OAc})+\text{OMe}]^+$ (a) theoretical simulation (b) experimental spectrum.

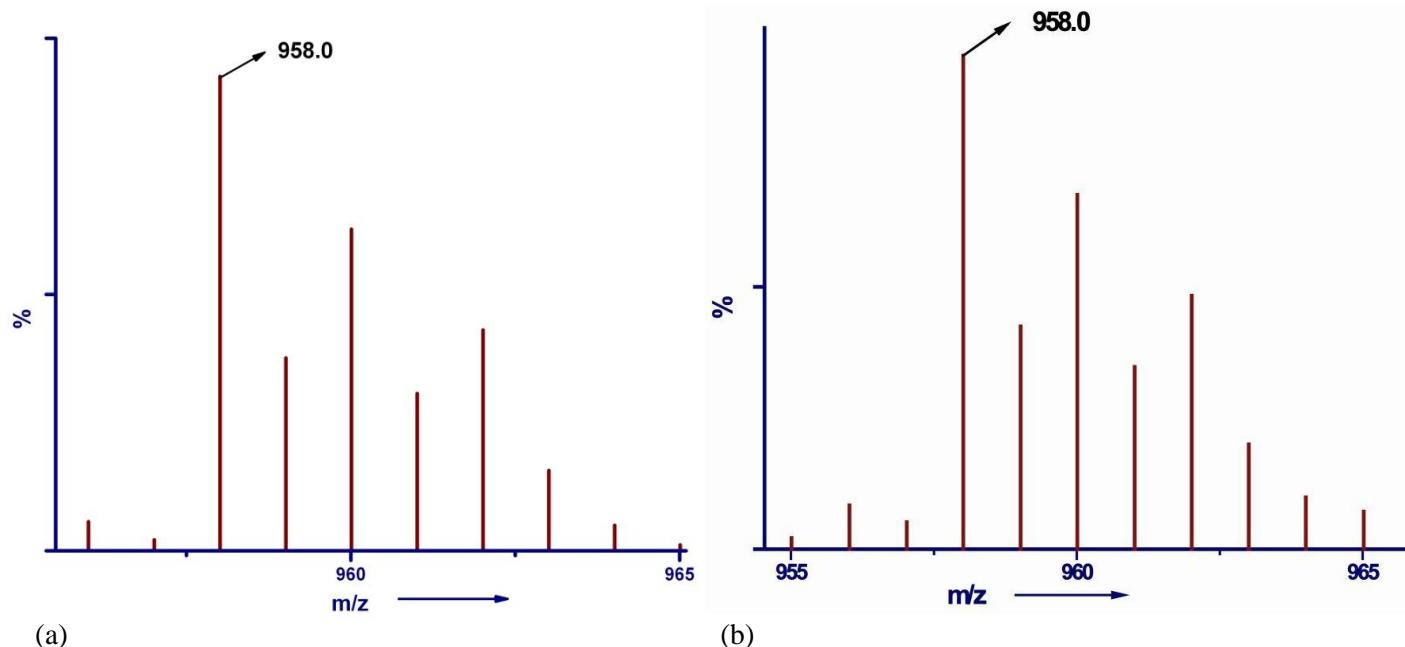


Figure S11. ESI-MS mass spectrum of **6** showing the fragment $[L\text{ZnHo}(\text{NO}_3)_2+\text{CH}_3\text{CN}]^+$: (a) theoretical simulation (b) experimental spectrum.

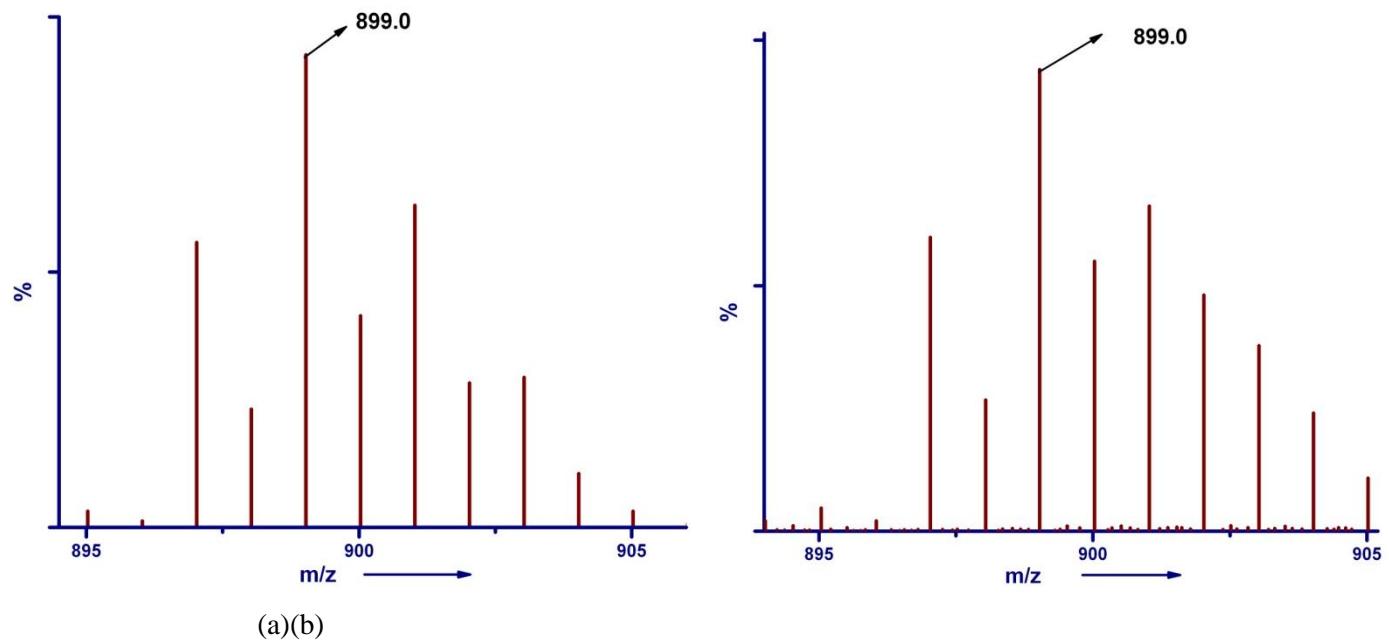


Figure S12. ESI-MS mass spectrum of **7** showing the species $[L\text{ZnEu}(\text{OAc})_2]^+$ (a) theoretical simulation, (b) experimental spectrum.

Electrochemistry

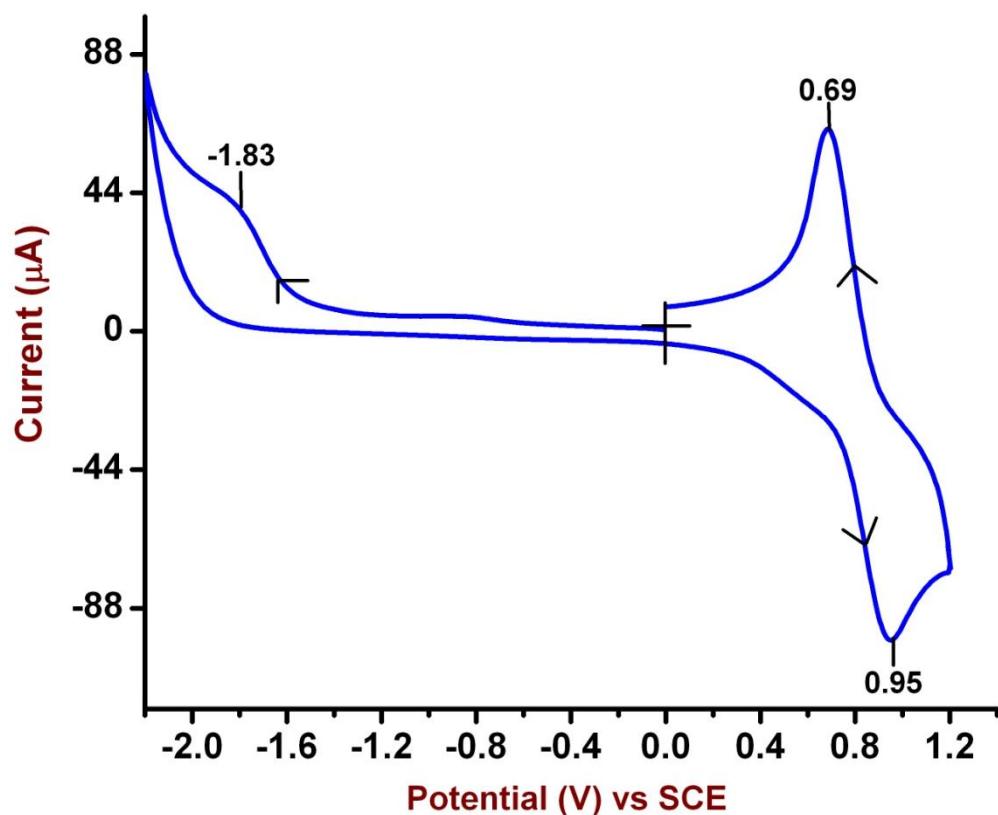


Figure S13. Cyclic voltammogram of $[L\text{Zn}(\mu\text{-OAc})\text{Tb}(\text{NO}_3)_2]$ in CH_2Cl_2 using a Glassy-Carbon working electrode and TBAP as supporting electrolyte(scan rate 100mV/s).

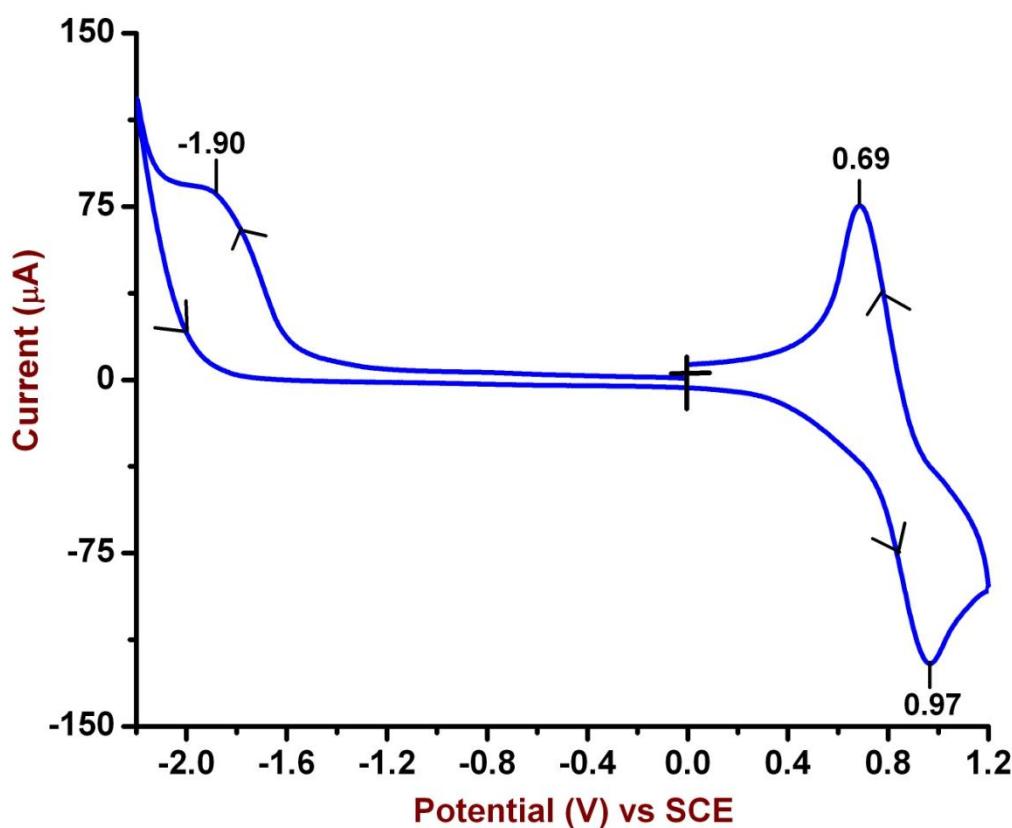


Figure S14. Cyclic voltammogram of $[\text{LZn}(\mu\text{-OAc})\text{Gd}(\text{NO}_3)_2]$ in CH_2Cl_2 using Glassy-Carbon working electrode and TBAP as supporting electrolyte(scan rate 100mV/s).

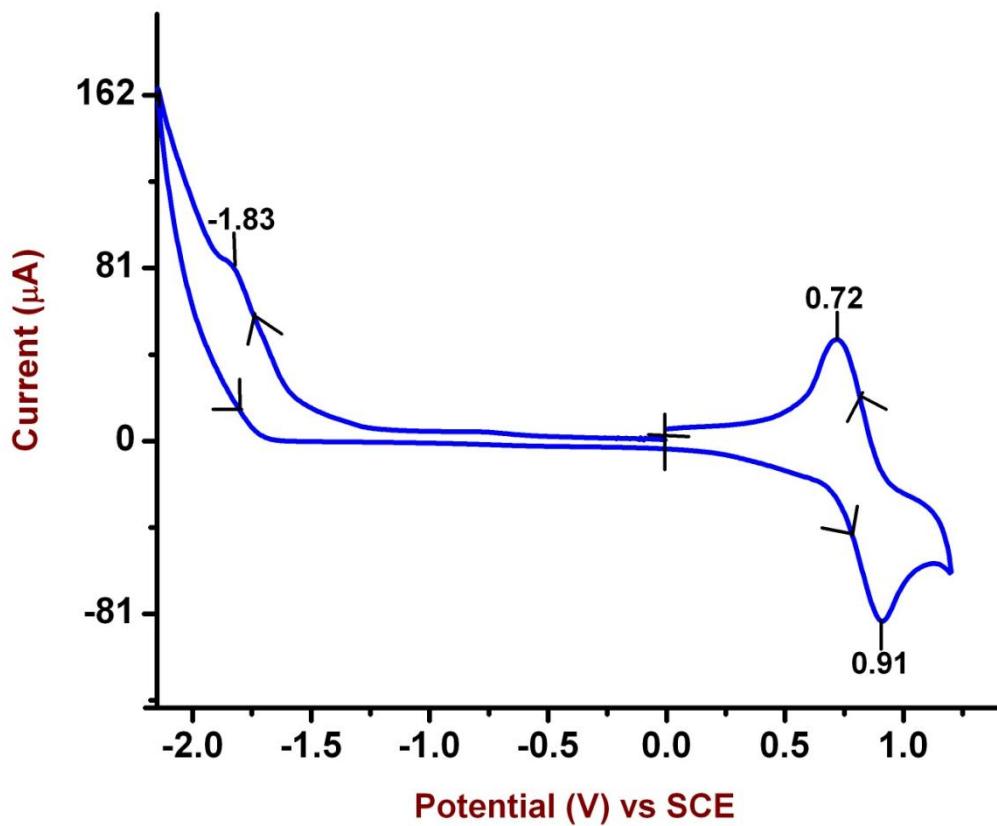


Figure S15. Cyclic voltammogram of $[\text{LZn}(\mu\text{-OAc})\text{Er}(\text{NO}_3)_2]$ in CH_2Cl_2 using Glassy-Carbon working electrode and TBAP as supporting electrolyte(scan rate 100mV/s).

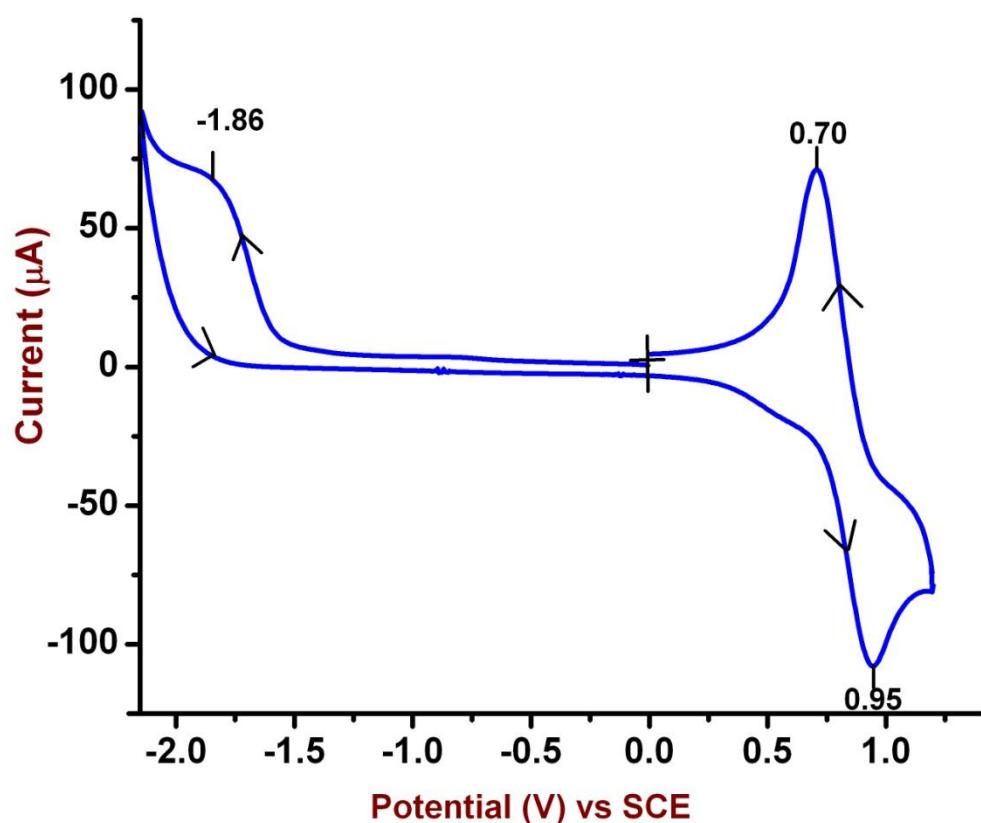


Figure S16. Cyclic voltammogram of $[\text{LZn}(\mu\text{-OAc})\text{Ho}(\text{NO}_3)_2]$ in CH_2Cl_2 using Glassy-Carbon working electrode and TBAP as supporting electrolyte (scan rate 100 mV/s).

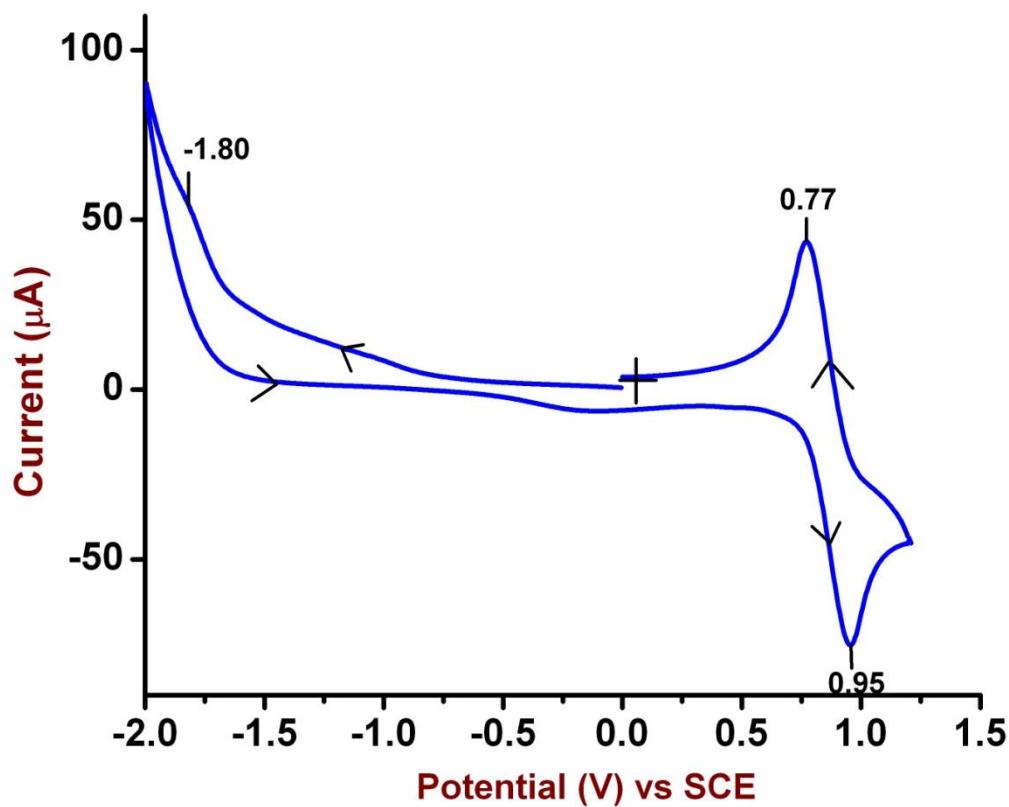
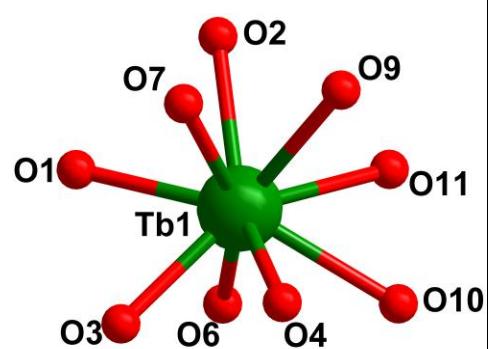


Figure S17. Cyclic voltammogram of $[L\text{Zn}(\mu\text{-OAc})\text{Eu}(\text{NO}_3)_2]$ in CH_2Cl_2 using Glassy-Carbon working electrode and TBAP as supporting electrolyte(Scan rate 100mV/s).

Table S1. Bond Parameters in 3

| Coordination environment around Tb(III) ion | Bond lengths around Tb[Å] | | Bond Angles around Tb[°] | |
|---|---------------------------|--|--------------------------|------------|
| Tb(1)-O(3) | 2.292(5) | | O(3)-Tb(1)-O(6) | 80.13(17) |
| Tb(1)-O(6) | 2.310(5) | | O(3)-Tb(1)-O(1) | 66.53(16) |
| Tb(1)-O(1) | 2.330(4) | | O(6)-Tb(1)-O(1) | 77.02(17) |
| Tb(1)-O(10) | 2.446(5) | | O(3)-Tb(1)-O(10) | 105.52(17) |
| Tb(1)-O(11) | 2.447(5) | | O(6)-Tb(1)-O(10) | 75.68(19) |
| Tb(1)-O(9) | 2.448(5) | | O(1)-Tb(1)-O(10) | 152.52(19) |
| Tb(1)-O(7) | 2.455(5) | | O(3)-Tb(1)-O(11) | 149.30(19) |
| Tb(1)-O(2) | 2.509(5) | | O(6)-Tb(1)-O(11) | 74.51(18) |
| Tb(1)-O(4) | 2.557(5) | | O(1)-Tb(1)-O(11) | 122.47(17) |
| Tb(1)-Zn(1) | 3.4554(9) | | O(10)-Tb(1)-O(11) | 51.67(17) |
| | | | O(3)-Tb(1)-O(9) | 128.84(17) |
| | | | O(6)-Tb(1)-O(9) | 148.62(17) |
| | | | O(1)-Tb(1)-O(9) | 122.30(17) |
| | | | O(10)-Tb(1)-O(9) | 83.74(18) |
| | | | O(11)-Tb(1)-O(9) | 74.15(17) |
| | | | O(3)-Tb(1)-O(7) | 85.87(17) |
| | | | O(6)-Tb(1)-O(7) | 156.62(17) |
| | | | O(1)-Tb(1)-O(7) | 80.26(16) |
| | | | O(10)-Tb(1)-O(7) | 126.50(17) |
| | | | O(11)-Tb(1)-O(7) | 123.51(17) |
| | | | O(9)-Tb(1)-O(7) | 52.31(16) |



| | O(3)-Tb(1)-O(2) | 130.21(15) |
|--|----------------------------|----------------------------|
| | O(6)-Tb(1)-O(2) | 97.07(17) |
| | O(1)-Tb(1)-O(2) | 64.49(15) |
| | O(10)-Tb(1)-O(2) | 122.06(16) |
| | O(11)-Tb(1)-O(2) | 70.78(17) |
| | O(9)-Tb(1)-O(2) | 74.01(17) |
| | O(7)-Tb(1)-O(2) | 77.84(16) |
| | O(3)-Tb(1)-O(4) | 64.64(15) |
| | O(6)-Tb(1)-O(4) | 117.78(18) |
| | O(1)-Tb(1)-O(4) | 124.45(15) |
| | O(10)-Tb(1)-O(4) | 67.60(17) |
| | O(11)-Tb(1)-O(4) | 113.02(17) |
| | O(9)-Tb(1)-O(4) | 73.92(17) |
| | O(7)-Tb(1)-O(4) | 71.52(17) |
| | O(2)-Tb(1)-O(4) | 144.93(16) |
| Bond angle containing both Tb and Zn[°] | | |
| | Zn(1)-O(3)-Tb(1) | 105.27(19) |
| | Zn(1)-O(1)-Tb(1) | 102.61(19) |
| Coordination environment around Zn(II) ion | Bond lengths around Zn [Å] | Bond Angles around Zn[°] |
| | Zn(1)-O(5) 1.989(5) | O(5)-Zn(1)-O(3) 101.67(19) |
| | Zn(1)-O(3) 2.052(4) | O(5)-Zn(1)-O(1) 95.37(19) |
| | Zn(1)-O(1) 2.093(4) | O(3)-Zn(1)-O(1) 75.41(18) |
| | Zn(1)-N(4) 2.110(6) | O(5)-Zn(1)-N(4) 109.8(2) |

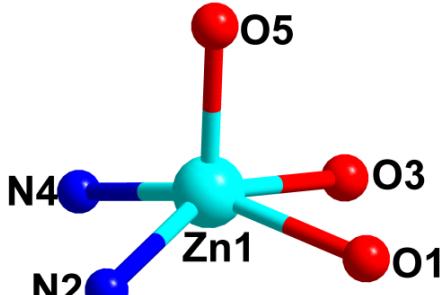
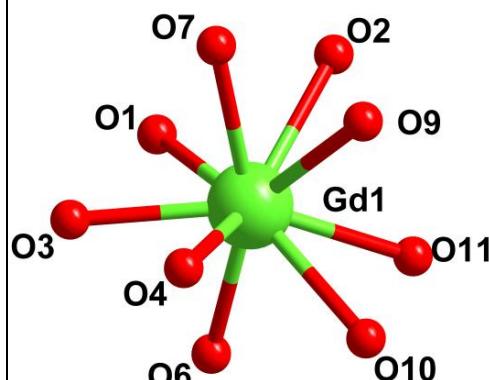
| | | | | |
|---|------------|----------|-----------------|----------|
|  | Zn(1)-N(2) | 2.115(5) | O(3)-Zn(1)-N(4) | 88.4(2) |
| | | | O(1)-Zn(1)-N(4) | 152.5(2) |
| | | | O(5)-Zn(1)-N(2) | 100.7(2) |
| | | | O(3)-Zn(1)-N(2) | 152.5(2) |
| | | | O(1)-Zn(1)-N(2) | 86.7(2) |
| | | | N(4)-Zn(1)-N(2) | 99.0(2) |

Table S2. Bond Parameters of 4

| Coordination environment around Gd(III) ion | Bond lengths around Gd [Å] | | Bond Angles around Gd[°] | |
|---|----------------------------|------------|--------------------------|------------|
| | Gd(1)-O(6) | 2.340(6) | O(6)-Gd(1)-O(3) | 76.22(19) |
| | Gd(1)-O(3) | 2.355(5) | O(6)-Gd(1)-O(1) | 78.8(2) |
| | Gd(1)-O(1) | 2.365(5) | O(3)-Gd(1)-O(1) | 65.06(17) |
| | Gd(1)-O(11) | 2.417(6) | O(6)-Gd(1)-O(11) | 75.9(2) |
| | Gd(1)-O(10) | 2.444(6) | O(3)-Gd(1)-O(11) | 151.65(19) |
| | Gd(1)-O(9) | 2.477(5) | O(1)-Gd(1)-O(11) | 104.52(19) |
| | Gd(1)-O(4) | 2.529(6) | O(6)-Gd(1)-O(10) | 74.9(2) |
| | Gd(1)-O(7) | 2.529(5) | O(3)-Gd(1)-O(10) | 122.21(19) |
| | Gd(1)-O(2) | 2.559(6) | O(1)-Gd(1)-O(10) | 149.19(19) |
| | Gd(1)-Zn(1) | 3.4933(10) | O(11)-Gd(1)-O(10) | 53.6(2) |
|  | | | O(6)-Gd(1)-O(9) | 147.71(19) |
| | | | O(3)-Gd(1)-O(9) | 124.98(18) |
| | | | O(1)-Gd(1)-O(9) | 130.43(18) |
| | | | O(11)-Gd(1)-O(9) | 82.39(18) |

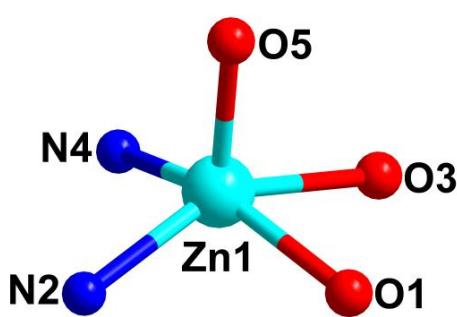
| | | |
|--|------------------|------------|
| | O(10)-Gd(1)-O(9) | 72.98(19) |
| | O(6)-Gd(1)-O(4) | 97.5(2) |
| | O(3)-Gd(1)-O(4) | 64.48(17) |
| | O(1)-Gd(1)-O(4) | 128.76(17) |
| | O(11)-Gd(1)-O(4) | 124.29(19) |
| | O(10)-Gd(1)-O(4) | 71.08(19) |
| | O(9)-Gd(1)-O(4) | 75.41(18) |
| | O(6)-Gd(1)-O(7) | 157.46(18) |
| | O(3)-Gd(1)-O(7) | 81.29(17) |
| | O(1)-Gd(1)-O(7) | 90.53(18) |
| | O(11)-Gd(1)-O(7) | 126.38(18) |
| | O(10)-Gd(1)-O(7) | 119.58(18) |
| | O(9)-Gd(1)-O(7) | 51.33(17) |
| | O(4)-Gd(1)-O(7) | 73.76(18) |
| | O(6)-Gd(1)-O(2) | 117.7(2) |
| | O(3)-Gd(1)-O(2) | 121.23(18) |
| | O(1)-Gd(1)-O(2) | 63.26(17) |
| | O(11)-Gd(1)-O(2) | 69.10(19) |
| | O(10)-Gd(1)-O(2) | 116.46(19) |
| | O(9)-Gd(1)-O(2) | 74.72(19) |
| | O(4)-Gd(1)-O(2) | 144.81(18) |
| | O(7)-Gd(1)-O(2) | 73.21(18) |

| | | Bond angle containing both Gd and Zn[°] | |
|---|---|--|--|
| | | Zn(1)-O(1)-Gd(1) 104.7(2) | |
| | | Zn(1)-O(3)-Gd(1) 103.3(2) | |
| Coordination environment around Zn(II) ion | Bond lengths around Zn [Å] | Bond Angles around Zn[°] | |
| | Zn(1)-O(5) 1.995(6) Zn(1)-O(1) 2.041(5) Zn(1)-O(3) 2.094(5) Zn(1)-N(4) 2.101(6) Zn(1)-N(2) 2.107(6) | O(5)-Zn(1)-O(1) 105.0(2) O(5)-Zn(1)-O(3) 94.6(2) O(1)-Zn(1)-O(3) 75.7(2) O(5)-Zn(1)-N(4) 100.5(2) O(1)-Zn(1)-N(4) 149.8(2) O(3)-Zn(1)-N(4) 86.4(2) O(5)-Zn(1)-N(2) 103.0(2) O(1)-Zn(1)-N(2) 88.4(2) O(3)-Zn(1)-N(2) 158.9(2) N(4)-Zn(1)-N(2) 101.5(2) | |

Table S3. Bond parameters of 5

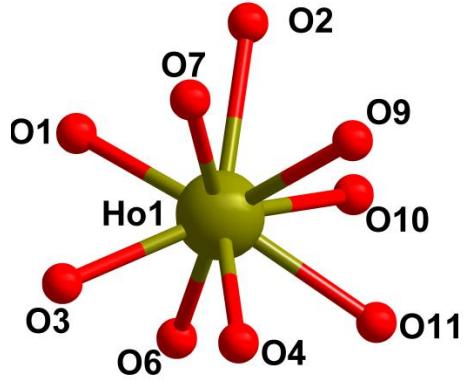
| Coordination environment around Er(III) ion | Bond lengths around Er[Å] | Bond Angles around Er[°] |
|--|---|---|
| | Er(1)-O(6) 2.260(6) Er(1)-O(3) 2.279(5) Er(1)-O(1) 2.302(5) Er(1)-O(9) 2.407(5) Er(1)-O(7) 2.414(6) | O(6)-Er(1)-O(3) 80.59(19) O(6)-Er(1)-O(1) 76.7(2) O(3)-Er(1)-O(1) 67.62(18) O(6)-Er(1)-O(9) 148.23(19) O(3)-Er(1)-O(9) 128.65(18) |

| | | | | |
|--|-------------|------------|-------------------|------------|
| | Er(1)-O(10) | 2.415(6) | O(1)-Er(1)-O(9) | 122.48(19) |
| | Er(1)-O(11) | 2.428(6) | O(6)-Er(1)-O(7) | 155.45(19) |
| | Er(1)-O(2) | 2.480(5) | O(3)-Er(1)-O(7) | 85.59(19) |
| | Er(1)-O(4) | 2.539(5) | O(1)-Er(1)-O(7) | 79.33(18) |
| | Er(1)-Zn(1) | 3.4265(14) | O(9)-Er(1)-O(7) | 53.42(18) |
| | | | O(6)-Er(1)-O(10) | 75.0(2) |
| | | | O(3)-Er(1)-O(10) | 102.89(19) |
| | | | O(1)-Er(1)-O(10) | 151.3(2) |
| | | | O(9)-Er(1)-O(10) | 85.03(19) |
| | | | O(7)-Er(1)-O(10) | 128.17(18) |
| | | | O(6)-Er(1)-O(11) | 73.7(2) |
| | | | O(3)-Er(1)-O(11) | 148.1(2) |
| | | | O(1)-Er(1)-O(11) | 122.40(19) |
| | | | O(9)-Er(1)-O(11) | 74.58(19) |
| | | | O(7)-Er(1)-O(11) | 124.89(18) |
| | | | O(10)-Er(1)-O(11) | 52.58(19) |
| | | | O(6)-Er(1)-O(2) | 96.6(2) |
| | | | O(3)-Er(1)-O(2) | 132.38(18) |
| | | | O(1)-Er(1)-O(2) | 65.54(16) |
| | | | O(9)-Er(1)-O(2) | 73.39(17) |
| | | | O(7)-Er(1)-O(2) | 77.97(18) |
| | | | O(10)-Er(1)-O(2) | 122.44(18) |
| | | | O(11)-Er(1)-O(2) | 70.23(18) |

| | | O(6)-Er(1)-O(4) | 119.2(2) | |
|---|----------------------------|--|-----------------|----------|
| | | O(3)-Er(1)-O(4) | 64.99(17) | |
| | | O(1)-Er(1)-O(4) | 125.43(17) | |
| | | O(9)-Er(1)-O(4) | 72.74(17) | |
| | | O(7)-Er(1)-O(4) | 71.70(18) | |
| | | O(10)-Er(1)-O(4) | 66.71(19) | |
| | | O(11)-Er(1)-O(4) | 112.11(19) | |
| | | O(2)-Er(1)-O(4) | 143.74(17) | |
| | | Bond angle containing both Er and Zn[°] | | |
| | | Zn(1)-O(1)-Er(1) | 102.7(2) | |
| | | Zn(1)-O(3)-Er(1) | 104.2(2) | |
| Coordination environment around Zn(II) ion | Bond lengths around Zn [Å] | Bond Angles around Zn[°] | | |
|  | Zn(1)-O(5) | 1.985(6) | O(5)-Zn(1)-O(3) | 100.9(2) |
| | Zn(1)-O(3) | 2.061(5) | O(5)-Zn(1)-O(1) | 95.0(2) |
| | Zn(1)-O(1) | 2.082(5) | O(3)-Zn(1)-O(1) | 75.9(2) |
| | Zn(1)-N(2) | 2.102(6) | O(5)-Zn(1)-N(2) | 100.8(2) |
| | Zn(1)-N(4) | 2.109(6) | O(3)-Zn(1)-N(2) | 152.8(2) |
| | | | O(1)-Zn(1)-N(2) | 86.1(2) |
| | | | O(5)-Zn(1)-N(4) | 110.6(2) |
| | | | O(3)-Zn(1)-N(4) | 87.7(2) |
| | | | O(1)-Zn(1)-N(4) | 152.0(2) |

| | | | |
|--|--|-----------------|---------|
| | | N(2)-Zn(1)-N(4) | 99.8(2) |
|--|--|-----------------|---------|

Table S4. Bond Parameters of 6

| Coordination environment around Ho(III) ion | Bond lengths around Ho [Å] | Bond Angles around Ho[°] |
|---|---|--|
|  | Ho(1)-O(1) 2.279(7) Ho(1)-O(6) 2.288(8) Ho(1)-O(3) 2.319(7) Ho(1)-O(10) 2.414(8) Ho(1)-O(11) 2.419(7) Ho(1)-O(9) 2.426(7) Ho(1)-O(7) 2.437(8) Ho(1)-O(4) 2.487(7) Ho(1)-O(2) 2.556(7) Ho(1)-Zn(1) 3.4416(13) | O(1)-Ho(1)-O(6) 80.9(3) O(1)-Ho(1)-O(3) 67.2(2) O(6)-Ho(1)-O(3) 77.0(3) O(1)-Ho(1)-O(10) 103.4(3) O(6)-Ho(1)-O(10) 75.7(3) O(3)-Ho(1)-O(10) 152.3(3) O(1)-Ho(1)-O(11) 148.8(3) O(6)-Ho(1)-O(11) 74.1(3) O(3)-Ho(1)-O(11) 123.0(3) O(10)-Ho(1)-O(11) 52.7(2) O(1)-Ho(1)-O(9) 128.1(3) O(6)-Ho(1)-O(9) 148.5(3) O(3)-Ho(1)-O(9) 122.2(3) O(10)-Ho(1)-O(9) 84.5(3) O(11)-Ho(1)-O(9) 74.5(3) O(1)-Ho(1)-O(7) 85.0(3) O(6)-Ho(1)-O(7) 155.9(3) O(3)-Ho(1)-O(7) 79.6(2) |

| | | |
|---|--|--|
| | O(10)-Ho(1)-O(7) O(11)-Ho(1)-O(7) O(9)-Ho(1)-O(7) O(1)-Ho(1)-O(4) O(6)-Ho(1)-O(4) O(3)-Ho(1)-O(4) O(10)-Ho(1)-O(4) O(11)-Ho(1)-O(4) O(9)-Ho(1)-O(4) O(7)-Ho(1)-O(4) O(1)-Ho(1)-O(2) O(6)-Ho(1)-O(2) O(3)-Ho(1)-O(2) O(10)-Ho(1)-O(2) O(11)-Ho(1)-O(2) O(9)-Ho(1)-O(2) O(7)-Ho(1)-O(2) O(4)-Ho(1)-O(2) | 126.9(2) 124.5(3) 52.9(2) 131.7(2) 96.1(3) 65.3(2) 122.6(2) 70.3(2) 74.1(3) 78.9(3) 64.5(2) 119.0(3) 124.6(2) 66.6(2) 112.4(2) 72.9(3) 70.9(3) 144.5(3) |
| Coordination environment around Zn(II) ion | Bond lengths around Zn [Å] | Bond Angles around Zn[°] Bond angle containing both Ho and Zn[°] Zn(1)-O(1)-Ho(1) 104.5(3) Zn(1)-O(3)-Ho(1) 102.6(3) |

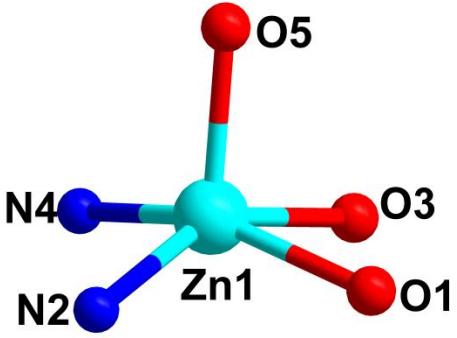
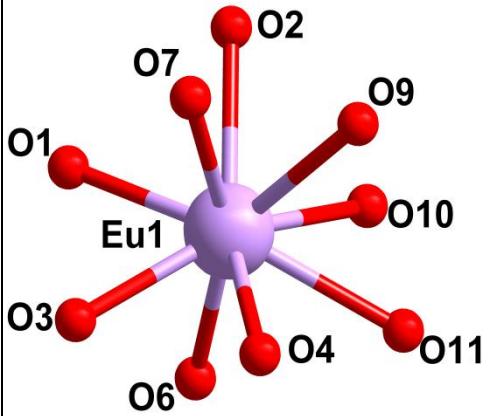
| | | | | |
|---|------------|----------|-----------------|----------|
|  | Zn(1)-O(5) | 2.007(8) | O(5)-Zn(1)-O(1) | 101.9(3) |
| | Zn(1)-O(1) | 2.071(7) | O(5)-Zn(1)-N(4) | 100.3(3) |
| | Zn(1)-N(4) | 2.074(9) | O(1)-Zn(1)-N(4) | 152.6(3) |
| | Zn(1)-O(3) | 2.087(7) | O(5)-Zn(1)-O(3) | 95.6(3) |
| | Zn(1)-N(2) | 2.105(9) | O(1)-Zn(1)-O(3) | 75.4(3) |
| | | | N(4)-Zn(1)-O(3) | 86.6(3) |
| | | | O(5)-Zn(1)-N(2) | 110.5(3) |
| | | | O(1)-Zn(1)-N(2) | 88.2(3) |
| | | | N(4)-Zn(1)-N(2) | 98.9(3) |
| | | | O(3)-Zn(1)-N(2) | 151.7(3) |

Table S5. Bond Parameters of 7

| Coordination environment around Eu(III) ion | Bond lengths around Eu[Å] | | Bond Angles around Eu[°] | |
|---|---------------------------|----------|--------------------------|------------|
| | Eu(1)-O(6) | 2.317(4) | O(6)-Eu(1)-O(1) | 79.79(13) |
| | Eu(1)-O(1) | 2.337(3) | O(6)-Eu(1)-O(3) | 76.51(13) |
| | Eu(1)-O(3) | 2.353(4) | O(1)-Eu(1)-O(3) | 66.34(12) |
| | Eu(1)-O(10) | 2.468(4) | O(6)-Eu(1)-O(10) | 76.24(14) |
| | Eu(1)-O(7) | 2.478(4) | O(1)-Eu(1)-O(10) | 105.96(13) |
| | Eu(1)-O(11) | 2.479(4) | O(3)-Eu(1)-O(10) | 152.62(14) |
| | Eu(1)-O(9) | 2.484(4) | O(6)-Eu(1)-O(7) | 156.58(13) |
| | Eu(1)-O(4) | 2.526(4) | O(1)-Eu(1)-O(7) | 86.40(13) |
| | Eu(1)-O(2) | 2.564(4) | O(3)-Eu(1)-O(7) | 80.65(13) |

| | | | | |
|---|-------------|------------|-------------------|------------|
|  | Eu(1)-Zn(1) | 3.4792(12) | O(10)-Eu(1)-O(7) | 126.14(13) |
| | | | O(6)-Eu(1)-O(11) | 75.39(13) |
| | | | O(1)-Eu(1)-O(11) | 149.75(14) |
| | | | O(3)-Eu(1)-O(11) | 122.71(13) |
| | | | O(10)-Eu(1)-O(11) | 51.43(13) |
| | | | O(7)-Eu(1)-O(11) | 122.49(12) |
| | | | O(6)-Eu(1)-O(9) | 149.25(13) |
| | | | O(1)-Eu(1)-O(9) | 128.62(13) |
| | | | O(3)-Eu(1)-O(9) | 122.42(13) |
| | | | O(10)-Eu(1)-O(9) | 83.51(14) |
| | | | O(7)-Eu(1)-O(9) | 51.61(13) |
| | | | O(11)-Eu(1)-O(9) | 73.89(13) |
| | | | O(6)-Eu(1)-O(4) | 96.99(13) |
| | | | O(1)-Eu(1)-O(4) | 129.84(12) |
| | | | O(3)-Eu(1)-O(4) | 64.32(11) |
| | | | O(10)-Eu(1)-O(4) | 121.99(12) |
| | | | O(7)-Eu(1)-O(4) | 77.47(12) |
| | | | O(11)-Eu(1)-O(4) | 70.90(13) |
| | | | O(9)-Eu(1)-O(4) | 74.36(12) |
| | | | O(6)-Eu(1)-O(2) | 117.23(14) |
| | | | O(1)-Eu(1)-O(2) | 64.13(12) |
| | | | O(3)-Eu(1)-O(2) | 124.10(12) |
| | | | O(10)-Eu(1)-O(2) | 67.73(13) |

| | | O(7)-Eu(1)-O(2) | 72.10(13) |
|--|---|---|------------|
| | | O(11)-Eu(1)-O(2) | 113.11(13) |
| | | O(9)-Eu(1)-O(2) | 74.41(12) |
| | | O(4)-Eu(1)-O(2) | 145.66(13) |
| Bond angle containing both Eu and Zn[°] | | | |
| | | Zn(1)-O(1)-Eu(1) | 104.28(14) |
| | | Zn(1)-O(3)-Eu(1) | 102.84(14) |
| Coordination environment around Zn(II) ion | Bond lengths around Zn[Å] | Bond Angles around Zn[°] | |
| | Zn(1)-O(5) 1.993(4) Zn(1)-O(1) 2.065(4) Zn(1)-O(3) 2.092(3) Zn(1)-N(2) 2.103(4) Zn(1)-N(4) 2.103(4) | O(5)-Zn(1)-O(1) 102.57(15) O(5)-Zn(1)-O(3) 95.15(15) O(1)-Zn(1)-O(3) 76.23(14) O(5)-Zn(1)-N(2) 109.65(16) O(1)-Zn(1)-N(2) 87.72(15) O(3)-Zn(1)-N(2) 152.99(16) O(5)-Zn(1)-N(4) 100.39(16) O(1)-Zn(1)-N(4) 152.29(16) O(3)-Zn(1)-N(4) 86.49(15) N(2)-Zn(1)-N(4) 98.99(17) | |

UV-vis Spectra:

UV-Vis and emission spectra of all compound was recorded in CHCl_3 at 10^{-5}M concentration (Figure S18) and the observed λ_{\max} and corresponding ε_{\max} are given in Table S6. The free ligand H_2L exhibit absorption band around 306 and 364 nm whereas the metal complex shows strong absorption around 286 and 360 nm. Absorption in case of the metal complex is assigned as ligand centered spin allowed $\pi-\pi^*$ transition. All the compound **1-7** shows emission at 403 and 426 nm in CHCl_3 solution($c \sim 1.0 \times 10^{-6}$) (Figure S18). The solution state quantum yield was calculated^{S1} using 8,1-ANS [8-(phenylamino)- 1 -naphthalenesulfonate] in water as standard, (Table S6).^{S2}

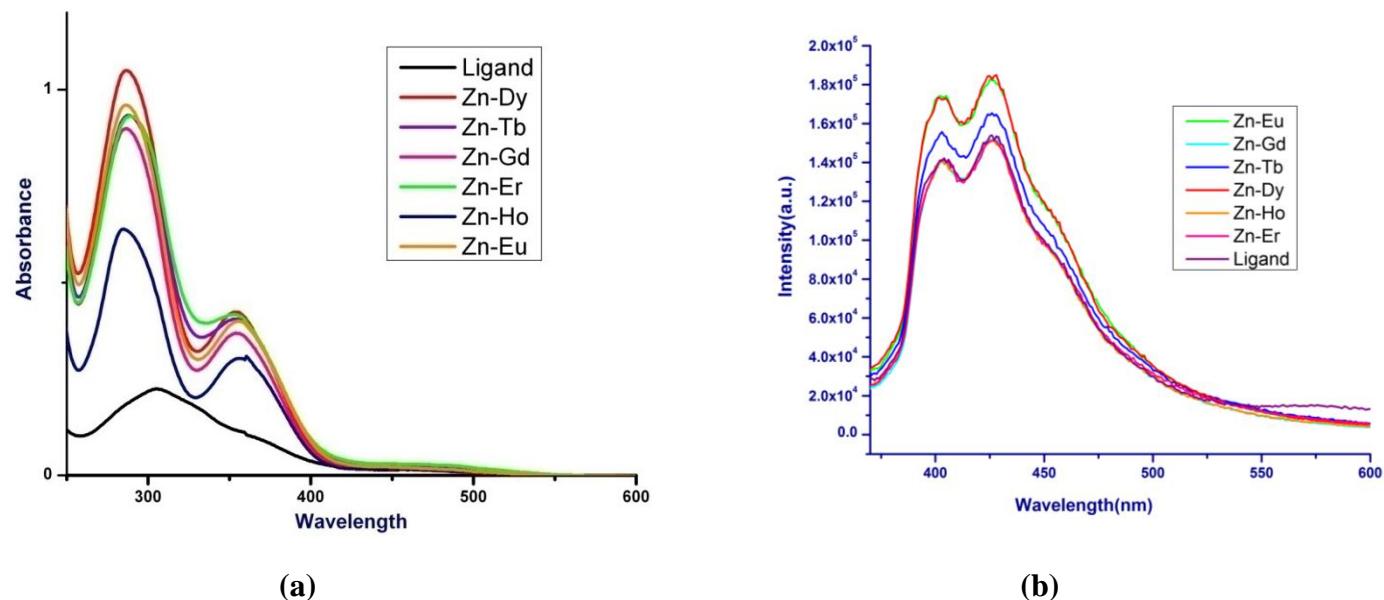


Figure S18. (a) UV/Vis absorption spectra of **1-7**. (b) Emission spectra of **1-7**.

Table S6: Spectroscopic data for **1-7** recorded in CHCl₃

| Complex | ligand | Zn-Dy | Zn-Tb | Zn-Gd | Zn-Er | Zn-Ho | Zn-Eu |
|--|--------|--|---------------------------------------|---------------------------------------|---------------------------------------|---------------------------------------|---------------------------------------|
| $\lambda_{\text{max}}(10^{-4}\epsilon_{\text{max}})$ | | 306(2.24), 287(10.49), 364(1.00), 353(4.23), 469(0.14) | 288(9.33), 352(4.05), 453(0.22) | 286(8.99), 354(3.69), 450(0.25) | 289(9.31), 352(4.17), 467(0.28) | 286(6.39), 355(3.03), 451(0.16) | 286(9.60), 355(4.00), 449(0.21) |
| Solution state | | 1.74X10 ⁻³ | 2.02X10 ⁻³ | 2.12X10 ⁻³ | 1.65X10 ⁻³ | 1.69X10 ⁻³ | 1.65X10 ⁻³ |
| Quantum yield(Φ) | | | | | | | |

References

- S1. J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, third ed., Springer, New York.
S2. J. Lee and G. W. Robinson, *J. Am. Chem. Soc.*, 1985, **107**, 6153.