Electronic Supporting Information for:

Schiff-base coordination complexes with Pu(IV) and Ce(IV)

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Experimental

General Considerations

Caution! *^{239}Pu [$t_{1/2}$ = 24,110(30) y] is a serious health threat, due to its radioactive decay, as well as that of its daughters. Hence, all studies with plutonium were conducted with appropriate controls for the safe handling and manipulation of radioactive materials, i.e. in a radiation laboratory equipped with a HEPA filtered hood. All free-flowing solids that contained plutonium were handled in negative-pressure gloveboxes or were covered in oil.*

All operations were performed in an open atmosphere with no attempt to exclude air and moisture. ^{239}Pu was MT-52 and obtained from Los Alamos National Laboratory as PuO_2 and converted to $PuCl_3$•xH_2O by repeated dissolution in concentrated HCl. $CeCl_3$•7H_2O (Sigma-Aldrich), 1,2-phenylenediammine (Sigma-Aldrich), 4-Diethylaminosalicylaldehyde (Sigma-Aldrich), NEt_3 (Sigma-Aldrich), and $CDCl_3$ (Sigma-Aldrich) were purchased from commercial sources and used as received.

UV/vis/NIR spectroscopic data were obtained from single crystals using a CRAIC Technologies UV/vis/NIR microspectrophotometer. Crystals were placed on quartz slides under Krytox oil and data were collected from 200 nm to 1400 nm. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker 600 MHz spectrometer operating at 600.1 and 150.9 MHz, respectively, at 298 K unless otherwise stated. ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced internally to solvent resonances. Electrochemical data was recorded on a CH Instruments Model 600E Series potentiostat. A three-electrode configuration comprising a platinum disk working electrode (2 mm diameter), a platinum wire counter electrode, and silver wire pseudo-reference electrode were used in all experiments. Cyclic voltammetric scans were conducted in DCM with 0.1 M [N^{n}Bu$_4$][PF_6] electrolyte for characterization of the ligand species, cerium, and plutonium complexes. Melting point data was performed using open capillaries on a Mel-Temp using an uncalibrated mercury thermometer. Elemental analyses for C, H, and N were carried out by Midwest Microlab, Indianapolis, IN. Single crystals selected for data collection were mounted on and optically aligned on a Bruker D8 Discover X-ray diffractometer, using a digital camera. Crystallographic data were collected at room temperature using a Mo-Kα (λ = 0.71069 Å) X-ray source and a graphite monochromator. The APEX III software[1] was used for the determination of the unit cells and data collection control. The raw data frames were

processed using SAINT[2] and SADABS.[3] Subsequent calculations were carried out using the OLEX2 program.[4] The structures were solved by olex2.solve and refined by full-matrix least-squares on F^2 techniques.

Synthesis of *N,N'* –bis[(4, 4' -diethylamino)salicylidene]-1, 2-phenylenediamine (H_2L)

H_2L was synthesized in a manner similar to procedures utilized with other Schiff-base salen ligands molecules previously reported.[5-9] To a stirred solution of 1,2-phenylenediamine, o-$C_6H_4(NH_2)_2$ (0.500 g, 4.62 mmol) in methanol (10 mL), 4-diethylamino-salicylaldehyde $HC(O)C_6H_3$,2-OH,4-NEt_2 (1.79 g, 9.25 mmol) in methanol (15 mL), was added and refluxed for 8 h. The mixture was cooled to room temperature and concentrated under vacuum. The crude product was washed with methanol and dried under vacuum, giving H_2L as a fine yellow powder (1.17 g, 55%). ^{1}H NMR ($CDCl_3$): δ 13.69 (s, 2H, O-*H*), 8.45 (s, 2H, *H*-C(Ar)=N), 7.22 (s, 4H, Ar-*H*), 7.15 (s, 2H, Ar-*H*), 6.26 (s, 2H, Ar-*H*), 6.24 (s, 2H, Ar-*H*), 3.40 (s, 8H, NC*H*$_2$CH$_3$), 1.21 (s, 12H, CH$_2$C*H*$_3$); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 164.61 (Ar-*C*), 160.90 (Ar-*C*), 151.91 (Ar-*C*), 142.58 (Ar-*C*), 133.81 (Ar-*C*), 126.17 (Ar-*C*), 119.32 (Ar-*C*), 109.61 (Ar-*C*), 103. 71 (Ar-*C*), 98.23 (Ar-*C*), 44.65 (*C*H$_2$), 12.88 (*C*H$_3$).

Synthesis of PuL_2

H_2L (25 mg, 0.050 mmol) and NEt_3 (200 μL, 1.43 mmol) in DCM (1 mL) were added to a solution of $PuCl_3$•xH_2O (10 mg, 0.029 mmol, based on elemental Pu content) in methanol (1 mL). The color of the solution immediately changed from light violet to black. Pentane (5 mL) was carefully layered on top of the solution and after 1 d at room temperature, X-ray quality crystals of PuL_2 were isolated as black block-like crystals, washed with pentane and dried in air. Due to radioactivity, elemental analysis was not obtained.

Synthesis of CeL_2

H_2L (25 mg, 0.050 mmol) and NEt_3 (200 μL, 1.43 mmol) in DCM (1 mL) were added to a solution of $CeCl_3$•7H_2O (10 mg, 0.025 mmol) in methanol (1 mL). The color of the solution immediately changed from orange to black. Pentane (5 mL) was carefully layered on top of the solution and after 1 d at room temperature, X-ray quality crystals of CeL_2 were isolated as black block-like crystals, washed with pentane and dried in air (14 mg, 60%). ^{1}H NMR ($CDCl_3$): δ 8.34 (s, 4H, *H*-C(Ar)=N), 7.04 (s, 12H, Ar-*H*), 5.99 (s, 4H, Ar-*H*), 5.40 (s, 4H, Ar-*H*), 3.26 (s, 16H, C*H*$_2$CH$_3$), 2.93 (s, 16H, C*H*$_2$CH$_3$), 1.24 (s, 24H, CH$_2$C*H*$_3$), 1.09 (s, 24*H*, C*H*$_2$), ; ^{13}C{^{1}H} NMR ($CDCl_3$): δ 169.48 (Ar-*C*), 158.19 (Ar-*C*), 152.86 (Ar-*C*), 146.33 (Ar-*C*),

135.21 (Ar-*C*), 125.2 (Ar-*C*), 116.96 (Ar-*C*), 114.70 (Ar-*C*), 103.37 (Ar-*C*), 99.11 (Ar-*C*), 45.89 (*C*H_2), 44.21 (*C*H_2), 13.05 (*C*H_3), 8.65 (*C*H_3). Anal. Cal'd For $C_{56}H_{64}CeN_8O_4 \cdot 2CH_2Cl_2$; C, 56.95; H, 5.60; N, 9.16. Found, C, 57.22; H, 5.78; N, 9.25. Melting point 250-255 ˚C.

NMR Spectra

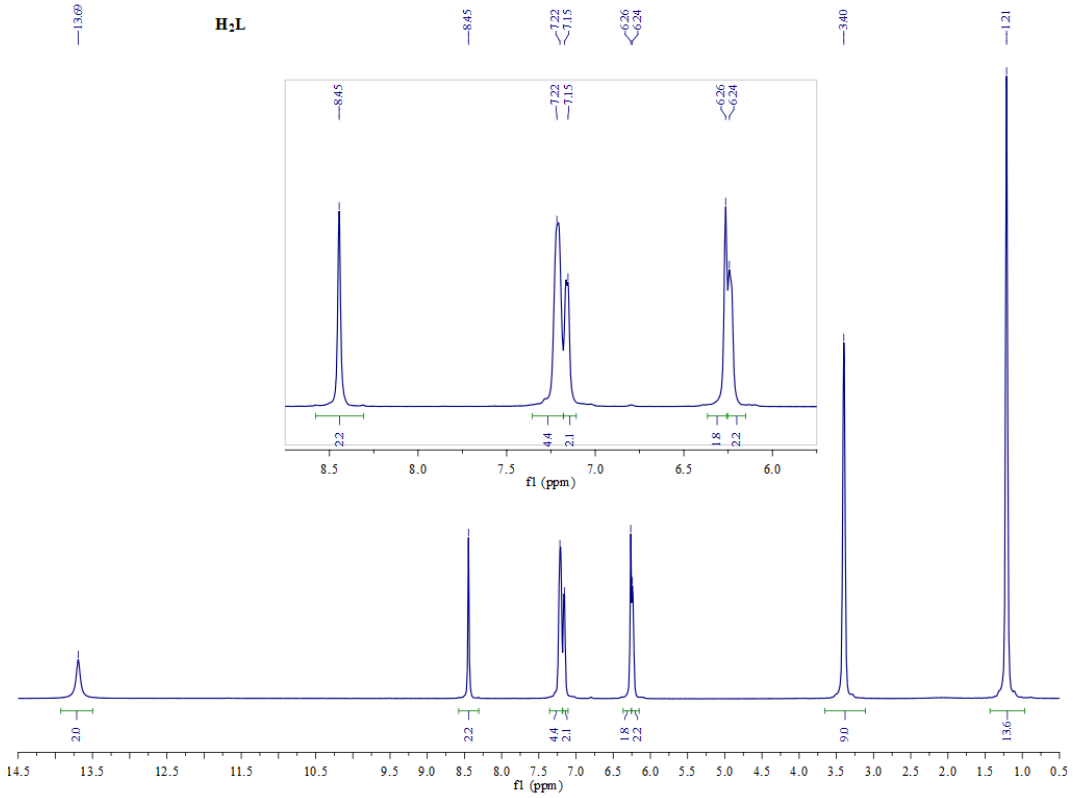

Figure S1. ^{1}H NMR spectrum of H_2L in $CDCl_3$ at 298 K.

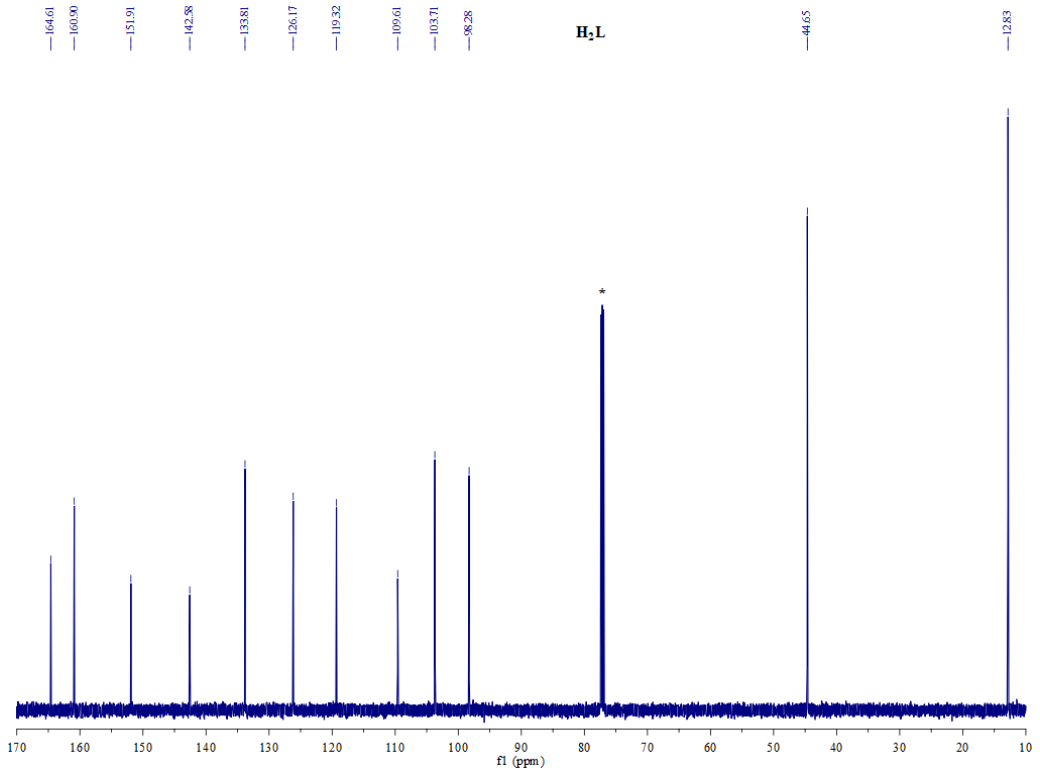

Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of H_2L in $CDCl_3$ at 298 K with * denoting solvent resonance.

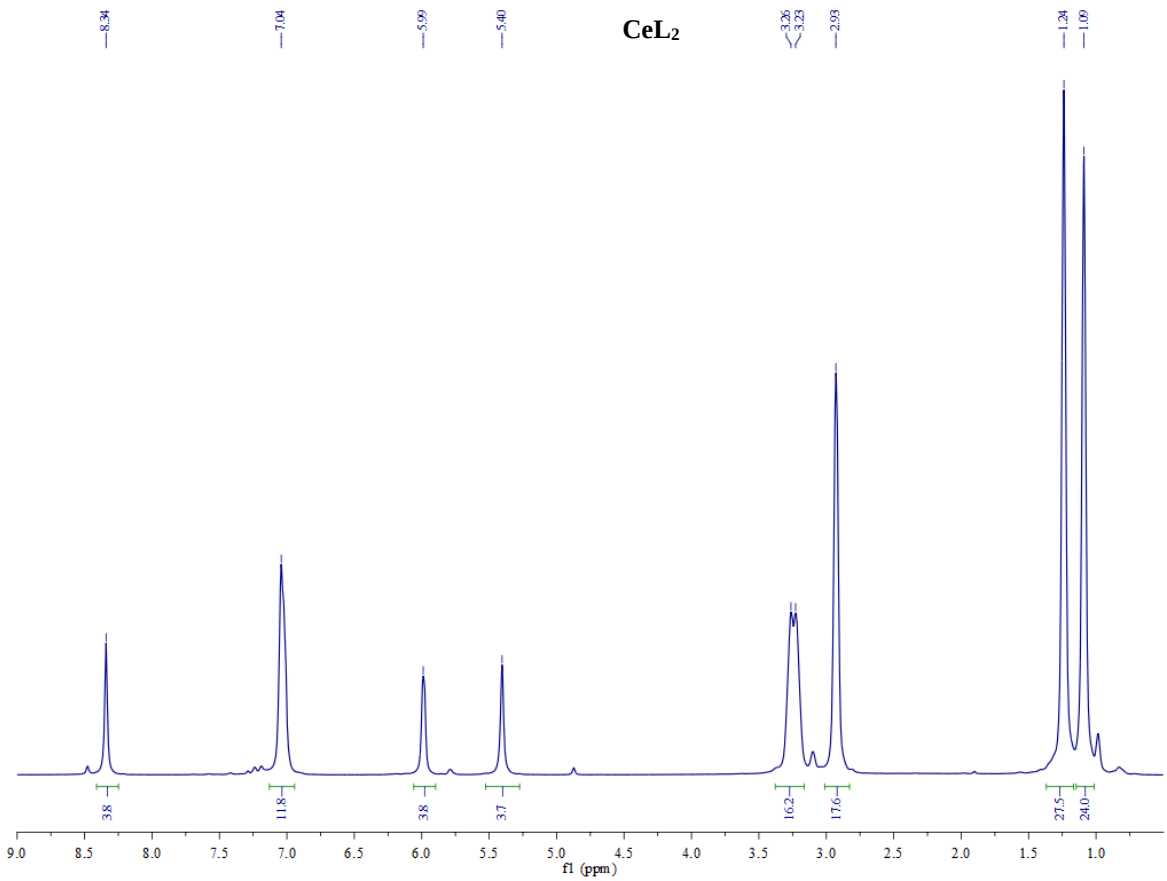

Figure S3. ^{1}H NMR spectrum of CeL_2 in $CDCl_3$ at 298K.

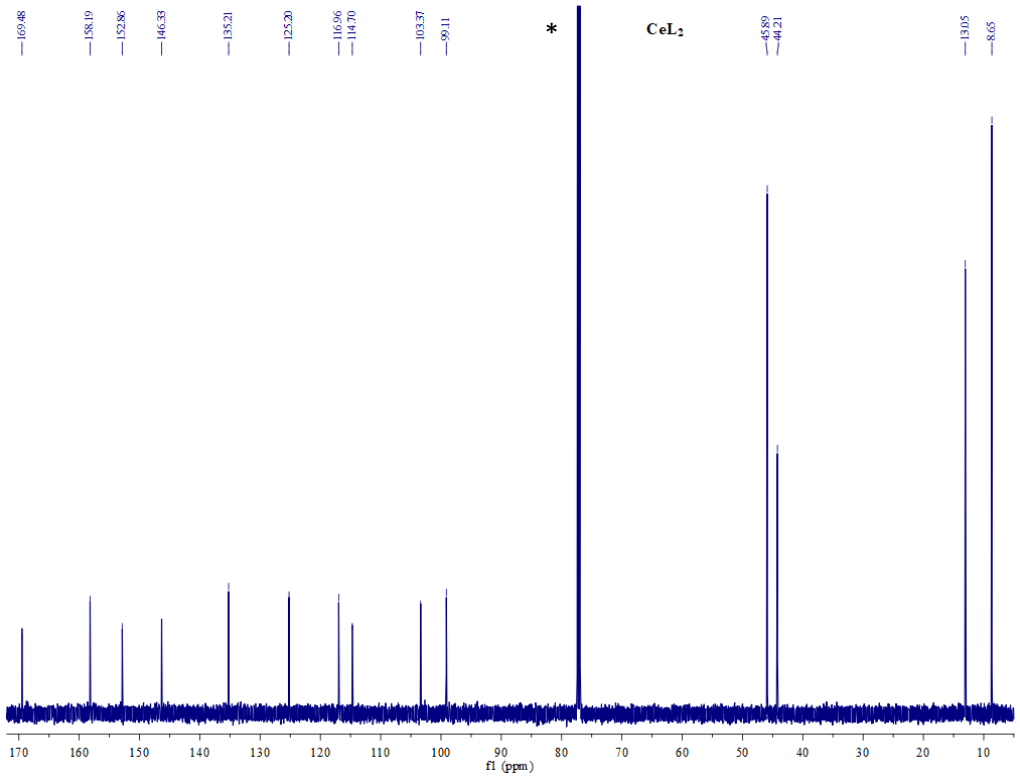

Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum of CeL_2 in $CDCl_3$ at 298K with * denoting solvent resonance.

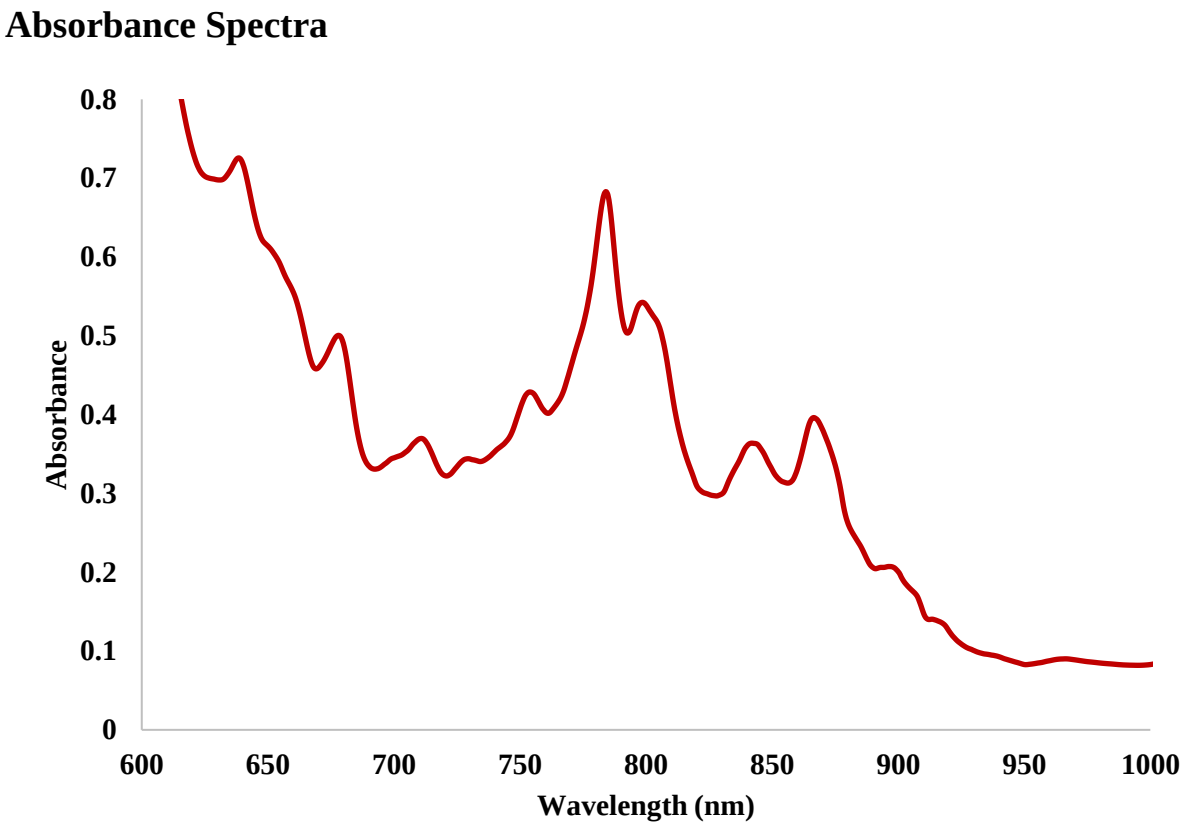

Figure S5. Absorption spectra of PuL_2 (L = *N*,*N'*–bis[(4,4'-diethylamino)salicylidene]-1,2-phenylenediamine).

Cyclic Voltammetry

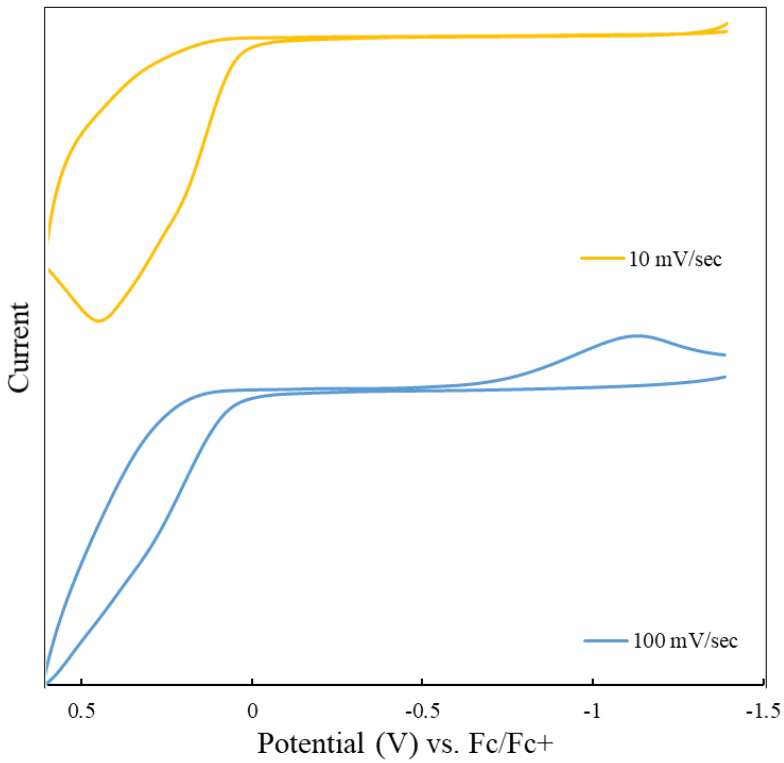

Figure S6. Cyclic voltammograms showing H_2L at a concentration of $5x10^{-3}$ M and ν = 10 mV/sec and ν = 100 mV/sec. Both scans are taken at 298 K with 0.1 M $[N^nBu_4][PF_6]$ in DCM.

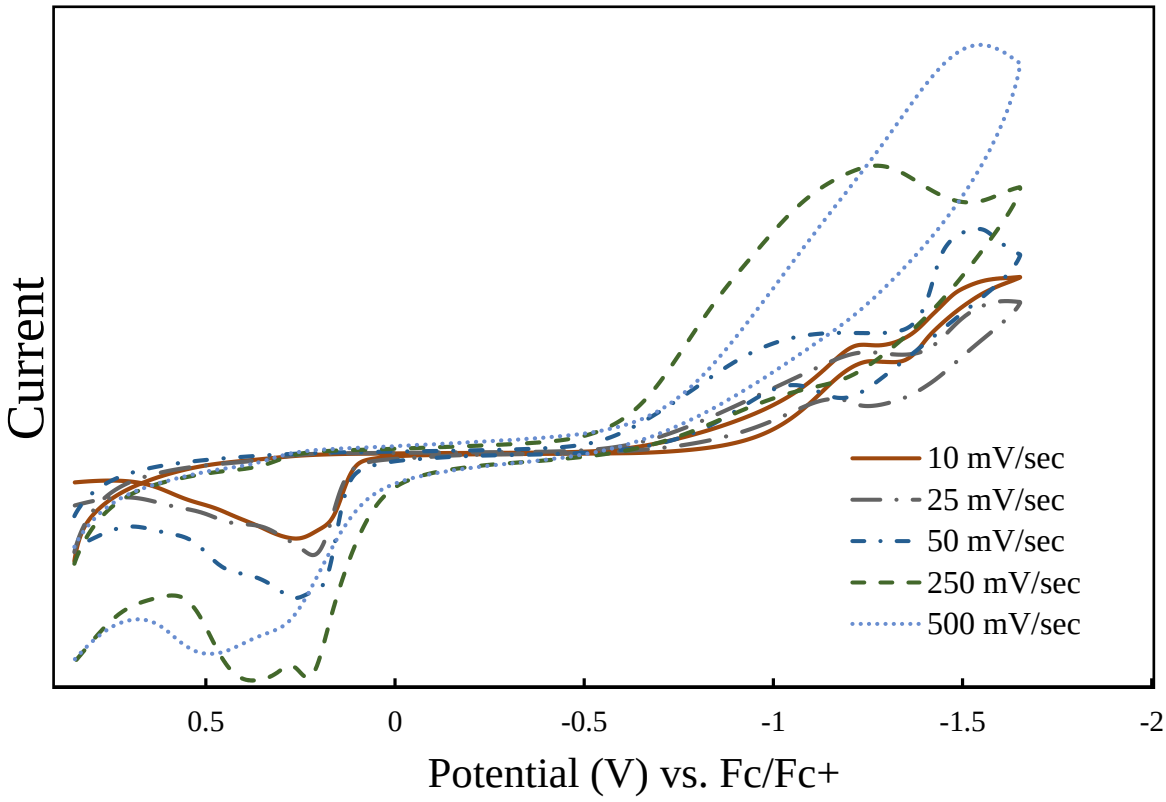

Figure S7. Cyclic voltammograms showing CeL_2 at a concentration of $5x10^{-3}$ M at various scan rates at 298 K with 0.1 M $[N^nBu_4][PF_6]$ in DCM.

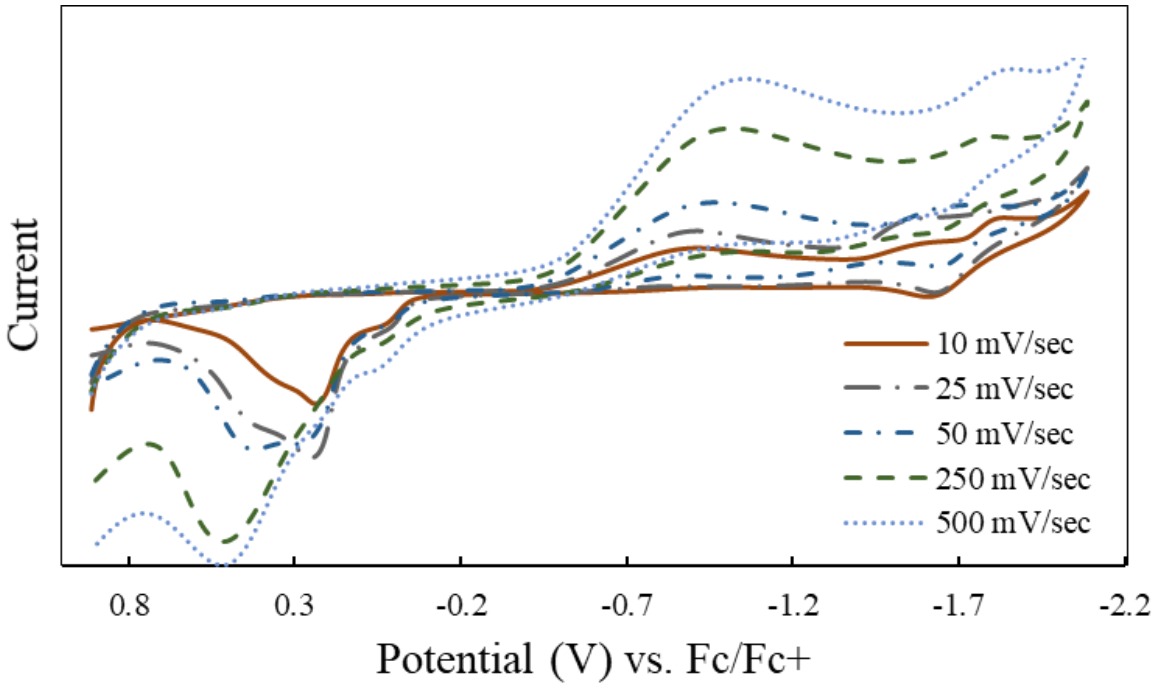

Figure S8. Cyclic voltammograms showing PuL_2 at a concentration of $5x10^{-3}$ M at various scan rates at 298 K with 0.1 M $[N^nBu_4][PF_6]$ in DCM.

Crystallographic Details

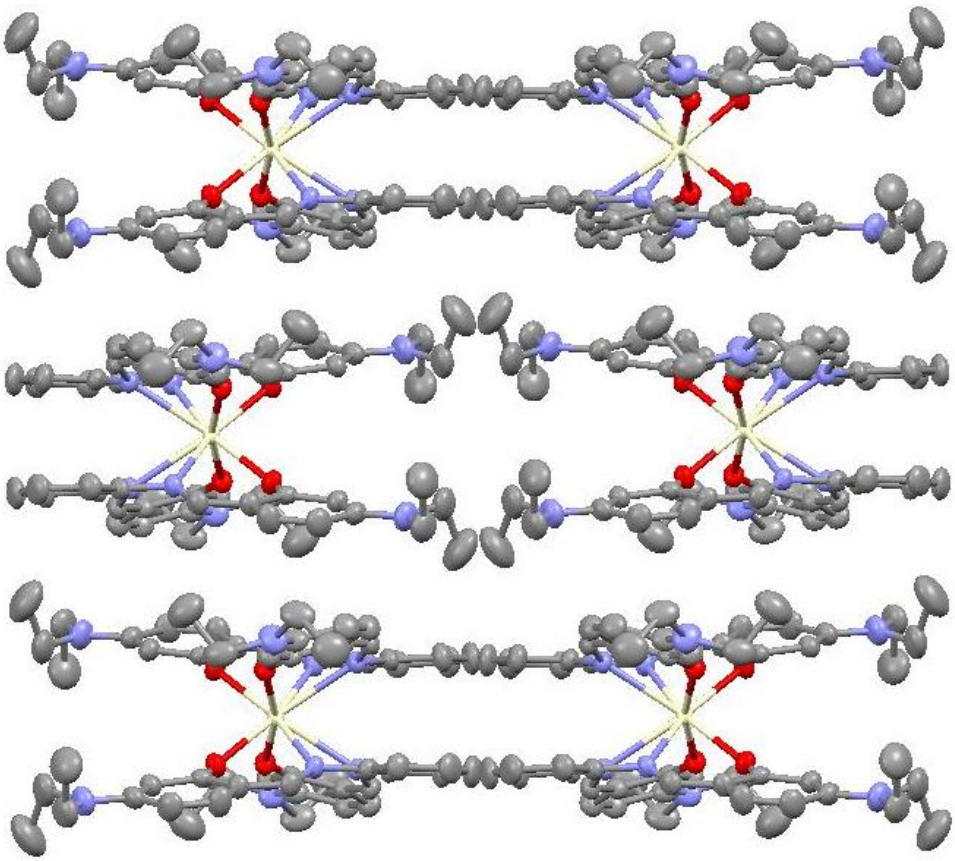

Figure S9. Packing diagram of CeL_2 shown down the c axis. Drawn at the 50% probability level with hydrogen atoms and lattice solvent omitted for clarity.

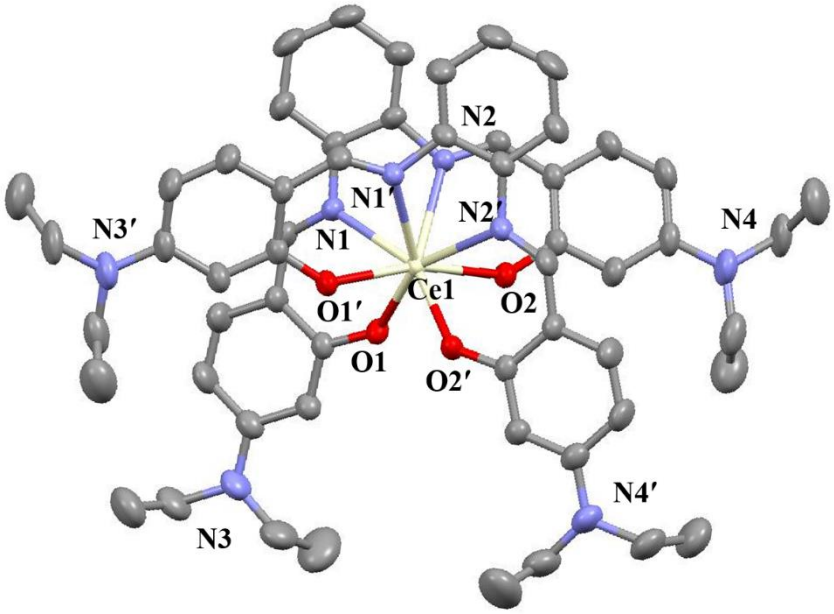

Figure S10. Molecular structure of CeL_2 drawn at the 50% probability level with hydrogen atoms and lattice solvent omitted for clarity.

Table S1. Crystallographic information for ML_2 (M = Ce, Pu)

Compound	**CeL_2**	**PuL_2**
Empirical Formula	$C_{58}H_{68}Cl_4N_8O_4Ce$	$C_{58}H_{68}Cl_4N_8O_4Pu$
Color	Black	Red
Habit	Block	Irregular
Temperature (K)	299(2)	298(2)
Crystal System	Monoclinic	Monoclinic
Space Group	*C*2/*c*	*C*2/*c*
a (Å)	15.120(6)	15.0632(9)
b (Å)	25.007(9)	24.9196(15)
c (Å)	15.405(6)	15.3540(9)
α (deg)	90	90
β (deg)	95.137(9)	95.012(2)
γ (deg)	90	90
Volume (Å^3)	5801(4)	5741.4(6)
Z	4	4
ρ_{calcd} (Mg/m^3)	1.400	1.533
μ (mm^{-1})	1.021	1.387
R1[a] ($I > 2.0\sigma$(I))	0.0412	0.0491
wR2 (all data)	0.0868	0.0906

[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.

Table S2. Bond lengths [Å] and angles [°] for PuL_2.

Pu(1)-O(2)#1	2.224(3)	O(2)#1-Pu(1)-N(2)	152.05(10)
Pu(1)-O(2)	2.224(3)	O(2)-Pu(1)-N(2)	71.76(10)
Pu(1)-O(1)#1	2.225(3)	O(1)#1-Pu(1)-N(2)	74.20(10)
Pu(1)-O(1)	2.225(3)	O(1)-Pu(1)-N(2)	112.80(11)
Pu(1)-N(2)#1	2.538(3)	N(2)#1-Pu(1)-N(2)	133.38(14)
Pu(1)-N(2)	2.538(3)	O(2)#1-Pu(1)-N(1)#1	110.89(10)
Pu(1)-N(1)#1	2.572(3)	O(2)-Pu(1)-N(1)#1	145.97(10)
Pu(1)-N(1)	2.572(3)	O(1)#1-Pu(1)-N(1)#1	71.11(10)
		O(1)-Pu(1)-N(1)#1	124.27(10)
O(2)#1-Pu(1)-O(2)	87.75(14)	N(2)#1-Pu(1)-N(1)#1	61.57(10)
O(2)#1-Pu(1)-O(1)#1	84.87(10)	N(2)-Pu(1)-N(1)#1	79.95(10)
O(2)-Pu(1)-O(1)#1	83.08(10)	O(2)#1-Pu(1)-N(1)	145.98(10)
O(2)#1-Pu(1)-O(1)	83.09(10)	O(2)-Pu(1)-N(1)	110.89(10)
O(2)-Pu(1)-O(1)	84.87(10)	O(1)#1-Pu(1)-N(1)	124.27(10)
O(1)#1-Pu(1)-O(1)	163.27(14)	O(1)-Pu(1)-N(1)	71.11(10)
O(2)#1-Pu(1)-N(2)#1	71.77(10)	N(2)#1-Pu(1)-N(1)	79.95(10)
O(2)-Pu(1)-N(2)#1	152.05(10)	N(2)-Pu(1)-N(1)	61.57(10)
O(1)#1-Pu(1)-N(2)#1	112.80(11)	N(1)#1-Pu(1)-N(1)	69.39(14)
O(1)-Pu(1)-N(2)#1	74.19(10)		

Table S2. Bond lengths [Å] and angles [°] for CeL_2.

Ce(1)-O(2)#1	2.2376(16)	O(2)#1-Ce(1)-O(1)#1	85.82(6)
Ce(1)-O(2)	2.2376(16)	O(2)-Ce(1)-O(1)#1	83.62(6)
Ce(1)-O(1)#1	2.2418(15)	O(2)#1-Ce(1)-O(1)	83.62(6)
Ce(1)-O(1)	2.2418(15)	O(2)-Ce(1)-O(1)	85.82(6)
Ce(1)-N(2)#1	2.6031(18)	O(1)#1-Ce (1)-O(1)	88.79(8)
Ce(1)-N(2)	2.6031(18)	O(2)#1-Ce(1)-N(2)#1	70.54(6)
Ce(1)-N(1)#1	2.5760(19)	O(2)-Ce(1)-N(2)#1	123.03(5)
Ce(1)-N(1)	2.5760(19)	O(1)#1-Ce(1)-N(2)#1	110.36(6)
		O(1)-Ce(1)-N(2)#1	145.93(6)
O(2)#1-Ce(1)-O(2)	165.21(7)	O(2)#1-Ce(1)-N(2)	123.03(5)

O(2)-Ce(1)-N(2)	70.54(5)	N(2)-Ce(1)-N(1)#1	80.38(6)
O(1)#1-Ce(1)-N(2)	145.93(6)	O(2)#1-Ce(1)-N(1)	73.88(6)
O(1)-Ce(1)-N(2)	110.36(6)	O(2)-Ce(1)-N(1)	112.29(6)
N(2)#1-Ce(1)-N(2)	69.22(8)	O(1)#1-Ce (1)-N(1)	152.61(6)
O(2)#1-Ce (1)-N(1)#1	112.29(6)	O(1)-Ce(1)-N(1)	71.14(6)
O(2)-Ce(1)-N(1)#1	73.88(6)	N(2)#1-Ce(1)-N(1)	80.38(6)
O(1)#1-Ce(1)-N(1)#1	71.14(6)	N(2)-Ce(1)-N(1)	61.09(6)
O(1)-Ce(1)-N(1)#1	152.62(6)	N(1)#1-Ce(1)-N(1)	133.45(8)
N(2)#1-Ce(1)-N(1)#1	61.09(6)		

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