Supporting Information for:

Experimental and Theoretical Comparison of Tetravalent Transition Metal and Actinide Schiff-Base Coordination Complexes

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Absorbance Spectroscopy

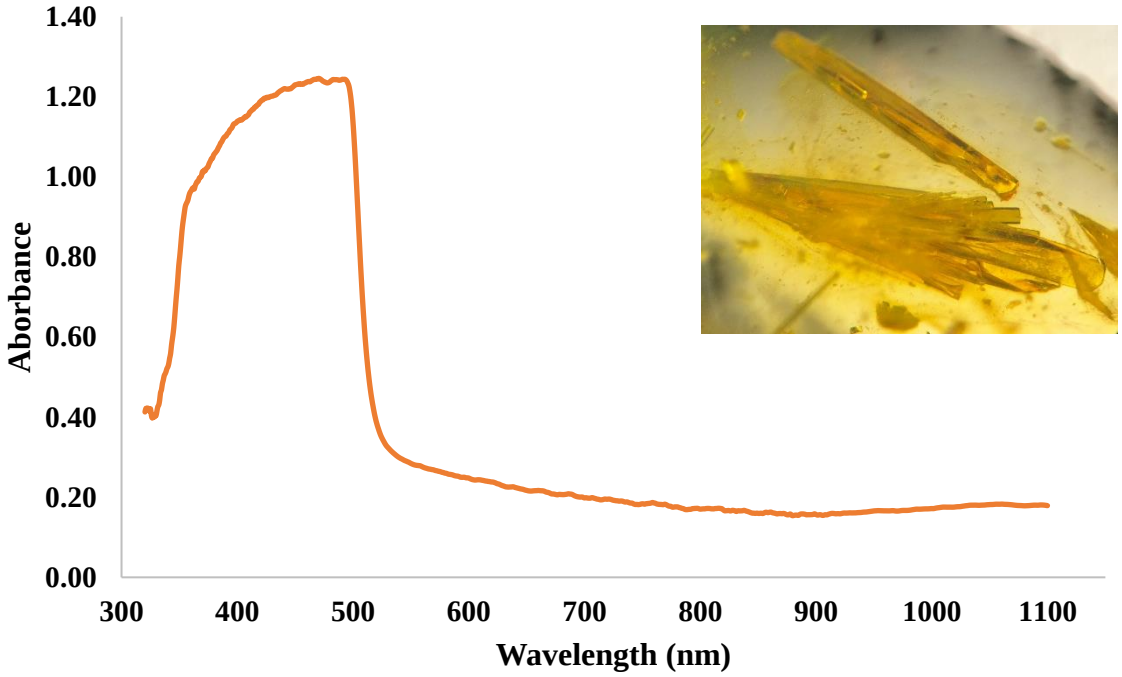

Figure S1. Solid state UV/vis/NIR absorbance spectrum and photograph of **ZrL$_2$** {L = *N*,*N*′–bis[(4,4'-diethylamino)salicylidene]-1,2-phenylenediamine}.

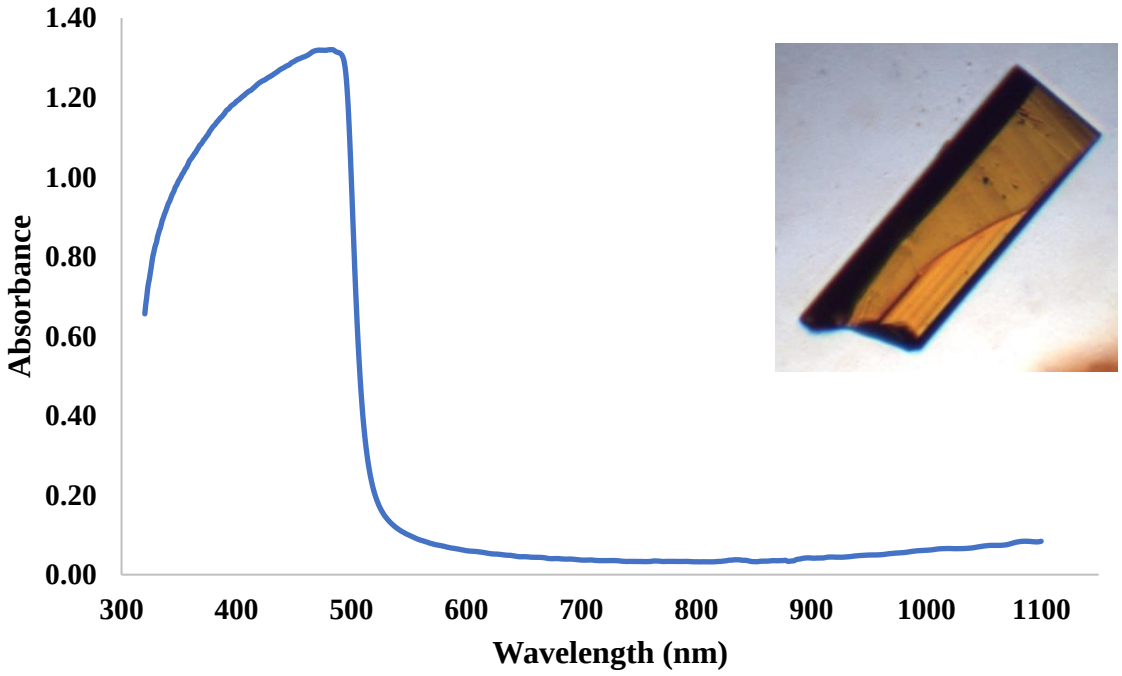

Figure S2. Solid state UV/vis/NIR absorbance spectrum and photograph of **HfL_2**.

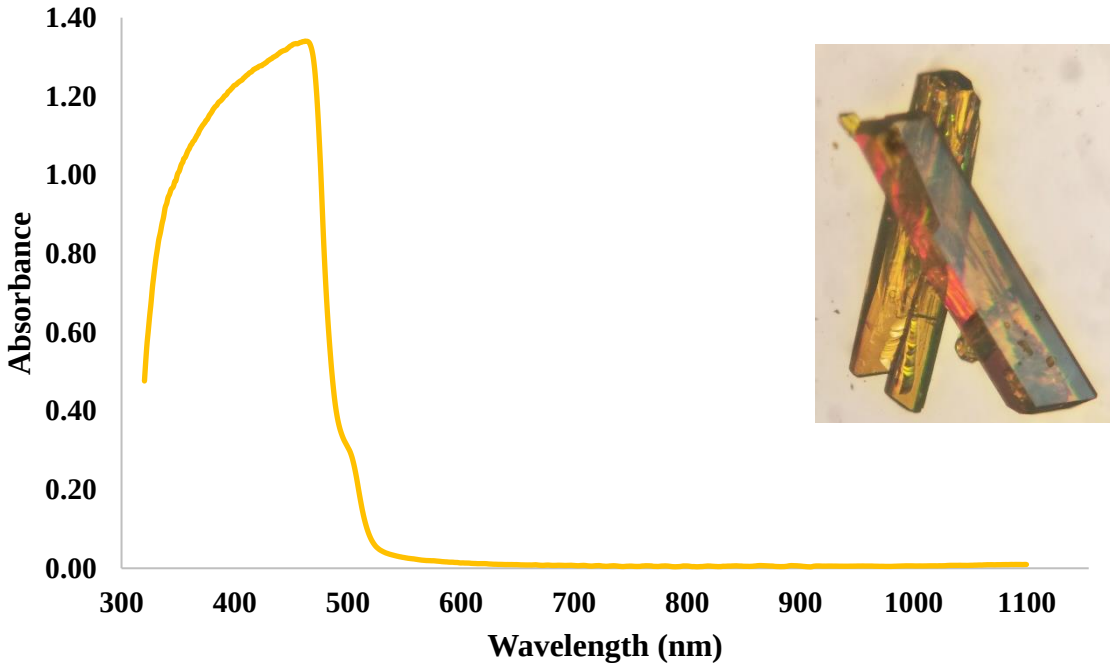

Figure S3. Solid state UV/vis/NIR absorbance spectrum and photograph of **ThfL$_2$**.

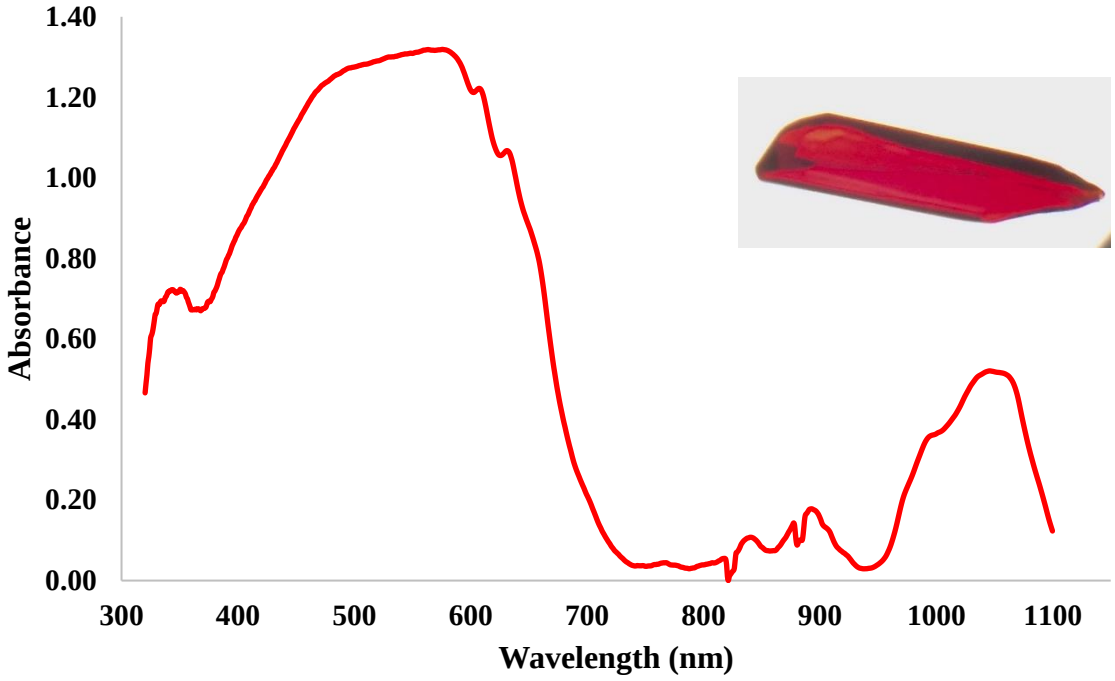

Figure S4. Solid state UV/vis/NIR absorbance spectrum and photograph of **UfL$_2$**.

Cyclic Voltammetry

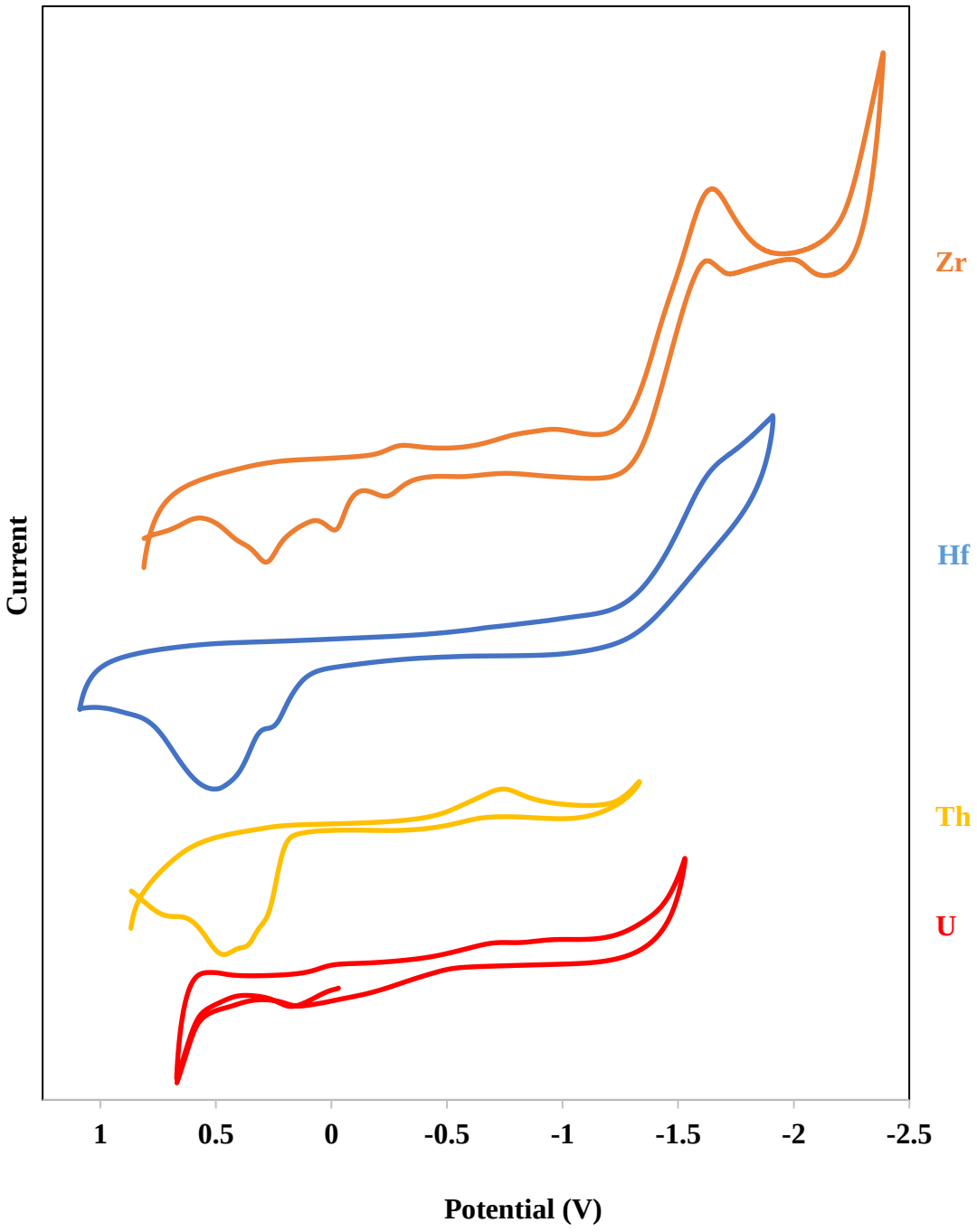

Figure S5. Cyclic voltammograms of **ML_2** (M = Zr, Hf, Th, U) vs. Fc/Fc^+ at 25 mV/sec in DCM with 0.1 M $[N^nBu_4][PF_6]$ at 23 ˚C.

NMR Spectroscopy

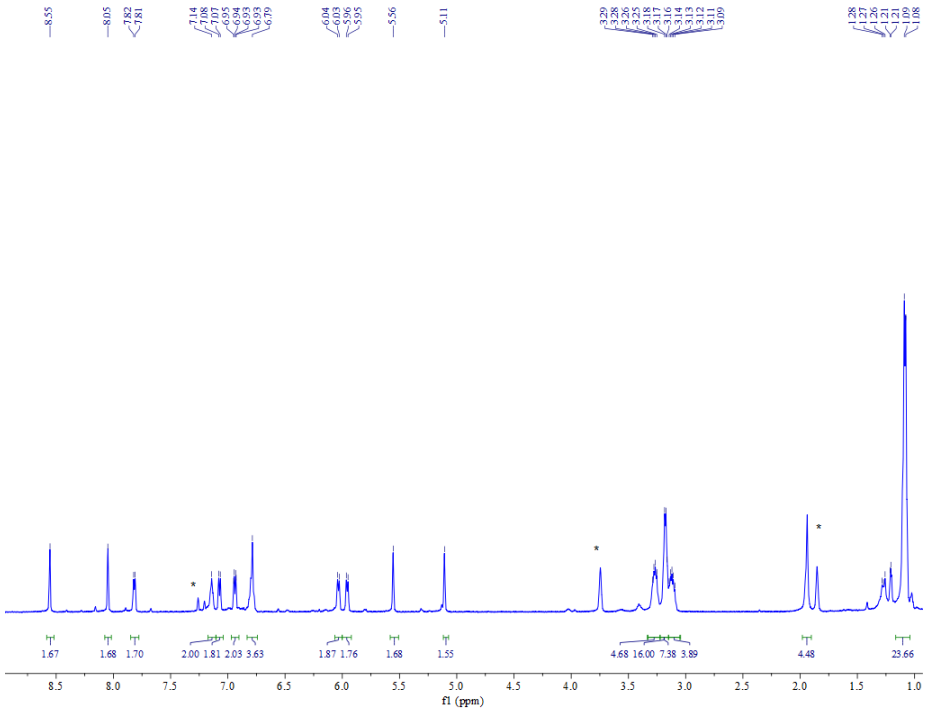

Figure S6. ^{1}H NMR spectrum of **ZrL$_2$** in $CDCl_3$ at 298 K with * denoting resonances from solvents.

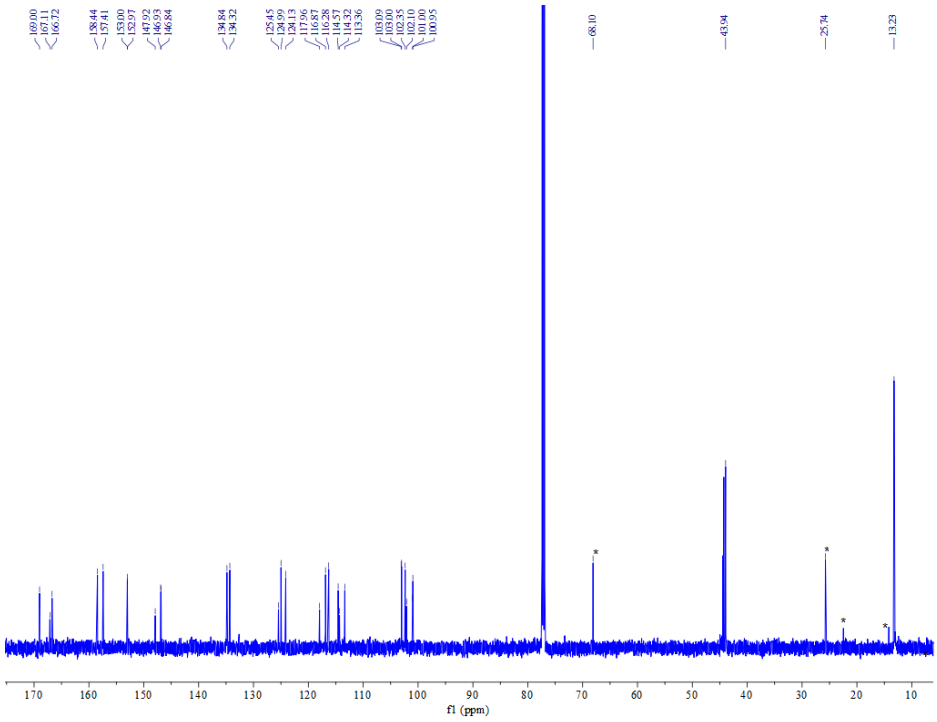

Figure S7. ^{13}C{^{1}H} NMR spectrum of **ZrL$_2$** in $CDCl_3$ at 298 K with * denoting resonances from solvents.

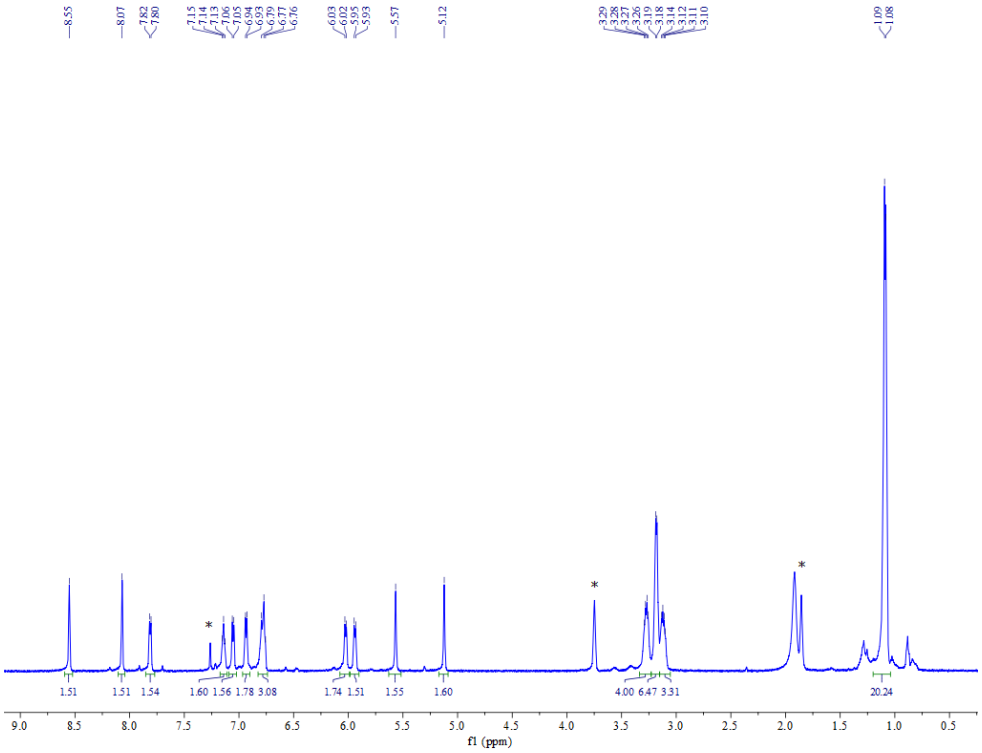

Figure S8. ^{1}H NMR spectrum of **HfL₂** in $CDCl_3$ at 298 K with * denoting resonances from solvents.

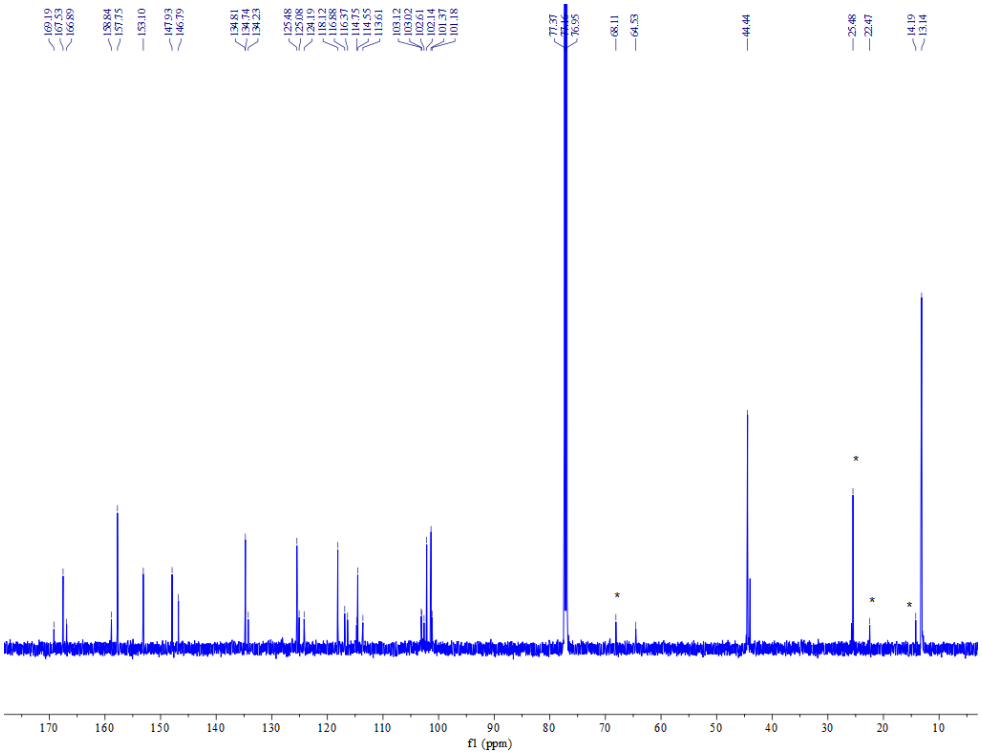

Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum of **HfL₂** in $CDCl_3$ at 298 K with * denoting resonances from solvents.

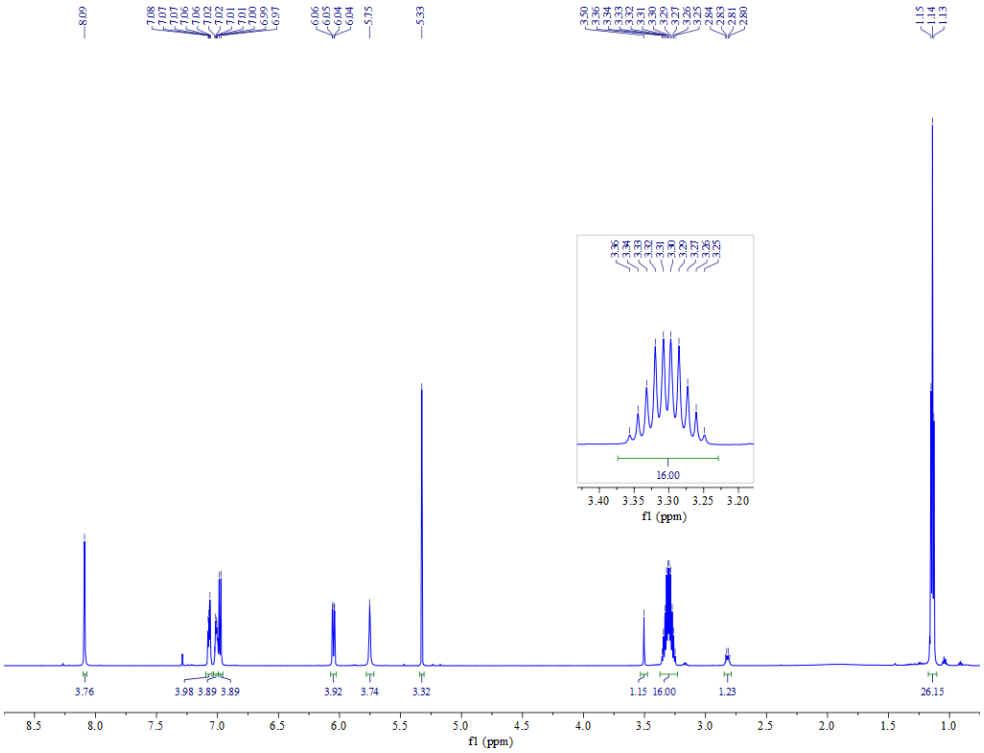

Figure S10. ^{1}H NMR spectrum of **ThL$_2$** in $CDCl_3$ at 298 K with * denoting resonances from solvents.

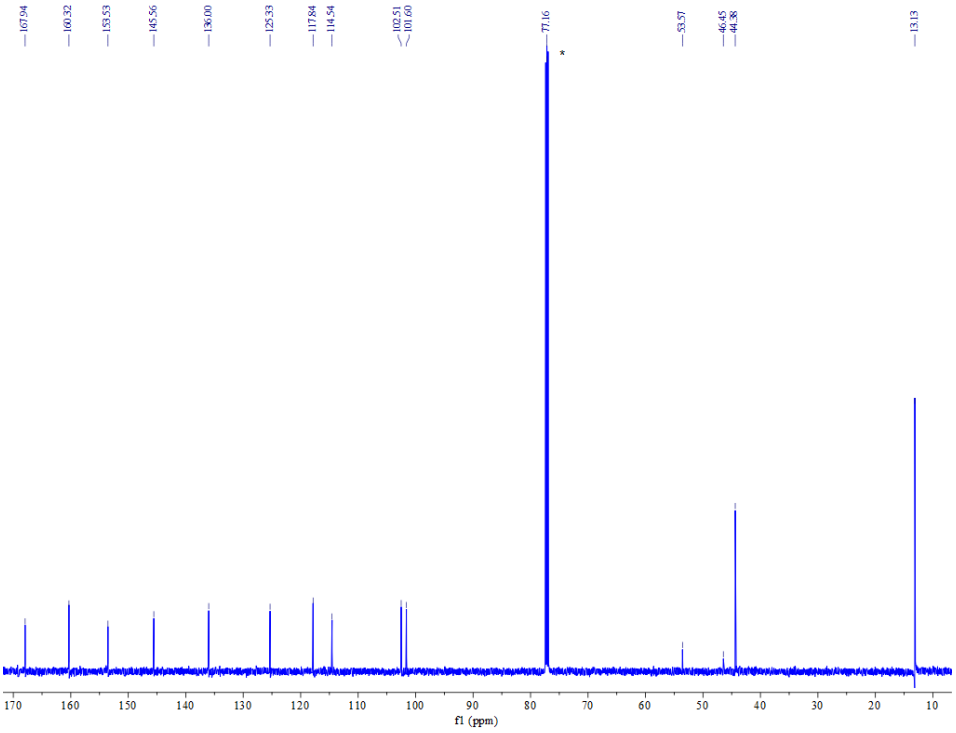

Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum of **ThL$_2$** in $CDCl_3$ at 298 K with * denoting resonances from solvents.

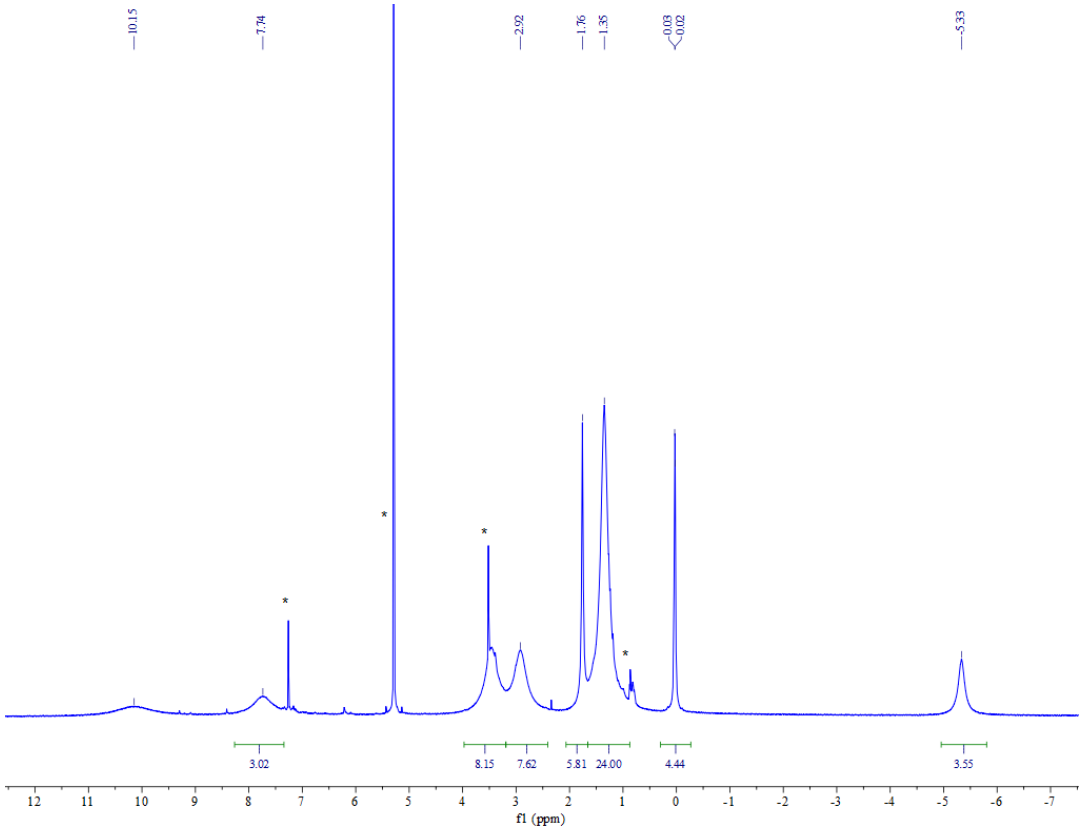

Figure S12. ^{1}H NMR spectrum of **UL$_2$** in $CDCl_3$ at 298 K with * denoting resonances from solvents.

Theory

Table S1. Transitions assignment for main bands in absorbance spectra from Figure 5 in the main text.

Band	Wavelength (nm)	Assignment
1a	498	$\pi \rightarrow f\pi$ (LMCT)[a]
		$\pi \rightarrow f$ (LMCT)
		$f\pi \rightarrow \pi$ (MLCT)[b]
1b	570	$\pi \rightarrow f\pi$ (LMCT)[a]
		$\pi \rightarrow f$ (LMCT)
2a	798	$f \rightarrow f$
		$f \rightarrow f\pi$
2b	800	$f \rightarrow f\pi$
		$f\pi \rightarrow f\pi$
3a	1138	$f \rightarrow f$
		$f \rightarrow f\pi$
3b	1090	$f \rightarrow f$
		$f \rightarrow f\pi$

[a] Not formally a ligand-to-metal charge transfer transition due to strong mixing between orbitals

[b] Not formally a metal-to-ligand charge transfer transition due to strong mixing between orbitals

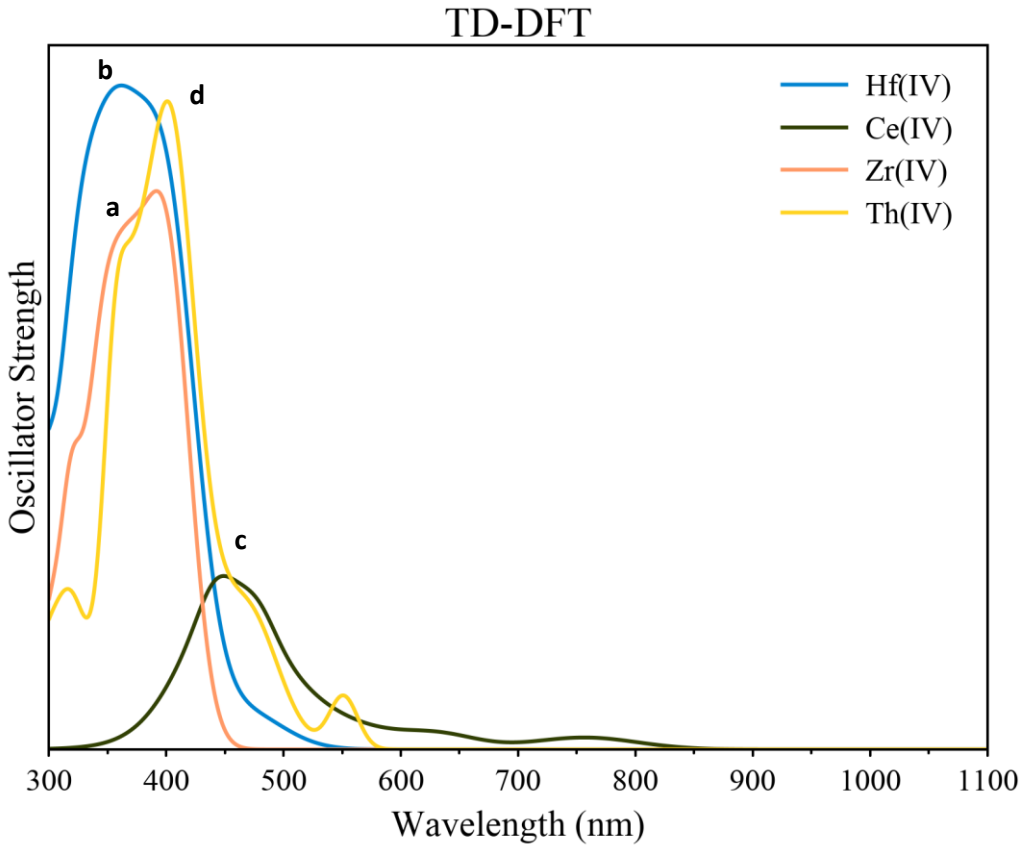

Figure S13. Calculated TD-DFT absorbance spectra of **ZrL$_2$**, **HfL$_2$**, **CeL$_2$**, and **ThL$_2$**. Solid lines correspond to the gaussian fit of the calculated transition. Labeled peaks correspond to transition assignments described in Table S2.

Table S2. Transitions assignment for main bands in absorbance spectra from Figure S13.

Band	Wavelength (nm)	Assignment
a	390	$\pi \rightarrow \pi^*$
		$\pi \rightarrow d\pi$ (LMCT)[a]
b	370	$\pi \rightarrow \pi^*$
		$\pi \rightarrow d\pi$ (LMCT)[a]
c	460	$\pi \rightarrow f$ (LMCT)
		$\pi \rightarrow f\pi$ (LMCT)[a]
d	405	$\pi \rightarrow \pi^*$
		$\pi \rightarrow d\pi$ (LMCT)[a]
		$\pi \rightarrow f\pi$ (LMCT)[a]

[a] Not formally a LMCT transition due to strong mixing between orbitals

Table S3. Bonding metrics derived from QTAIM theory. M−O and M−N data correspond to the weaker bonds for each oxygen and nitrogen bond.

	ρ(r)	|V(r)|/G(r)	H(r)	H(r)/ρ(r)
Hf−O(avg)	0.0870	1.1461	−0.0156	−0.1794
Ce−O(1)	0.0845	1.1827	−0.0159	−0.1885
Th−O(2)	0.0800	1.1849	−0.0151	−0.1883
U−O(1)	0.0878	1.1826	−0.0171	−0.1947
Pu−O(1)	0.0900	1.1681	−0.0173	−0.1921
Hf−N(avg)	0.0597	1.1722	−0.0094	−0.1575
Ce−N(2)	0.0459	1.0899	−0.0031	−0.0685
Th−N(1)	0.0469	1.1487	−0.0051	−0.1085
U−N(2)	0.0501	1.1348	−0.0052	−0.1039
Pu−N(1)	0.0495	1.1254	−0.0056	−0.1130

Crystallographic Details

Table S4. Crystallographic information for **ML_2** (M = Zr, Hf, Th, U)

Compound	**ZrL_2•$(THF)_{0.25}$**	**HfL_2•$(THF)_{0.25}$**	**ThL_2•$2(CH_2Cl_2)$**	**UL_2•$2(CH_2Cl_2)$**
Empirical Formula	$C_{228}H_{264}N_{32}O_{17}Zr_4$	$C_{228}H_{264}N_{32}O_{17}Hf_4$	$C_{58}H_{68}Cl_4N_8O_4Th$	$C_{58}H_{68}Cl_4N_8O_4U$
Color	Yellow	Yellow	Yellow	Red
Habit	Columnar	Columnar	Columnar	Columnar
Temperature (K)	120(2)	120(2)	120(2)	150(2)
Crystal System	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space Group	*$P2_1/c$*	*$P2_1/c$*	*C2/c*	*C2/c*
***a* (Å)**	14.846(2)	14.8530(19)	14.880(3)	14.855(2)
***b* (Å)**	19.683(3)	19.686(3)	24.966(5)	24.820(3)
***c* (Å)**	35.574(5)	35.692(5)	15.406(5)	15.374(3)
α (deg)	90	90	90	90
β (deg)	91.188(5)	91.044(4)	95.145	95.234(2)
γ (deg)	90	90	90	90
Volume ($Å^3$)	10393(3)	10434(2)	5700(2)	5645(1)
Z	2	2	4	4
ρ_{calcd} (Mg/m^3)	1.307	1.413	1.532	1.554
μ (mm^{-1})	0.266	2.054	2.857	3.119
R1[a] (*I* > 2.0σ(I))	0.0544	0.0361	0.0193	0.0185
wR2 (all data)	0.1324	0.0803	0.0455	0.0434

[a]Definitions: R1 = $\Sigma||F_o| - |F_c||/\Sigma|F_o|$, wR2 = $[\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Goof = S = $[\Sigma[w(F_o^2-F_c^2)^2] / (n-p)]^{1/2}$ where n is the number of reflections and p is the total number of parameters refined.

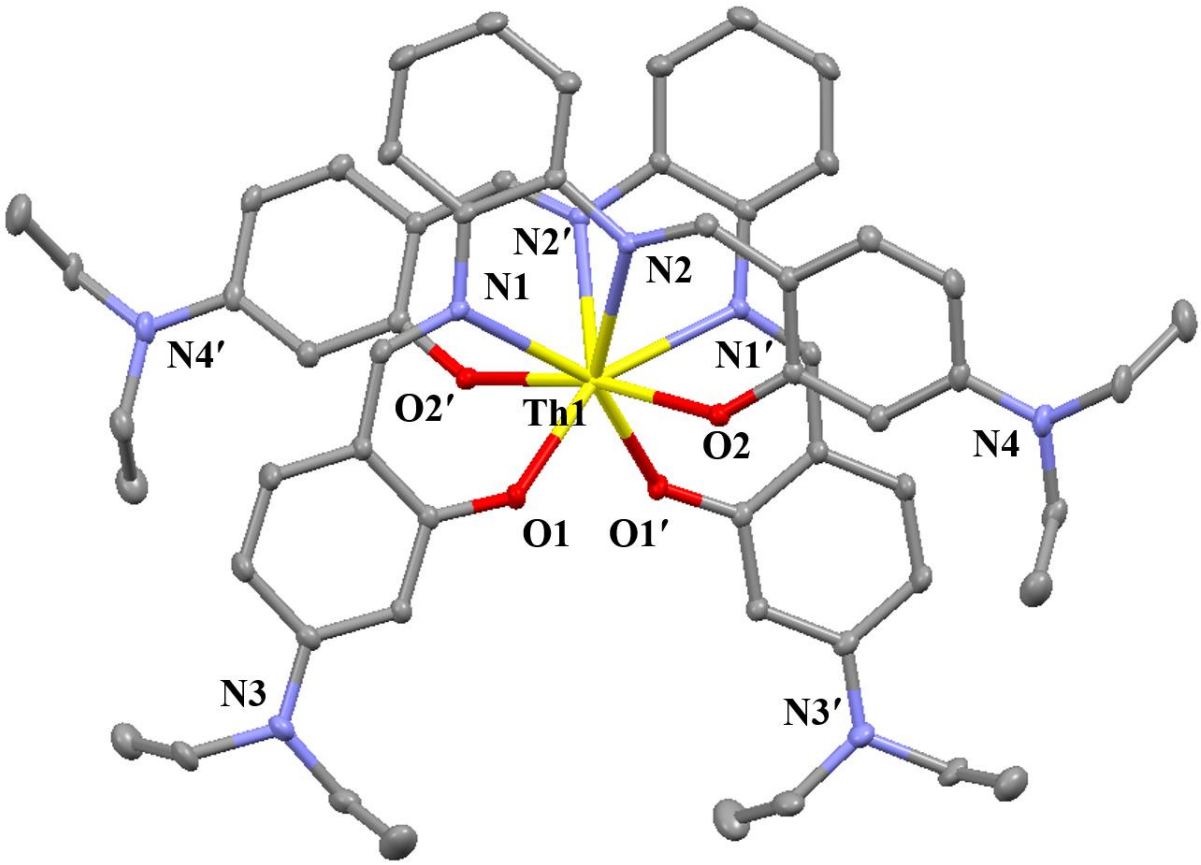

Figure S14. Molecular structure of **ThL$_2$** (L = *N*,*N*′–bis[(4,4'-diethylamino)salicylidene]-1,2-phenylenediamine) drawn at the 50% probability level with hydrogen atoms and lattice solvent omitted for clarity.

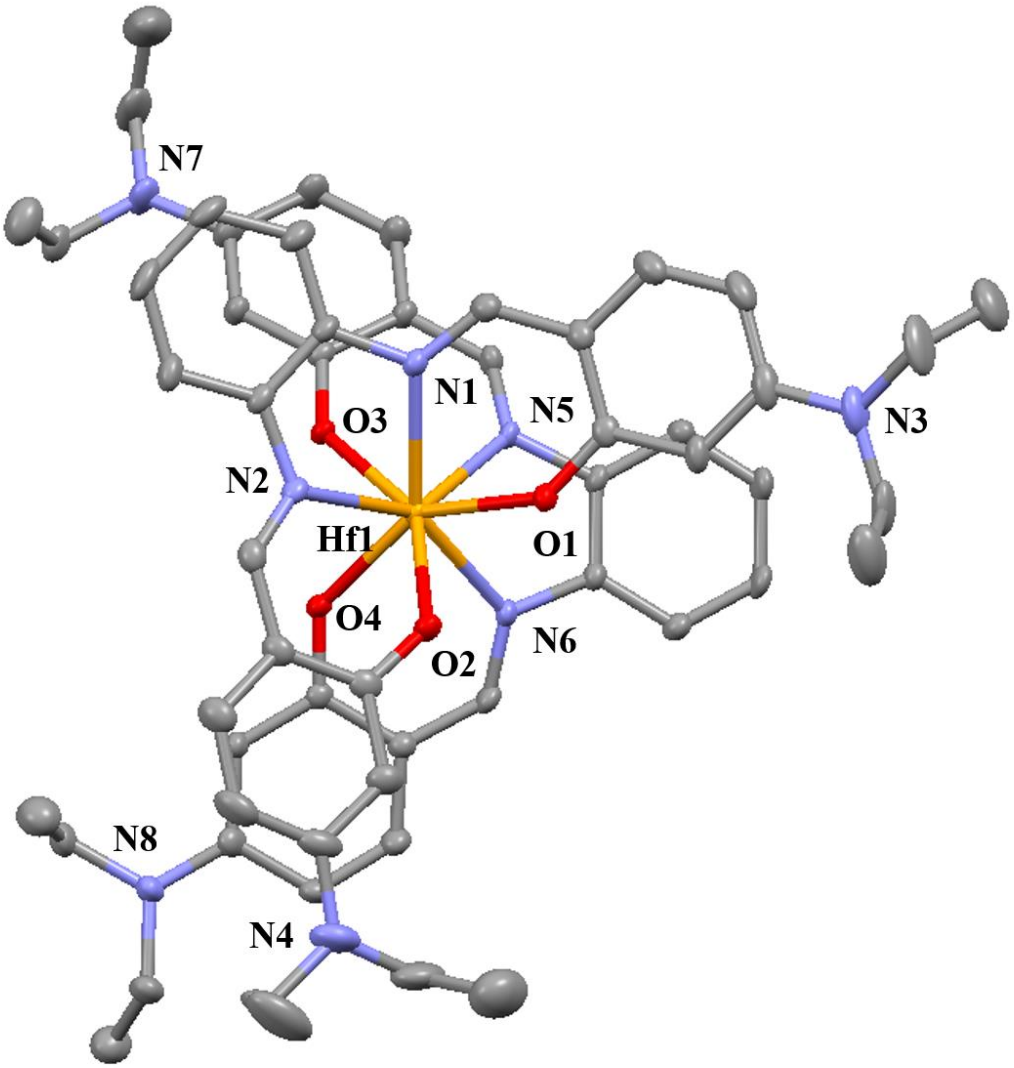

Figure S15. Molecular structure of **HfL_2** (L = *N*,*N'*–bis[(4,4'-diethylamino)salicylidene]-1,2-phenylenediamine) drawn at the 50% probability level with hydrogen atoms and lattice solvent omitted for clarity.

Table S5. Bond lengths [Å] and angles [°] for **ZrL_2**

Zr1	O4	2.103(2)		O2	Zr1	N1	113.80(8)
Zr1	O1	2.110(2)		O2	Zr1	N6	82.25(8)
Zr1	O3	2.091(2)		N2	Zr1	N1	65.61(8)
Zr1	O2	2.139(2)		N5	Zr1	N2	141.36(8)
Zr1	N2	2.386(2)		N5	Zr1	N1	81.82(8)
Zr1	N5	2.372(2)		N6	Zr1	N2	150.72(8)
Zr1	N1	2.399(2)		N6	Zr1	N5	66.73(8)
Zr1	N6	2.363(2)		N6	Zr1	N1	142.25(8)
Zr2	O7	2.113 (2)		O7	Zr2	O8	73.83(7)
Zr2	O8	2.126(2)		O7	Zr2	N9	73.25(8)
Zr2	O5	2.101(2)		O7	Zr2	O6	144.61(8)
Zr2	N9	2.364(2)		O7	Zr2	N10	79.00(8)
Zr2	O6	2.118(2)		O7	Zr2	N14	112.48(8)
Zr2	N10	2.358(2)		O7	Zr2	N13	74.30(8)
Zr2	N14	2.381(2)		O8	Zr2	N9	138.44(8)
Zr2	N13	2.373(2)		O8	Zr2	N10	82.70(8)
				O8	Zr2	N14	74.73(8)
O4	Zr1	O1	143.98(8)	O8	Zr2	N13	112.86(8)
O4	Zr1	O2	77.06(8)	O5	Zr2	O7	138.15(8)
O4	Zr1	N2	81.78(8)	O5	Zr2	O8	146.03(7)
O4	Zr1	N5	115.13(8)	O5	Zr2	N9	73.92(8)
O4	Zr1	N1	139.64(8)	O5	Zr2	O6	74.83(8)
O4	Zr1	N6	75.52(8)	O5	Zr2	N10	110.45(8)
O1	Zr1	O2	75.31(7)	O5	Zr2	N14	80.17(8)
O1	Zr1	N2	112.23(8)	O5	Zr2	N13	75.81(8)
O1	Zr1	N5	75.28(8)	N9	Zr2	N14	142.33(8)
O1	Zr1	N1	73.79(8)	N9	Zr2	N13	81.47(8)
O1	Zr1	N6	78.26(8)	O6	Zr2	O8	78.72(7)
O3	Zr1	O4	74.96(7)	O6	Zr2	N9	117.26(8)
O3	Zr1	O1	139.04(7)	O6	Zr2	N10	75.72(8)
O3	Zr1	O2	143.01(7)	O6	Zr2	N14	80.50(8)
O3	Zr1	N2	77.69(8)	O6	Zr2	N13	138.30(8)
O3	Zr1	N5	74.25(7)	N10	Zr2	N9	66.70(8)
O3	Zr1	N1	75.34(8)	N10	Zr2	N14	149.92(8)
O3	Zr1	N6	113.08(8)	N10	Zr2	N13	143.18(8)
O2	Zr1	N2	74.77(8)	N13	Zr2	N14	65.79(8)
O2	Zr1	N5	140.74(8)				

Table S6. Bond lengths [Å] and angles [°] for **HfL$_2$**

Hf1	O3	2.102(2)
Hf1	O4	2.124(2)
Hf1	O1	2.098(2)
Hf1	O2	2.113(2)
Hf1	N1	2.355(3)
Hf1	N2	2.342(3)
Hf1	N5	2.356(3)
Hf1	N6	2.360(3)
Hf2	O8	2.101(2)
Hf2	O7	2.087(2)
Hf2	O5	2.105(2)
Hf2	N14	2.345(3)
Hf2	N13	2.355(3)
Hf2	N9	2.387(3)
Hf2	O6	2.132(2)
Hf2	N10	2.363(3)

O3	Hf1	O4	73.16(8)
O3	Hf1	O2	144.47(8)
O3	Hf1	N1	73.57(9)
O3	Hf1	N2	78.97(9)
O3	Hf1	N5	74.63(8)
O3	Hf1	N6	112.49(9)
O4	Hf1	N1	138.08(8)
O4	Hf1	N2	82.14(9)
O4	Hf1	N5	113.32(9)
O4	Hf1	N6	74.97(8)
O1	Hf1	O3	138.98(8)
O1	Hf1	O4	146.06(8)
O1	Hf1	O2	74.35(9)
O1	Hf1	N1	74.12(9)
O1	Hf1	N2	110.35(9)
O1	Hf1	N5	76.02(9)
O1	Hf1	N6	80.23(9)
O2	Hf1	O4	78.65(8)
O2	Hf1	N1	117.86(9)
O2	Hf1	N2	76.13(9)
O2	Hf1	N5	137.85(8)
O2	Hf1	N6	79.65(9)
N1	Hf1	N5	81.11(9)
N1	Hf1	N6	142.49(9)
N2	Hf1	N1	67.03(9)
N2	Hf1	N5	143.23(9)
N2	Hf1	N6	149.42(9)
N5	Hf1	N6	66.26(9)
O8	Hf2	O5	143.80(8)
O8	Hf2	N14	75.68(9)
O8	Hf2	N13	115.39(9)
O8	Hf2	N9	139.44(8)
O8	Hf2	O6	77.20(8)
O8	Hf2	N10	81.40(9)
O7	Hf2	O8	74.49(8)
O7	Hf2	O5	139.86(8)
O7	Hf2	N14	113.21(9)
O7	Hf2	N13	74.55(8)
O7	Hf2	N9	75.61(9)
O7	Hf2	O6	143.06(8)
O7	Hf2	N10	77.52(9)
O5	Hf2	N14	78.21(9)
O5	Hf2	N13	75.64(9)
O5	Hf2	N9	74.00(9)
O5	Hf2	O6	74.54(8)
O5	Hf2	N10	112.15(9)
N14	Hf2	N13	67.06(9)
N14	Hf2	N9	142.34(9)
N14	Hf2	N10	150.40(9)
N13	Hf2	N9	81.65(9)
N13	Hf2	N10	141.36(9)
O6	Hf2	N14	81.60(9)
O6	Hf2	N13	140.29(9)
O6	Hf2	N9	114.03(9)
O6	Hf2	N10	75.20(9)
N10	Hf2	N9	65.80(9)

Table S7. Bond lengths [Å] and angles [°] for **ThL$_2$**

Th(1)-O(2)#1	2.3067(11)	$O1^1$ Th1 N1	121.60(4)
Th(1)-O(2)	2.3067(11)	$O2^1$ Th1 O2	89.91(6)
Th(1)-O(1)#1	2.3039(13)	$O2^1$ Th1 N2	153.68(4)
Th(1)-O(1)	2.3039(13)	O2 Th1 N2	70.29(4)
Th(1)-N(2)#1	2.6290(14)	O2 Th1 $N2^1$	153.68(4)
Th(1)-N(2)	2.6290(14)	$O2^1$ Th1 $N2^1$	70.29(4)
Th(1)-N(1)#1	2.6480(13)	O2 Th1 $N1^1$	145.47(4)
Th(1)-N(1)	2.6480(13)	O2 Th1 N1	109.94(4)
		$O2^1$ Th1 N1	145.47(4)
O1 Th1 O2	87.40(4)	$O2^1$ Th1 $N1^1$	109.94(4)
O1 Th1 $O2^1$	83.95(4)	N2 Th1 $N2^1$	133.47(6)
$O1^1$ Th1 $O2^1$	87.40(4)	$N2^1$ Th1 $N1^1$	60.43(4)
$O1^1$ Th1 N2	73.78(5)	N2 Th1 N1	60.43(4)
O1 Th1 $N2^1$	73.78(4)	N2 Th1 $N1^1$	80.99(4)
O1 Th1 N2	111.32(5)	$N2^1$ Th1 N1	80.99(4)
$O1^1$ Th1 $N2^1$	111.32(5)	N1 Th1 $N1^1$	69.23(6)
O1 Th1 $N1^1$	121.60(4)		
O1 Th1 N1	69.60(4)		
$O1^1$ Th1 $N1^1$	69.60(4)		

Table S8. Bond lengths [Å] and angles [°] for **UL$_2$**

U1 O1	2.258(1)	O1^1 U1 N1^1	71.22(5)
U1 O1^1	2.258(1)	O1^1 U1 N2^1	110.74(5)
U1 O2^1	2.241(1)	O1 U1 N2	110.74(5)
U1 O2	2.241(1)	O1^1 U1 N2	145.79(4)
U1 N1^1	2.576(2)	O1 U1 N2^1	145.79(4)
U1 N1	2.576(2)	O2^1 U1 O1^1	86.23(5)
U1 N2^1	2.600(2)	O2^1 U1 O1	83.52(5)
U1 N2	2.600(2)	O2 U1 O1	86.23(5)
		O2 U1 O1^1	83.52(5)
O1^1 U1 O1	88.49(6)	O2^1 U1 O2	165.68(6)
O1 U1 N1	71.22(5)	O2 U1 N1	112.18(5)
O1^1 U1 N1	152.71(5)	O2^1 U1 N1	73.81(5)
O1 U1 N1^1	152.71(5)		
O2 U1 N1^1	73.81(5)	N1^1 U1 N1	133.40(7)
O2^1 U1 N1^1	112.18(5)	N1^1 U1 N2^1	61.09(5)
O2 U1 N2	70.41(4)	N1 U1 N2	61.09(5)
O2^1 U1 N2^1	70.41(4)	N1^1 U1 N2	80.28(5)
O2^1 U1 N2	122.74(4)	N1 U1 N2^1	80.29(5)
O2 U1 N2^1	122.74(4)	N2^1 U1 N2	68.94(7)