SUPPLEMENTARY INFORMATION

for

From Actinide Bonding to Extraction Performance: Trends in An(IV) N-Heterocyclic Diamide Complexes

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Table of Contents

1 Experimental part

Caution! Th and U are toxic heavy metals; ^{237}Np and ^{239}Pu are dangerous alpha-emitters ($T_{1/2} = 2 \cdot 10^6$ y and 24000 y, respectively). All manipulations were conducted in specialized facilities, following strict safety protocols.

1.1 Extraction experiments and preparation of the crystals

All purchased chemicals used in this study were of analytical grade and used without any further purification. All aqueous acidic solutions were prepared from deionized water (MilliPore Simplicity) and concentrated acid (analytical grade, Chimmed Group). N,N'-diethyl-N,N'-di(4-ethyl-phenyl)-diamide of 2,2'-dipyridyl-6,6'-dicarboxylic acid (^{4Et}DABipy) was prepared, purified, and characterized according to the published procedure[1]. Metanitrobenzotrifluoride (F-3) (OJSC "PIM-INVEST", >99%), acetonitrile (ACCROS, HPLC grade), $CsNO_3$ (Sigma-Aldrich, 99.9%), $Ce(NO_3)_3 \cdot 6H_2O$ (Sigma-Aldrich, 99.9%), $(NH_4)_2Ce(NO_3)_6$ (Sigma-Aldrich, 99.9%), $Th(NO_3)_4 \cdot 5H_2O$ (natural isotopic ratio), $UO_2(NO_3)_2 \cdot 6H_2O$ (natural isotopic ratio), $^{237}NpO_2$, $^{239}PuO_2$ (Company "Isotope") were used. Deuterated solvents CH_3CN-d_3 and $(CH_3)_2SO$-d_6 for NMR spectra registration were purchased from commercial sources and used without further purification.

$Cs_2An(NO_3)_6$ (An = U, Np, Pu) precursors were prepared as follows. U(IV) solution (1 M) in 3 M HNO_3 was prepared by controlled potential electrolysis at the mercury pool cathode; Np(IV) and Pu(IV) in 5-7 M HNO_3 were prepared by reducing with hydrazine at 50 – 60˚C. A saturated solution of $CsNO_3$ in 5-7 M HNO_3 was added to a solution of 0.5 – 1 M An(IV) in 5 – 7 M HNO_3 until the Cs:An molar ratio reached 3:1. The solution was stored at 6˚C for at least 3 hours. Crystals of $Cs_2An(NO_3)_6$ were then filtered, washed thrice with cold (6˚C) 3 M HNO_3 solution and dried in air.

Starting solutions of 0.1 M Th(IV), 0.1 M U(IV) and 0.025 M Pu(IV) were prepared by dissolving of $Th(NO_3)_4 \cdot 5H_2O$ and $Cs_2An(NO_3)_6$ (An = U, Pu) in 1 M HNO_3. In case of U(IV), 0.25 M $N_2H_4 \cdot HNO_3$ was added to prevent oxidation. Np(IV) was prepared from ^{237}Np stock solution in HNO_3. Neptunium was reduced to Np(IV) by adding an excess amount of $NH_2OH \cdot HCl$ and heating to 70˚C for nearly 4 h. The resulting solution of Np(IV) was diluted with 1 M HNO_3 and UV-vis spectrum was recorded to ensure that other oxidation states of neptunium are absent. Np(IV) concentration was calculated from the absorption at 961 nm to be 0.05 M. Starting solutions of 0.01 M Ce(III), Ce(IV) and U(VI) were prepared by dissolving $Ce(NO_3)_3 \cdot 6H_2O$, $(NH_4)_2Ce(NO_3)_6$ and $UO_2(NO_3)_2 \cdot 6H_2O$ in 0.5 M HNO_3. All the extraction experiments were repeated twice to ensure convergent result.

Extraction experiments were conducted in the polyethylene tubes with organic to aqueous phase ratio of 1:1 (each phase volume equaled 500 µl). For all experiments, initial cation concentration in the aqueous phase was close to 0.025 mM, HNO_3 concentration varied from 0.5 M to 5 M. Organic phase consisted of ^{4Et}DABipy solution in F-3 (metanitrobenzotrifluoride, Figure 1b) with ^{4Et}DABipy concentration from 2.5 mM to 50 mM. Phases were contacted sat 22±2°C using Vortex-shaker. Phases were then centrifuged for 1.5 min at 10000 rpm. Ce, Th and U concentration in the aqueous phase after contact was measured using inductively coupled plasma mass spectrometry (ICP-MS). Np and Pu concentrations were measured in aqueous phase by liquid scintillation counting using a PerkinElmer Tricarb 2810 TR Liquid Scintillation Analyzer. Alpha-beta discrimination was implied to distinguish counts attributed to ^{237}Np and ^{233}Pa. Samples were prepared by mixing 200 µl of the aqueous phase after extraction, 500 µl of distilled water and 3 ml of scintillation

cocktail (Ultima Gold). Distribution coefficients were calculated as the ratio of the difference in metal concentration between the initial and equilibrium aqueous phases, divided by the concentration of the metal in the equilibrium aqueous phase.

Single crystals of *[(^{4Et}DABipy)Ce(NO_3)$_3$]·[(^{4Et}DABipy)Ce(NO_3)$_4$]*, *[(^{4Et}DABipy)An(NO_3)$_4$]* suitable for SC-XRD analysis were synthesized by isothermal evaporation of the solvent from concentrated solutions of ^{4Et}DABipy and the corresponding metal nitrate salt ($(NH_4)_2Ce(NO_3)_6$, $Th(NO_3)_4$, $Cs_2An(NO_3)_6$ (An = U, Np, Pu) in acetonitrile.

1.2 Single crystal X-ray diffraction

Crystallographic data for [(^{4Et}DABipy)Ce(NO_3)$_3$]·[(^{4Et}DABipy)Ce(NO_3)$_4$], [(^{4Et}DABipy)Th(NO_3)$_4$], and [(^{4Et}DABipy)U(NO_3)$_4$] were collected on a Bruker D8 Venture diffractometer using graphite monochromatized Mo*K*α radiation (λ = 0.71073 Å) in ω-scan mode at 100 or 150 K. The data for [(^{4Et}DABipy)Np(NO_3)$_4$] and [(^{4Et}DABipy)Pu(NO_3)$_4$] were collected on a Bruker Kappa APEX II diffractometer with a CCD area detector using graphite-monochromatized Mo*K*α (λ = 0.71073 Å) radiation at 100 K.

Cell refinement and data reduction were conducted using the software SAINT (V8.38A, Bruker). Absorption correction based on measurements of equivalent reflections was applied (SADABS-2016/2, Bruker 2016/2). The structures were solved by direct methods (SHELXT 2018/2)[2] and refined by full matrix least-squares on F^2 (SHELXL 2018/3)[3] with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were placed in calculated positions and refined using a riding model. In the structure of cerium complex, disordered solvent molecules (acetonitrile) could not be modeled and a solvent mask was calculated as implemented in Olex2-1.5 to account for the electron density[4].

1.3 ICP-MS

The quantitative determination of ^{140}Ce, ^{232}Th and ^{238}U was performed using ICP-MS by PlasmaQuant MS Elite (Analytic Jena, Germany). All samples were diluted with the 3% nitric acid solution to concentrations within the calibration range. The dilution solution was prepared using ultra-high purity HNO_3 and deionized water obtained from a Milli-Q water purification system (resistivity 18.2 MΩ·cm). Calibration range was 0.1 – 100 µg/L. For signal correction and matrix effect compensation, an internal standard with ^{103}Rh was used.

Solvent extraction experiments with Th^{4+} and U^{4+} were repeated and remeasured at Agilent 7500 ce instrument following similar sample preparation procedure. The cross-validation yielded comparable results.

1.4 ^{1}H-NMR sample preparation and measurements

Two sets of samples were prepared for ^{1}H-NMR analysis. One set consisted of a series of solutions containing $Ce^{3+/4+}$ and An^{4+} (An = Th, U, Np, Pu) complexes with ^{4Et}DABipy in acetonitrile-d_3. The samples were prepared by mixing acetonitrile-d_3 solutions of ^{4Et}DABipy and the corresponding metal salt. In case of U^{4+}, $N_2H_4{\cdot}H_2O$ was added to the solvent prior to $Cs_2U(NO_3)_6$ dissolution. The second set of samples was prepared by extracting An^{4+} cations from 3 M HNO_3 to 0.01 M ^{4Et}DABipy in F-3. NMR spectrometer was calibrated using DMSO-d_6, which was placed in the inner capillary of the ampule.

The NMR spectra were measured with a BRUKER AVANCE-600 MHz NMR spectrometer at 298±0.3K in 5 mm probe tubes (with the solvents as internal reference). For experiments with F-3 used as solvent, capillary filled with DMSO-d_6 was placed inside the probe tube. The 2D homonuclear shift correlation using gradient pulse for selection experiments were made for protons assignment.

1.5 UV-vis spectroscopy

UV-vis spectra of the initial aqueous phases, acetonitrile solutions after ^{1}H-NMR experiments and of organic phases after extraction were recorded using Shimadzu UV 1800 spectrometer at 298.0±0.1 K in quartz cuvettes. The scanning range was 750 – 400 nm for U, 1100 – 400 nm for Np and 850 – 400 nm Pu for samples.

As reference of 12-coordinate An(IV) species, $[N(CH_3)_4]_2An^{IV}(NO_3)_6$ (An^{IV} = U, Np, Pu) complexes were prepared by adding a solution of $[N(CH_3)_4]NO_3$ (2 equivalents) in 4 M HNO_3 to An(IV) solutions in 4 M HNO_3 (1 equivalent). The solutions were left overnight ta 4˚C for precipitation. The precipitates were washed twice with 3 M HNO_3, dried under vacuum and then dissolved in acetonitrile. Chemical identity of the complexes was confirmed by comparison of the obtained UV-vis spectra with literature data, namely $[(C_2H_5)_4]_2An(NO_3)_6$ (An = U, Np, Pu)[5] and $[N(n\text{-}Bu_4)]_2Pu(NO_3)_6$[6].

1.6 IR spectroscopy

Infrared spectra of Ce^{3+}, Th^{4+}, U^{4+} and Np^{4+} crystals were measured using the FT-801 IR Fourier spectrometer (Simex, Russia). Crystals were mixed with calcined NaCl in a mass ratio of 1:100 and pressed into a thin pellet. IR data were recorded from the pellets in a range 500-2000 cm^{-1}, with a spectral resolution of 4 cm^{-1}. In total, 16 scans were recorded and averaged for each sample. IR spectra are presented in Figure S3. All spectra are identical, except for the 935 cm^{-1} band of $[(^{4Et}DABipy)U(NO_3)_4]$ compound, which likely indicates that U(IV) was oxidized during sample preparation and the peak corresponds to ν_3 vibrations of UO_2^{2+}.

1.7 Computational methodology

Simplified starting models of Ce(IV), Th(IV), U(IV), Np(IV), and Pu(IV) complexes assigned as $[(DABipy)M(NO_3)_4]$, where 4-EtC_6H_4 substituents were replaced by Ph groups, were constructed based on X-ray data (see section 2.2), with hydrogen atoms placed in idealized positions accordingly to neutron diffraction statistics[7]. Further DFT calculations with full geometry optimization were performed in ORCA 5.0 program[8] using PBE0[9]-D3[10] functional with the Douglas–Kroll–Hess 2nd order scalar relativistic (DKH) calculations requested relativistic core Hamiltonian[11,12] and full-electron jorge-TZP-DKH[13–15] (for metals) and jorge-DZP-DKH[15–18] (for other elements) basis sets with the “resolution of identity” algorithm[19] in conjunction with the AutoAux-generated[20] auxiliary basis sets. The SCF calculations were tightly converged (TightSCF). In all cases, vibrational analysis showed no imaginary frequencies.

Bader topological analysis of electron density distributions[21–23] for all calculated wavefunctions as well as atoms-in-molecules (AIM) [24–26] charge calculations was performed in Multiwfn 3.8 program[27,28]. Wiberg bond indexes (WBI) [29–31] and natural population analysis (NPA)[32,33] atomic charges in natural atomic partitioning scheme were calculated using GENNBO utility in NBO 7.0[34] based on .47 files generated in Multiwfn 3.8.

2 Crystal Data

Table S1. Crystal data and structure refinement for Ce, Th and U complexes.

CCDC code	2534238	2534240	2534239
Empirical formula	$C_{33.5}H_{36.06}CeN_{8.25}O_{12.5}$	$C_{32}H_{34}N_8O_{14}Th$	$C_{32}H_{34}N_8O_{14}U$
Formula weight	894.38	986.71	992.70
Temperature/K	100	100	150
Crystal system	monoclinic	monoclinic	monoclinic
Space group	C2/c	$P2_1/n$	C2/c
a/Å	51.7998(15)	11.9377(4)	51.3341(15)
b/Å	16.5422(5)	24.7740(10)	8.5076(3)
c/Å	18.0168(5)	13.5637(5)	17.5282(6)
α/°	90	90	90
β/°	95.6060(10)	112.1650(10)	101.6010(10)
γ/°	90	90	90
Volume/Å^3	15364.4(8)	3715.0(2)	7498.7(4)
Z	16	4	8
ρ_{calc}g/cm^3	1.547	1.764	1.759
μ/mm^{-1}	1.258	4.092	4.406
F(000)	7245.0	1936.0	3888.0
Crystal size/mm^3	0.34 × 0.09 × 0.05	0.28 × 0.24 × 0.12	0.2 × 0.12 × 0.01
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.586 to 55.842	3.636 to 55.994	4.696 to 56
Reflections collected	83195	33895	34027
Independent reflections	18392 [R_{int} = 0.0731, R_{sigma} = 0.0652]	8949 [R_{int} = 0.0352, R_{sigma} = 0.0349]	9045 [R_{int} = 0.0449, R_{sigma} = 0.0460]
Data/restraints/parameters	18392/8/982	8949/0/500	9045/0/500
Goodness-of-fit on F^2	1.057	1.064	1.100
Final R indexes [I>=2σ (I)]	R_1 = 0.0423, wR_2 = 0.0853	R_1 = 0.0347, wR_2 = 0.0901	R_1 = 0.0350, wR_2 = 0.0739
Final R indexes [all data]	R_1 = 0.0713, wR_2 = 0.0935	R_1 = 0.0433, wR_2 = 0.0936	R_1 = 0.0474, wR_2 = 0.0776
Largest diff. peak/hole / e Å^{-3}	1.23/-1.57	1.68/-1.80	1.04/-1.77

Table S2. Crystal data and structure refinement for Np and Pu complexes.

CCDC code	2534233	2534234
Empirical formula	$C_{32}H_{34}N_8NpO_{14}$	$C_{32}H_{34}N_8PuO_{14}$
Formula weight	991.67	996.67
Temperature/K	100	100
Crystal system	monoclinic	monoclinic
Space group	C2/c	C2/c

a/Å	51.287(16)	51.224(2)
b/Å	8.499(3)	8.4955(4)
c/Å	17.467(5)	17.4214(8)
α/°	90	90
β/°	101.542(12)	101.452(2)
γ/°	90	90
Volume/Å^3	7460(4)	7430.4(6)
Z	8	8
ρ_{calc}g/cm^3	1.766	1.782
μ/mm^{-1}	2.863	1.852
F(000)	3896.0	3904.0
Crystal size/mm^3	0.3 × 0.18 × 0.04	0.18 × 0.14 × 0.04
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	7.238 to 54.998	6.926 to 55
Reflections collected	63586	55550
Independent reflections	8537 [R_{int} = 0.1275, R_{sigma} = 0.0841]	8507 [R_{int} = 0.1045, R_{sigma} = 0.0738]
Data/restraints/parameters	8537/0/500	8507/0/500
Goodness-of-fit on F^2	1.029	1.032
Final R indexes [I>=2σ (I)]	R_1 = 0.0441, wR_2 = 0.0797	R_1 = 0.0397, wR_2 = 0.0594
Final R indexes [all data]	R_1 = 0.0746, wR_2 = 0.0915	R_1 = 0.0681, wR_2 = 0.0679
Largest diff. peak/hole / e Å^{-3}	2.59/-2.30	1.51/-1.71

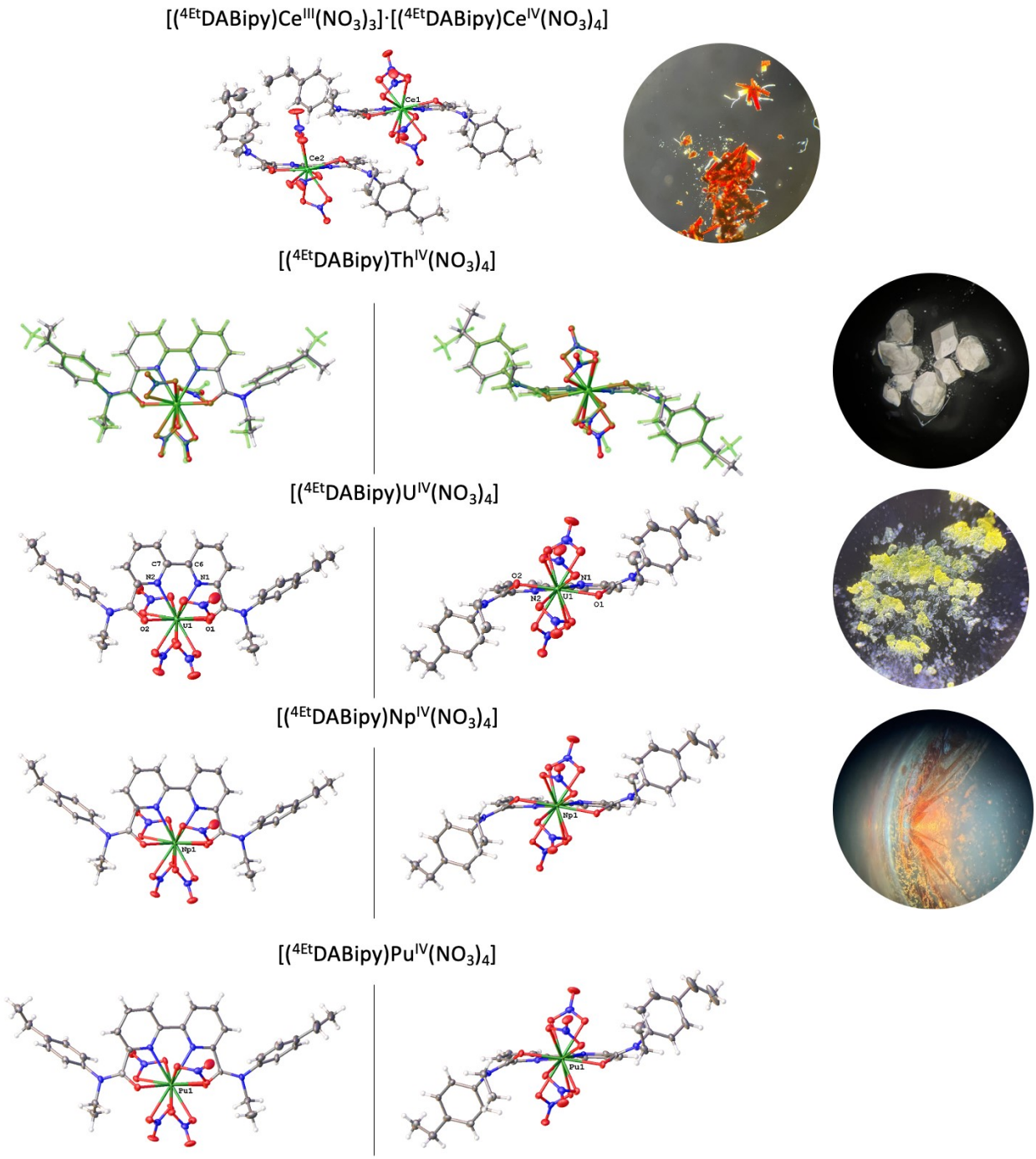

Figure S1. Molecular structures of [(4EtDABipy)An^{IV}(NO$_3$)$_4$] (An^{IV} = Th, U, Np, Pu) in two projections and asymmetric unit of [(4EtDABipy)Ce^{IV}(NO$_3$)$_4$]·[(4EtDABipy)Ce^{III}(NO$_3$)$_3$]. Displacement ellipsoids for all non-hydrogen atoms are shown at the 50% probability level. The structure of [(4EtDABipy)Th^{IV}(NO$_3$)$_4$] is superimposed on previously reported modification (CCDC 2395348).

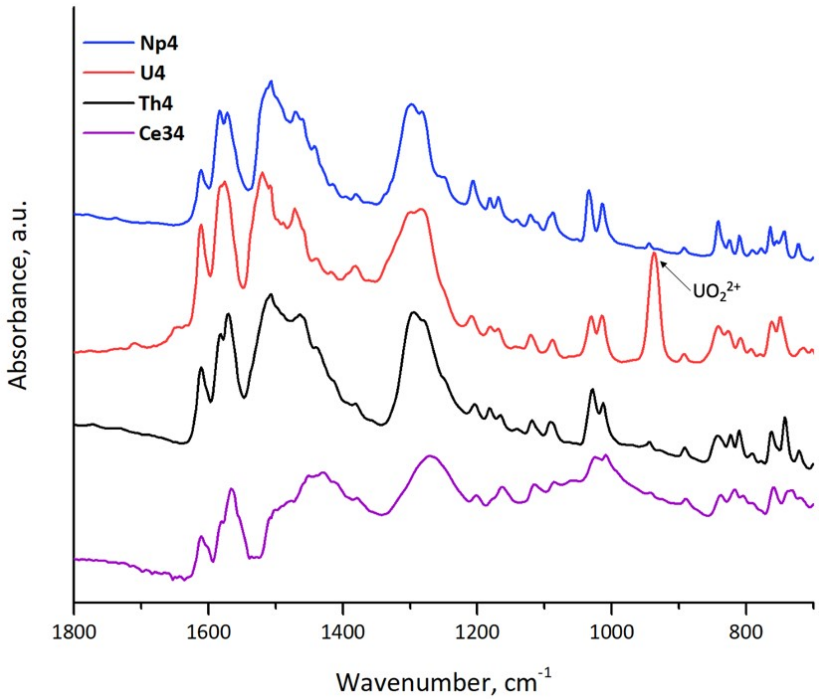

Figure S2. IR spectra of [(^{4Et}DABipy)$Ce^{IV}(NO_3)_4$]·[(^{4Et}DABipy)$Ce^{III}(NO_3)_3$] (**Ce34)**, [(^{4Et}DABipy)$An^{IV}(NO_3)_4$] (**Th4**, **U4** and **Np4**) crystals.

3 Computational part

Table S3. Electron density ρ (in e/Bohr^3), Laplacian $\nabla^2\rho$ (in e/Bohr^5), potential energy density V, Lagrangian kinetic energy G (in Hartree/Bohr^3) at the bond critical points (3, –1), corresponding to the M–N and M–O bonds with DABipy ligand. Experimental and optimized lengths of the bonds l_{exp} and l_{opt} are in Å.

Metal	Bond	l_{exp}	l_{opt}	ρ	$\nabla^2\rho$	G	V	|V|/G	WBI
Ce	Ce–O	2.441	2.444	0.051	0.187	0.049	-0.051	1.039	0.269
		2.383	2.448	0.051	0.186	0.048	-0.050	1.036	0.268
	Ce–N	2.603	2.653	0.040	0.120	0.031	-0.032	1.028	0.210
		2.616	2.654	0.040	0.120	0.031	-0.032	1.027	0.210
Th	Th–O	2.454	2.462	0.051	0.231	0.058	-0.057	0.998	0.148
		2.432	2.466	0.050	0.228	0.057	-0.057	0.996	0.147
	Th–N	2.676	2.692	0.039	0.129	0.034	-0.035	1.040	0.101
		2.667	2.692	0.039	0.129	0.034	-0.035	1.040	0.101
U	U–O	2.382	2.439	0.054	0.241	0.060	-0.060	1.001	0.154
		2.405	2.440	0.054	0.240	0.060	-0.060	1.000	0.153
	U–N	2.616	2.638	0.043	0.152	0.038	-0.038	0.997	0.117
		2.624	2.639	0.043	0.151	0.038	-0.038	0.997	0.117
Np	Np–O	2.398	2.427	0.054	0.240	0.059	-0.059	0.993	0.155
		2.374	2.425	0.055	0.240	0.060	-0.059	0.995	0.157
	Np–N	2.605	2.641	0.041	0.145	0.036	-0.035	0.986	0.115
		2.611	2.641	0.041	0.145	0.036	-0.035	0.987	0.114
Pu	Pu–O	2.391	2.412	0.054	0.231	0.057	-0.057	0.993	0.138
		2.371	2.414	0.054	0.230	0.057	-0.056	0.992	0.138
	Pu–N	2.601	2.626	0.042	0.140	0.035	-0.034	0.992	0.105
		2.594	2.626	0.042	0.140	0.035	-0.034	0.991	0.105

Table S4. Electron density ρ (in e/Bohr^3), Laplacian $\nabla^2\rho$ (in e/Bohr^5), potential energy density V, Lagrangian kinetic energy G (in Hartree/Bohr^3) at the bond critical points (3, –1), corresponding to the M–O bonds with nitrate ligands. Experimental and optimized lengths of the bonds l_{exp} and l_{opt} are in Å.

Metal	Bond	l_{exp}	l_{opt}	ρ	$\nabla^2\rho$	G	V	|V|/G	WBI
Ce	Ce–4O	2.574	2.525	0.046	0.160	0.040	-0.041	1.009	0.285
	Ce–5O	2.529	2.521	0.047	0.159	0.040	-0.040	1.008	0.300
	Ce–7O	2.576	2.453	0.055	0.174	0.047	-0.050	1.071	0.356
	Ce–8O	2.509	2.435	0.058	0.176	0.048	-0.053	1.091	0.371
	Ce–10O	2.537	2.522	0.046	0.159	0.040	-0.040	1.007	0.299
	Ce–11O	2.507	2.521	0.047	0.161	0.041	-0.041	1.013	0.287
	Ce–13O	2.557	2.439	0.057	0.175	0.048	-0.052	1.086	0.369
	Ce–14O	2.565	2.449	0.056	0.175	0.047	-0.051	1.075	0.358
Th	Th–4O	2.606	2.579	0.043	0.170	0.042	-0.042	0.998	0.142
	Th–5O	2.628	2.584	0.043	0.167	0.042	-0.042	1.002	0.138
	Th–7O	2.619	2.512	0.050	0.200	0.051	-0.052	1.023	0.182
	Th–8O	2.549	2.501	0.052	0.203	0.053	-0.055	1.038	0.186
	Th–10O	2.583	2.586	0.043	0.166	0.042	-0.042	1.002	0.137
	Th–11O	2.588	2.577	0.043	0.171	0.043	-0.043	0.998	0.142

	Th–13O	2.593	2.505	0.051	0.201	0.052	-0.054	1.036	0.185
	Th–14O	2.607	2.508	0.051	0.202	0.052	-0.053	1.024	0.184
U	U–4O	2.582	2.548	0.046	0.188	0.045	-0.044	0.963	0.156
	U–5O	2.564	2.542	0.047	0.185	0.045	-0.043	0.964	0.165
	U–7O	2.501	2.470	0.056	0.213	0.055	-0.057	1.032	0.205
	U–8O	2.578	2.440	0.061	0.218	0.058	-0.061	1.059	0.227
	U–10O	2.548	2.543	0.046	0.185	0.045	-0.043	0.963	0.164
	U–11O	2.549	2.543	0.047	0.190	0.046	-0.045	0.967	0.158
	U–13O	2.552	2.444	0.060	0.217	0.057	-0.061	1.056	0.226
	U–14O	2.558	2.465	0.057	0.215	0.056	-0.058	1.035	0.206
Np	Np–4O	2.569	2.519	0.048	0.193	0.047	-0.045	0.969	0.168
	Np–5O	2.548	2.549	0.045	0.180	0.043	-0.041	0.947	0.159
	Np–7O	2.494	2.432	0.059	0.226	0.059	-0.061	1.038	0.227
	Np–8O	2.561	2.409	0.063	0.232	0.062	-0.066	1.061	0.248
	Np–10O	2.535	2.529	0.047	0.185	0.044	-0.043	0.960	0.170
	Np–11O	2.530	2.538	0.046	0.189	0.045	-0.043	0.956	0.158
	Np–13O	2.547	2.427	0.061	0.225	0.059	-0.062	1.048	0.235
	Np–14O	2.542	2.435	0.059	0.225	0.059	-0.061	1.038	0.223
Pu	Pu–4O	2.553	2.518	0.046	0.183	0.044	-0.042	0.954	0.145
	Pu–5O	2.530	2.525	0.045	0.176	0.042	-0.040	0.949	0.147
	Pu–7O	2.482	2.435	0.057	0.214	0.054	-0.055	1.017	0.194
	Pu–8O	2.550	2.411	0.061	0.219	0.057	-0.059	1.040	0.211
	Pu–10O	2.513	2.528	0.045	0.175	0.042	-0.039	0.947	0.146
	Pu–11O	2.513	2.513	0.047	0.185	0.044	-0.043	0.957	0.146
	Pu–13O	2.534	2.415	0.060	0.218	0.056	-0.059	1.036	0.208
	Pu–14O	2.520	2.429	0.058	0.216	0.055	-0.057	1.022	0.197

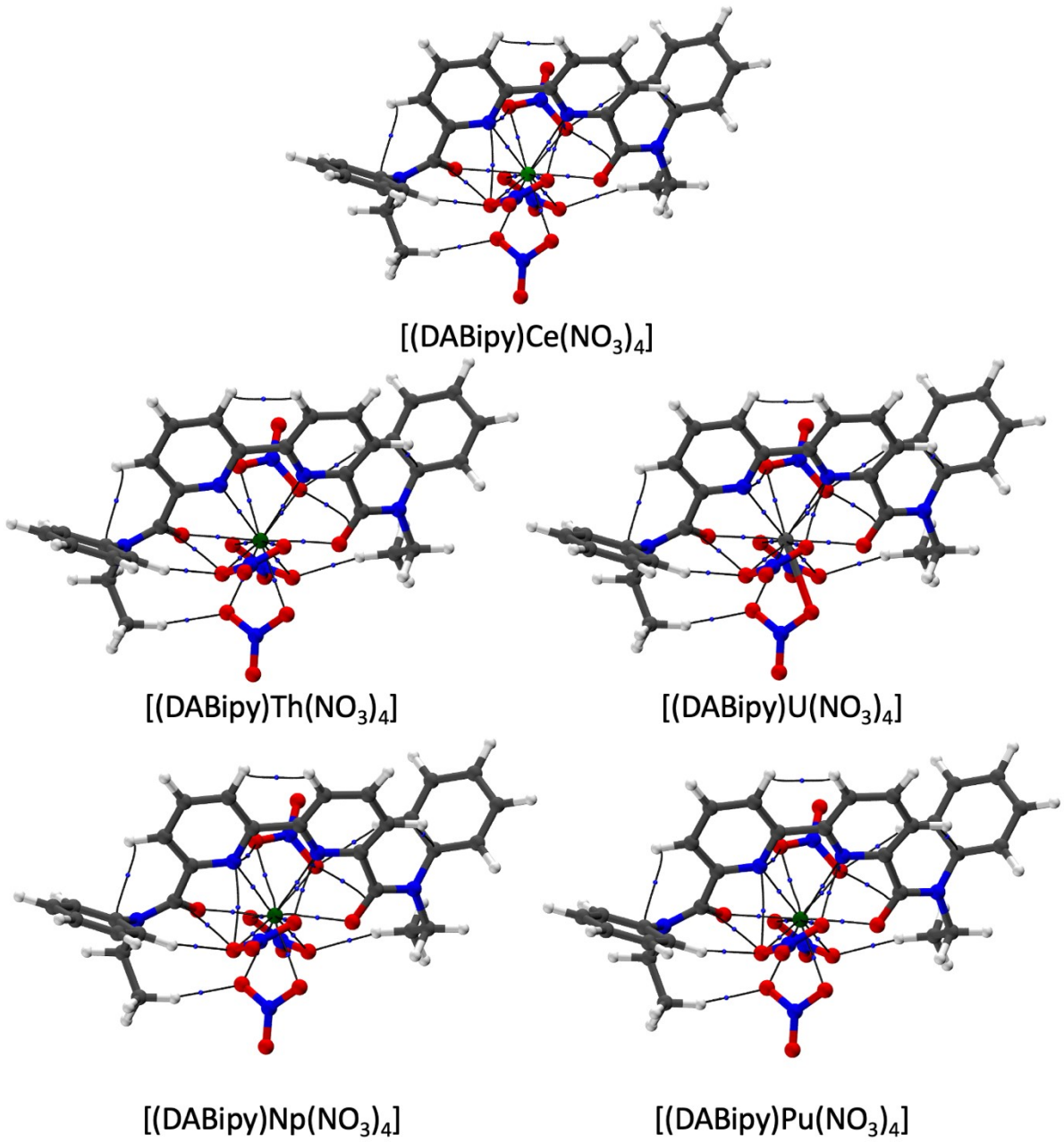

Figure S3. Representation of the optimized structures [(DABipy)M(NO_3)$_4$] (M = Ce, Th, U, Np, Pu) with assigned black bond paths and (3,–1) BCPs (black dots) for metal-ligand and other intramolecular interactions.

Table S5. Optimized XYZ coordinates.

[(DABipy)Ce(NO_3)$_4$]			
Ce	3.494194000	4.029429000	6.844990000
O	3.313599000	2.702643000	8.889678000
O	3.681537000	5.332275000	4.780580000
O	5.583063000	4.097527000	8.262506000
O	5.203164000	5.861114000	7.126551000
O	6.872145000	5.826579000	8.519868000
O	4.837992000	1.978514000	6.770096000
O	5.539590000	3.609995000	5.593170000
O	6.676665000	1.756675000	5.630894000

O	1.190189000	4.276755000	7.839947000
O	1.276815000	4.435855000	5.716124000
O	-0.614507000	4.768376000	6.730600000
O	2.124671000	2.024281000	6.611783000
O	3.118454000	2.670438000	4.842604000
O	1.831497000	0.918851000	4.762682000
N	3.232190000	5.307305000	9.155383000
N	2.668835000	6.551342000	6.868505000
N	4.416009000	2.380751000	10.837189000
N	2.346146000	6.412981000	3.310389000
N	5.931902000	5.289242000	7.982342000
N	5.732464000	2.414737000	5.977253000
N	0.562812000	4.496151000	6.768550000
N	2.333749000	1.822241000	5.376040000
C	3.753236000	3.150751000	9.959566000
C	3.418716000	4.586576000	10.266252000
C	3.160418000	5.082689000	11.543103000
H	3.322062000	4.459129000	12.424351000
C	2.677305000	6.382260000	11.654089000
H	2.443527000	6.804169000	12.636819000
C	2.478228000	7.131678000	10.502129000
H	2.074466000	8.144120000	10.570689000
C	2.771531000	6.559483000	9.258813000
C	2.558126000	7.281777000	7.984378000
C	2.292953000	8.655381000	7.937419000
H	2.234432000	9.245493000	8.854543000
C	2.136881000	9.271150000	6.702651000
H	1.942611000	10.346711000	6.640483000
C	2.247472000	8.507948000	5.545159000
H	2.138938000	8.957297000	4.556365000
C	2.519515000	7.147558000	5.680745000
C	2.854912000	6.225381000	4.538665000
C	4.611344000	0.961793000	10.494285000
H	3.738488000	0.653727000	9.898688000
H	4.606379000	0.403063000	11.445562000
C	5.897823000	0.726969000	9.723511000
H	5.867154000	1.246546000	8.752298000
H	6.015567000	-0.352869000	9.530346000
H	6.776445000	1.072010000	10.295909000
C	5.251068000	2.932422000	11.855809000
C	6.256800000	3.840050000	11.511138000
H	6.400925000	4.111567000	10.459413000
C	7.061054000	4.379291000	12.515000000
C	6.881275000	3.997976000	13.845432000
H	7.521033000	4.418931000	14.628738000
C	5.891769000	3.068388000	14.177195000
H	5.752219000	2.760284000	15.219026000

C	5.073259000	2.533508000	13.183981000
H	4.283848000	1.816190000	13.435103000
C	2.793505000	5.506749000	2.238727000
H	3.835523000	5.233626000	2.464598000
H	2.773377000	6.088760000	1.301741000
C	1.924635000	4.265889000	2.140059000
H	1.990220000	3.678647000	3.069676000
H	2.281060000	3.633564000	1.309224000
H	0.870277000	4.529235000	1.945405000
C	1.148171000	7.156762000	3.084676000
C	1.150114000	8.197057000	2.150516000
H	2.073574000	8.443368000	1.614465000
C	-0.018439000	8.923214000	1.927931000
C	-1.182708000	8.611446000	2.635590000
H	-2.098849000	9.186404000	2.462049000
C	-1.179489000	7.561127000	3.554626000
H	-2.092097000	7.301641000	4.101692000
C	-0.019116000	6.819392000	3.775762000
H	-0.006141000	5.978558000	4.478219000
H	-0.018037000	9.742377000	1.200790000
H	7.844370000	5.095432000	12.244578000
	[(DABipy)Th(NO_3)$_4$]		
Th	3.516162000	4.005879000	6.822739000
O	3.328355000	2.712285000	8.908592000
O	3.681796000	5.362247000	4.769829000
O	5.621589000	4.118271000	8.308422000
O	5.251380000	5.888081000	7.171776000
O	6.899445000	5.852727000	8.593365000
O	4.930420000	1.931013000	6.748354000
O	5.639927000	3.574138000	5.574486000
O	6.791976000	1.728197000	5.639843000
O	1.150420000	4.304300000	7.822527000
O	1.245953000	4.471024000	5.695780000
O	-0.644724000	4.824231000	6.706426000
O	2.086213000	1.967190000	6.554556000
O	3.088394000	2.615751000	4.779373000
O	1.772092000	0.884148000	4.693113000
N	3.237647000	5.311607000	9.160588000
N	2.674613000	6.562459000	6.862395000
N	4.400335000	2.385239000	10.870217000
N	2.339439000	6.435504000	3.301942000
N	5.970972000	5.315515000	8.036417000
N	5.835989000	2.378918000	5.966490000
N	0.528106000	4.534623000	6.749488000
N	2.290113000	1.773257000	5.313891000
C	3.760560000	3.159765000	9.985618000
C	3.437804000	4.601510000	10.278205000

C	3.201336000	5.112254000	11.552727000
H	3.372659000	4.497386000	12.438256000
C	2.728134000	6.415890000	11.657219000
H	2.512911000	6.849992000	12.638799000
C	2.516006000	7.154101000	10.500823000
H	2.122253000	8.170242000	10.567433000
C	2.785634000	6.568029000	9.258651000
C	2.554989000	7.286652000	7.982111000
C	2.258341000	8.653929000	7.941063000
H	2.189759000	9.240552000	8.859324000
C	2.078374000	9.270242000	6.710223000
H	1.858006000	10.341015000	6.653973000
C	2.196116000	8.514026000	5.548922000
H	2.067165000	8.964104000	4.562926000
C	2.500273000	7.160517000	5.676959000
C	2.844841000	6.250687000	4.527085000
C	4.559793000	0.956066000	10.544438000
H	3.661774000	0.651881000	9.985113000
H	4.576435000	0.417955000	11.507017000
C	5.815367000	0.682606000	9.736463000
H	5.756356000	1.163492000	8.746445000
H	5.915926000	-0.405071000	9.580783000
H	6.716443000	1.037920000	10.266038000
C	5.252017000	2.929644000	11.880222000
C	6.270161000	3.816331000	11.518502000
H	6.405166000	4.079543000	10.462982000
C	7.093181000	4.347709000	12.511284000
C	6.918356000	3.979058000	13.845911000
H	7.573075000	4.393317000	14.620371000
C	5.914846000	3.070411000	14.193785000
H	5.779516000	2.772578000	15.239124000
C	5.077653000	2.542946000	13.212287000
H	4.278213000	1.841432000	13.475977000
C	2.812880000	5.552974000	2.219665000
H	3.866654000	5.317782000	2.433945000
H	2.762951000	6.145086000	1.290492000
C	1.990569000	4.281641000	2.111210000
H	2.113646000	3.660461000	3.012784000
H	2.340906000	3.695791000	1.244317000
H	0.920619000	4.509257000	1.962197000
C	1.130903000	7.164018000	3.076042000
C	1.120698000	8.207693000	2.145878000
H	2.041000000	8.469752000	1.611933000
C	-0.057973000	8.917574000	1.924505000
C	-1.218964000	8.585433000	2.628508000
H	-2.143123000	9.147529000	2.455370000
C	-1.202237000	7.531629000	3.543261000

H	-2.111446000	7.256463000	4.088169000
C	-0.031658000	6.805958000	3.764150000
H	-0.004903000	5.965173000	4.466626000
H	-0.068307000	9.739748000	1.200916000
H	7.886636000	5.047422000	12.228064000
		[(DABipy)U(NO_3)$_4$]	
U	3.485073000	4.041854000	6.856326000
O	3.338341000	2.715817000	8.897521000
O	3.644899000	5.326774000	4.788255000
O	5.591246000	4.118028000	8.288196000
O	5.193836000	5.895345000	7.181265000
O	6.881797000	5.846995000	8.555974000
O	4.856723000	1.988979000	6.776183000
O	5.541323000	3.631786000	5.608418000
O	6.694350000	1.783644000	5.625849000
O	1.160806000	4.331627000	7.847093000
O	1.247848000	4.456247000	5.721287000
O	-0.647266000	4.802426000	6.728203000
O	2.104303000	2.039099000	6.622465000
O	3.088594000	2.671880000	4.845231000
O	1.803438000	0.914266000	4.781839000
N	3.230191000	5.302651000	9.159864000
N	2.661669000	6.549230000	6.866491000
N	4.415046000	2.378969000	10.856309000
N	2.342725000	6.423253000	3.301948000
N	5.938020000	5.314474000	8.021640000
N	5.747822000	2.431856000	5.980721000
N	0.529551000	4.531958000	6.770936000
N	2.306974000	1.822543000	5.384800000
C	3.772540000	3.158011000	9.974155000
C	3.447393000	4.595584000	10.275595000
C	3.220835000	5.107535000	11.551577000
H	3.403701000	4.495613000	12.436654000
C	2.744688000	6.409875000	11.658432000
H	2.537512000	6.844398000	12.641651000
C	2.520741000	7.146663000	10.503310000
H	2.127129000	8.162594000	10.572733000
C	2.778862000	6.559406000	9.259537000
C	2.541507000	7.274522000	7.985634000
C	2.238919000	8.640170000	7.942235000
H	2.168785000	9.228639000	8.859124000
C	2.055992000	9.253350000	6.710289000
H	1.832494000	10.323441000	6.651789000
C	2.174474000	8.495469000	5.550231000
H	2.042757000	8.944142000	4.564151000
C	2.480717000	7.142350000	5.680017000
C	2.826081000	6.226917000	4.537138000

C	4.586358000	0.954533000	10.517364000
H	3.692360000	0.648584000	9.952598000
H	4.605411000	0.406065000	11.474118000
C	5.845692000	0.700194000	9.708732000
H	5.786058000	1.203690000	8.730150000
H	5.949387000	-0.383463000	9.528852000
H	6.744347000	1.047395000	10.247754000
C	5.262030000	2.918481000	11.871994000
C	6.277133000	3.814062000	11.522899000
H	6.415721000	4.090094000	10.471547000
C	7.095341000	4.339453000	12.522883000
C	6.919631000	3.956419000	13.853320000
H	7.570838000	4.365792000	14.633317000
C	5.919352000	3.039926000	14.189293000
H	5.782700000	2.730804000	15.231185000
C	5.086843000	2.518860000	13.200354000
H	4.289503000	1.811756000	13.455208000
C	2.820600000	5.532514000	2.228727000
H	3.872499000	5.295960000	2.450919000
H	2.777720000	6.117255000	1.294524000
C	1.996742000	4.261451000	2.126550000
H	2.099677000	3.661619000	3.044980000
H	2.364179000	3.656048000	1.280417000
H	0.930760000	4.488903000	1.950905000
C	1.143057000	7.159607000	3.060707000
C	1.149336000	8.198842000	2.125292000
H	2.076756000	8.450174000	1.598612000
C	-0.020842000	8.918315000	1.889905000
C	-1.190604000	8.601379000	2.586095000
H	-2.107987000	9.171147000	2.402375000
C	-1.191141000	7.552642000	3.506910000
H	-2.107637000	7.289667000	4.045683000
C	-0.029339000	6.817091000	3.740900000
H	-0.018888000	5.980695000	4.448856000
H	-0.017309000	9.736440000	1.161646000
H	7.886180000	5.045926000	12.249063000
	[(DABipy)Np(NO_3)$_4$]		
Np	3.482842000	4.041918000	6.859152000
O	3.324847000	2.727386000	8.893087000
O	3.648443000	5.330181000	4.811733000
O	5.565887000	4.139825000	8.271730000
O	5.181005000	5.918809000	7.163746000
O	6.835399000	5.877344000	8.578974000
O	4.827457000	2.015757000	6.799036000
O	5.514665000	3.647569000	5.626549000
O	6.676485000	1.804109000	5.667105000
O	1.171692000	4.339921000	7.842097000

O	1.253021000	4.444202000	5.715533000
O	-0.626877000	4.852690000	6.727751000
O	2.103076000	2.056228000	6.650428000
O	3.094977000	2.682346000	4.877259000
O	1.775814000	0.950648000	4.802313000
N	3.231362000	5.308647000	9.163411000
N	2.642425000	6.545873000	6.877489000
N	4.415127000	2.378312000	10.843441000
N	2.350130000	6.413882000	3.312255000
N	5.907624000	5.342488000	8.018322000
N	5.725564000	2.452188000	6.007972000
N	0.542444000	4.549287000	6.767481000
N	2.297362000	1.843797000	5.412099000
C	3.770072000	3.162645000	9.967717000
C	3.450264000	4.599217000	10.276440000
C	3.223074000	5.105913000	11.554396000
H	3.410433000	4.491539000	12.436880000
C	2.739676000	6.405267000	11.665679000
H	2.532016000	6.836270000	12.650360000
C	2.507128000	7.142735000	10.512648000
H	2.104369000	8.154988000	10.584452000
C	2.768402000	6.560421000	9.267166000
C	2.522955000	7.273663000	7.994567000
C	2.221794000	8.639452000	7.949458000
H	2.152016000	9.228620000	8.865988000
C	2.041320000	9.251382000	6.716376000
H	1.818553000	10.321533000	6.656118000
C	2.164272000	8.492197000	5.557792000
H	2.037983000	8.939361000	4.570245000
C	2.468351000	7.138674000	5.690173000
C	2.825062000	6.223734000	4.551560000
C	4.577566000	0.953893000	10.502104000
H	3.685729000	0.657810000	9.928787000
H	4.584012000	0.401471000	11.456843000
C	5.841871000	0.691515000	9.703839000
H	5.794799000	1.199811000	8.727187000
H	5.938339000	-0.392228000	9.520625000
H	6.738451000	1.029187000	10.252277000
C	5.269934000	2.913728000	11.854614000
C	6.280222000	3.813139000	11.501197000
H	6.408357000	4.095890000	10.450319000
C	7.106152000	4.335361000	12.496325000
C	6.943297000	3.945138000	13.826340000
H	7.600613000	4.351836000	14.602605000
C	5.947679000	3.025159000	14.166520000
H	5.820707000	2.710810000	15.208078000
C	5.107182000	2.507555000	13.182521000

H	4.313305000	1.798034000	13.441392000
C	2.835975000	5.519309000	2.246048000
H	3.884948000	5.280690000	2.479402000
H	2.804134000	6.100944000	1.309442000
C	2.008671000	4.250793000	2.139974000
H	2.098470000	3.654990000	3.062267000
H	2.382897000	3.640404000	1.300425000
H	0.945626000	4.481659000	1.951403000
C	1.152684000	7.150018000	3.060098000
C	1.165862000	8.185130000	2.120154000
H	2.096647000	8.432614000	1.597613000
C	-0.001791000	8.905325000	1.874835000
C	-1.175859000	8.593611000	2.566179000
H	-2.091119000	9.164406000	2.375166000
C	-1.183150000	7.549262000	3.491900000
H	-2.102815000	7.290670000	4.027385000
C	-0.023998000	6.812564000	3.735354000
H	-0.019019000	5.979690000	4.447496000
H	0.007225000	9.720436000	1.143247000
H	7.892787000	5.045058000	12.218763000
	[(DABipy)Pu(NO_3)$_4$]		
Pu	3.471922000	4.069288000	6.877381000
O	3.309855000	2.757523000	8.895296000
O	3.647923000	5.344219000	4.834622000
O	5.549602000	4.145571000	8.298050000
O	5.156586000	5.923324000	7.196532000
O	6.858626000	5.862325000	8.553350000
O	4.806202000	2.033376000	6.809464000
O	5.519763000	3.677091000	5.667196000
O	6.658461000	1.820027000	5.684559000
O	1.168294000	4.366753000	7.874643000
O	1.263543000	4.484077000	5.752173000
O	-0.643068000	4.802372000	6.746360000
O	2.084645000	2.105616000	6.645593000
O	3.102070000	2.726564000	4.887367000
O	1.801131000	0.981673000	4.801566000
N	3.233388000	5.330504000	9.167970000
N	2.637771000	6.559623000	6.886851000
N	4.399593000	2.386836000	10.840509000
N	2.355290000	6.413472000	3.320464000
N	5.904952000	5.339610000	8.027599000
N	5.713008000	2.474006000	6.030234000
N	0.537434000	4.551742000	6.798030000
N	2.302959000	1.884272000	5.413454000
C	3.765761000	3.183950000	9.969751000
C	3.463964000	4.622966000	10.280701000
C	3.259008000	5.136456000	11.559426000

H	3.453751000	4.523895000	12.441744000
C	2.787965000	6.440320000	11.673072000
H	2.599237000	6.876800000	12.659058000
C	2.543090000	7.174944000	10.520970000
H	2.151174000	8.191410000	10.594517000
C	2.779404000	6.585360000	9.274024000
C	2.518268000	7.291688000	8.001335000
C	2.195220000	8.652317000	7.951777000
H	2.120818000	9.244193000	8.866318000
C	1.995670000	9.254995000	6.717357000
H	1.754813000	10.320953000	6.653629000
C	2.122182000	8.492081000	5.561355000
H	1.982119000	8.933046000	4.572773000
C	2.447466000	7.144198000	5.697668000
C	2.817487000	6.228463000	4.564547000
C	4.533795000	0.960056000	10.495721000
H	3.633403000	0.681495000	9.927044000
H	4.534996000	0.406960000	11.450062000
C	5.788161000	0.673904000	9.689998000
H	5.739862000	1.173059000	8.708559000
H	5.867811000	-0.412810000	9.516355000
H	6.693851000	1.003535000	10.228274000
C	5.269165000	2.904735000	11.848096000
C	6.292005000	3.788308000	11.490797000
H	6.415841000	4.072292000	10.439694000
C	7.134062000	4.291879000	12.482021000
C	6.973482000	3.899627000	13.811716000
H	7.644283000	4.290492000	14.584557000
C	5.963656000	2.996704000	14.155680000
H	5.838938000	2.680177000	15.196839000
C	5.107816000	2.496989000	13.175662000
H	4.302309000	1.801975000	13.437745000
C	2.875596000	5.537638000	2.255178000
H	3.924615000	5.316233000	2.504866000
H	2.849565000	6.128735000	1.324274000
C	2.076121000	4.254461000	2.118463000
H	2.177350000	3.638405000	3.026440000
H	2.466312000	3.672661000	1.265897000
H	1.008800000	4.465964000	1.931201000
C	1.149927000	7.132144000	3.057156000
C	1.154368000	8.163007000	2.112429000
H	2.084325000	8.421117000	1.593660000
C	-0.021347000	8.866763000	1.858007000
C	-1.194907000	8.542572000	2.544360000
H	-2.116407000	9.100891000	2.346651000
C	-1.193345000	7.502033000	3.474442000
H	-2.112217000	7.234321000	4.006776000

C	-0.025790000	6.782368000	3.728088000
H	-0.011982000	5.953434000	4.444898000
H	-0.018955000	9.679121000	1.123310000
H	7.932085000	4.987559000	12.201494000

4 UV-vis data

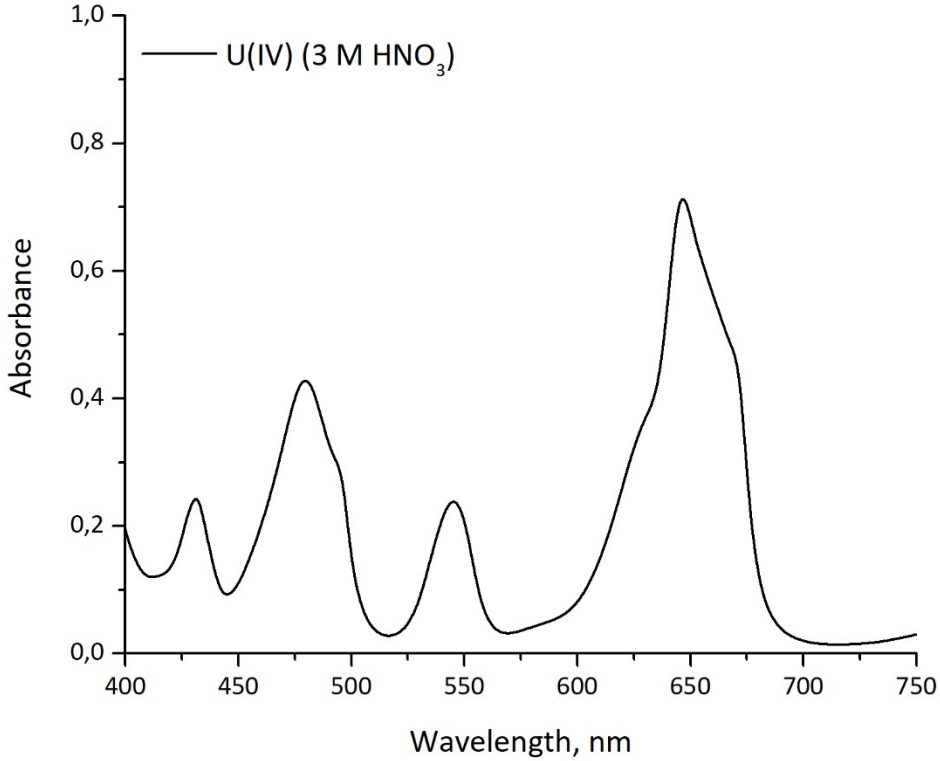

Figure S4. UV-vis absorption spectrum of the initial aqueous solution of U(IV) in 3 M HNO_3.

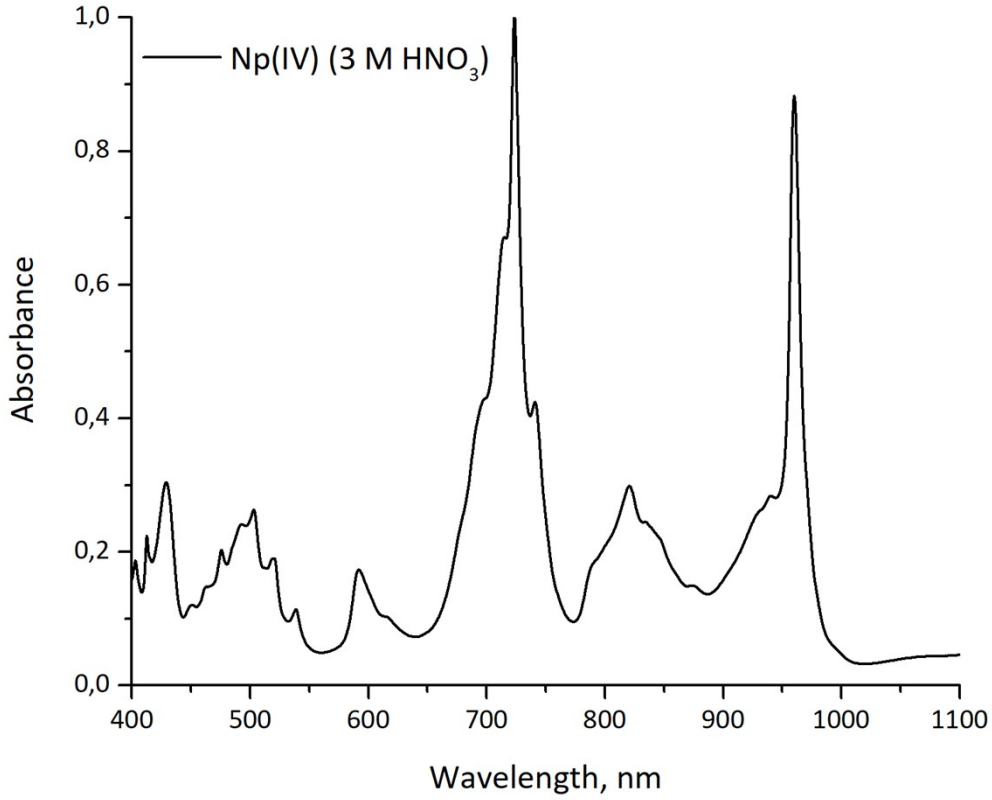

Figure S5. UV-vis absorption spectrum of the initial aqueous solution of Np(IV) in 3 M HNO_3.

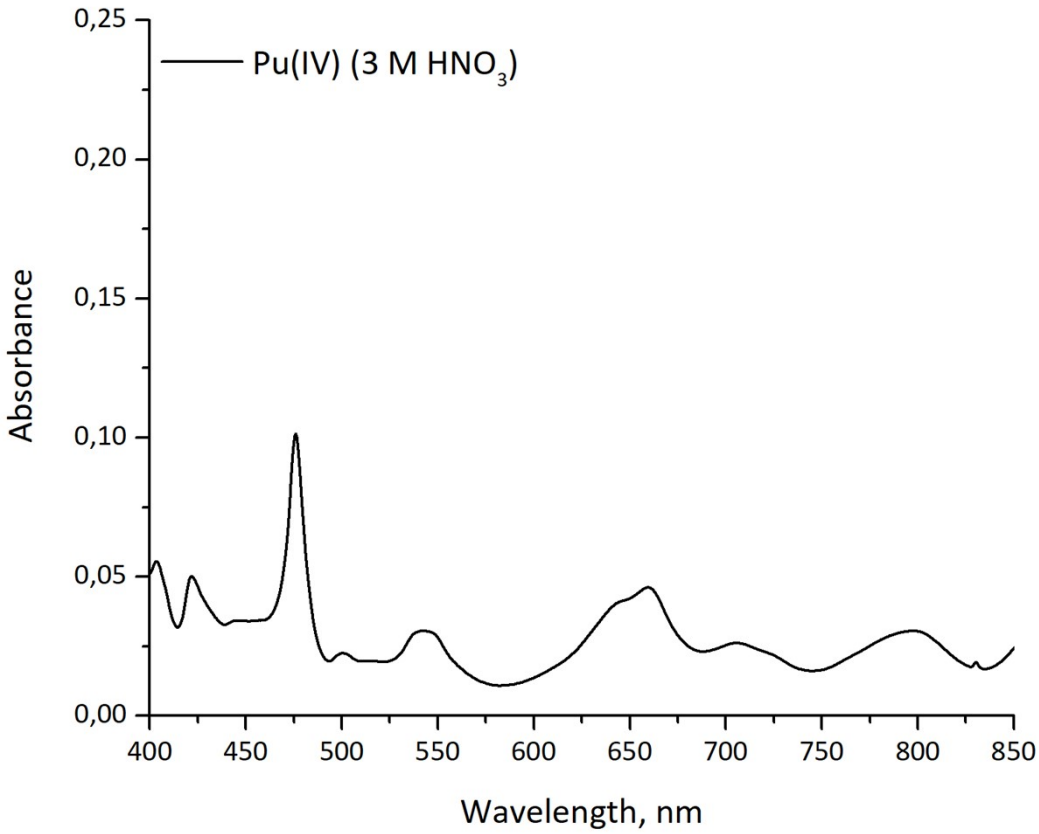

Figure S6. UV-vis absorption spectrum of the initial aqueous solution of Pu(IV) in 3 M HNO_3.

5 ^{1}H-NMR data

Table S6. Chemical shifts assignment of (^{4Et}DABipy)$M^{IV}(NO_3)_4$ complexes in CH_3CN-d_3 (M^{IV} = Ce, Th, U, Np, Pu).

M^{IV}	3Py	4Py	5Py	2,6Ar	3,5Ar	EtN-CH_2	EtN-CH_3	EtAr-CH_2	EtAr-CH_3
Ce	8.30	7.89	6.93	7.36		4.14	1.30	2.71	2.23
Th	8.29	7.91	7.00	7.34		4.13	1.31	2.70	2.23
U	12.47	9.93	6.03	10.55	8.37	17.28	6.56	1.67	3.30
Np	10.72	9.08	6.33	8.82	7.75	13.03	3.90	2.93	1.18
Pu	8.88	8.43	7.39	7.06		4.23	1.26	2.76	1.26

Table S7. Chemical shifts assignment of (^{4Et}DABipy)$M^{IV}(NO_3)_4$ complexes in F-3 (M^{IV} = Ce, Th, U, Np, Pu) with internal standard DMSO-d_6.

M^{IV}	3Py	4Py	5Py	2,6Ar	3,5Ar	EtN-CH_2	EtN-CH_3	EtAr-CH_2	EtAr-CH_3	H_2O
Ce	under F-3	7.44	6.61	6.99	6.78	3.69	0.76	2.08	0.61	3.45
Th	7.50	6.76	6.55	6.70		3.68	0.77	2.07	0.61	3.45
U	11.54	9.68	7.14	9.73	under F-3	15.04	6.45	2.80	1.20	5.22
Np	10.07	8.84	6.34	under F-3		11.65	3.07	2.50	0.95	5.33
Pu	8.57	8.13	7.18	7.32	6.98	3.89	1.02	2.30	0.82	5.29

Table S8. Chemical shifts assignment of ^{4Et}DABipy in F-3 and ^{4Et}DABipy in F-3 after contact with 3 M HNO_3 with internal standard DMSO-d_6.

	3Py	4Py	5Py	2,6Ar	3,5Ar	EtN-CH_2	EtN-CH_3	EtAr-CH_2	EtAr-CH_3	H_2O
^{4Et}DABipy	7.10	7.28	6.94	6.56		3.53	0.76	1.97	0.53	5.38; 1.60
^{4Et}DABipy contacted with 3 M HNO_3	6.54; 6.49			6.41		3.45*	0.66	1.84	0.39	3.46

*under H_2O

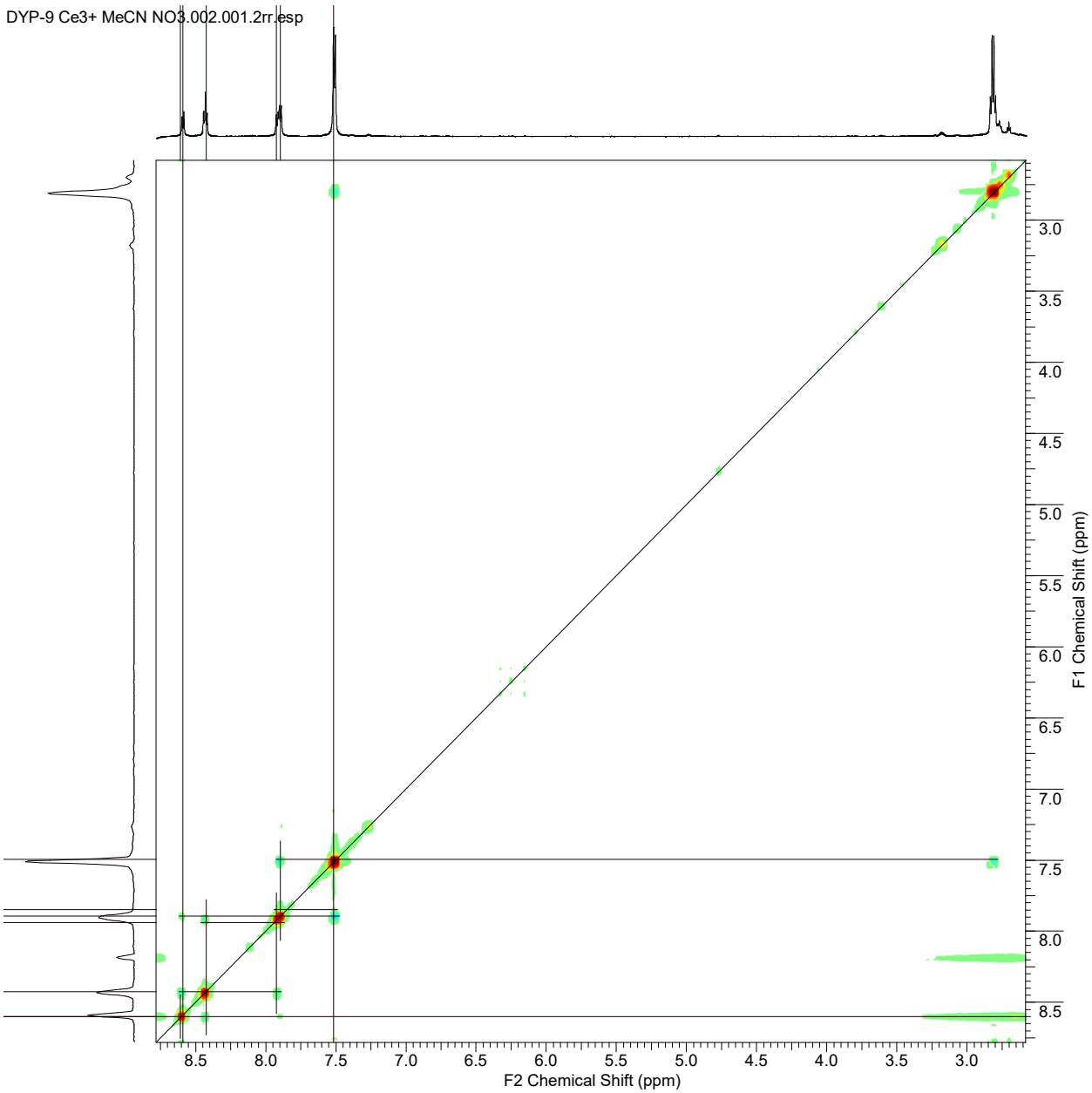

Figure S7. $^{1}H^{1}H$-NOESY Ce^{4+} (600.13MHz for ^{1}H, CH_3CN-d_3, 303K).

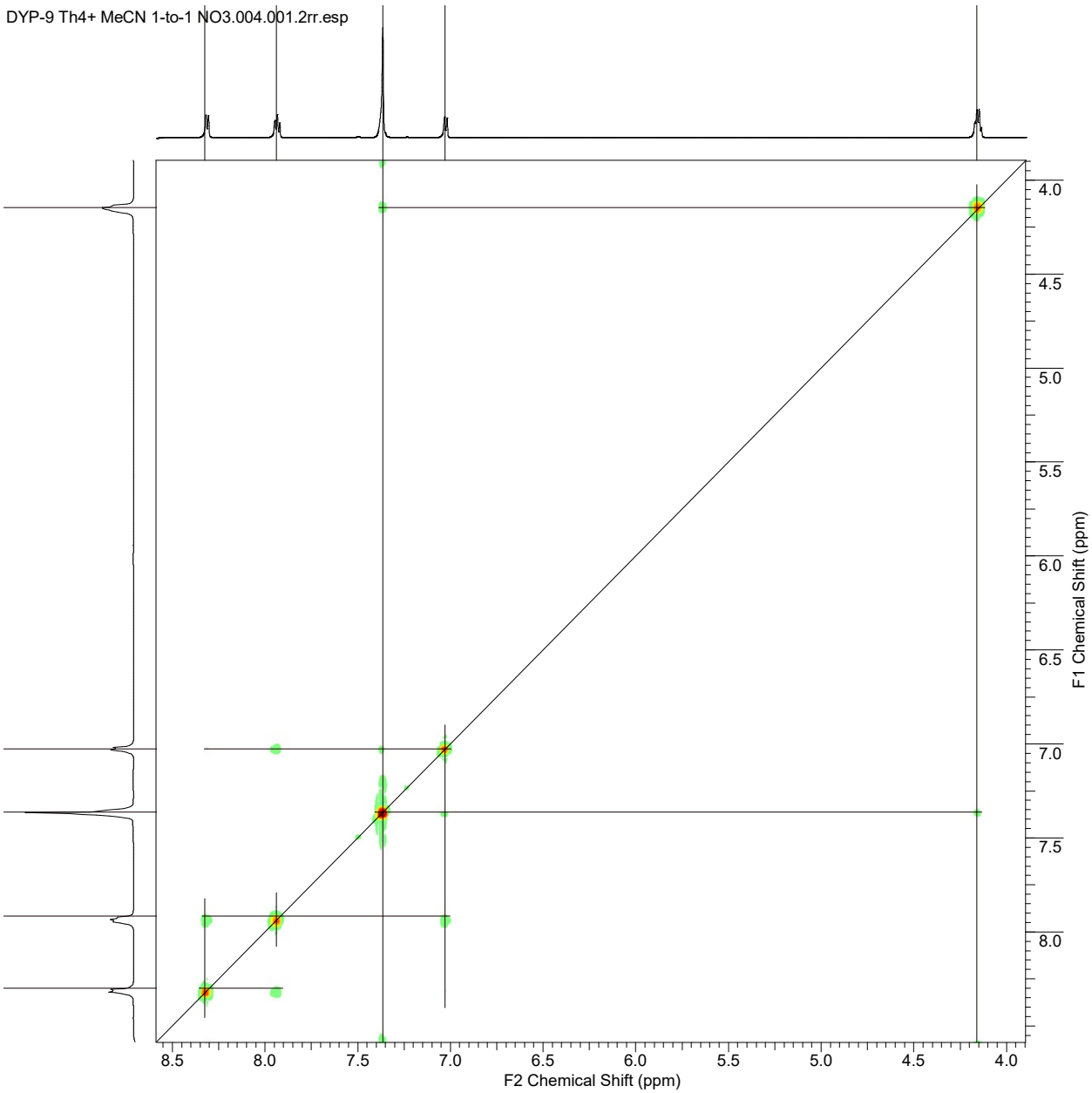

Figure S8. ^{1}H-^{1}H ROESY Th^{4+} (600.13MHz for ^{1}H, CH_3CN-d_3, 303K).

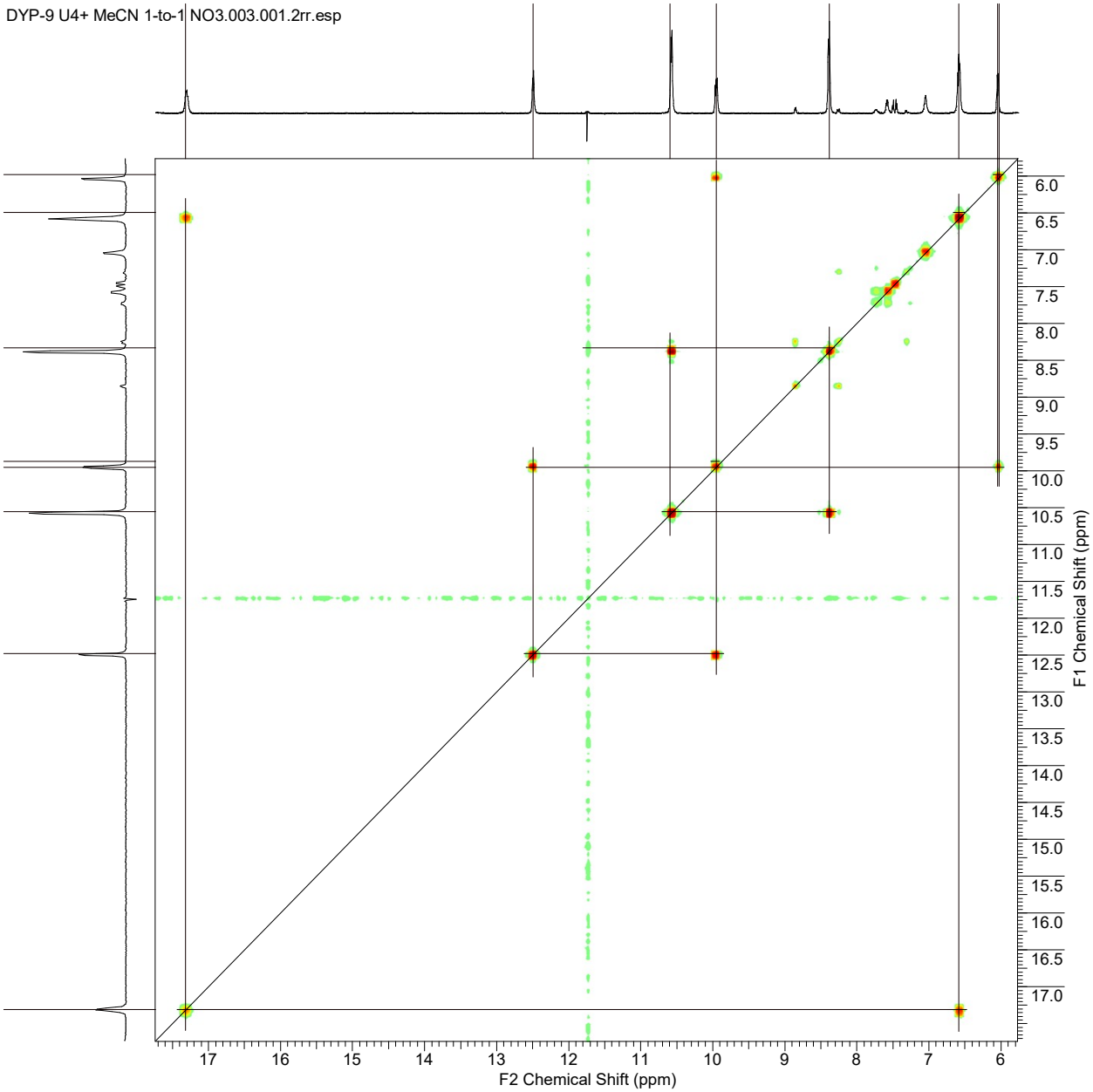

Figure S9. ^{1}H-^{1}H COSY U^{4+} (600.13MHz for ^{1}H, CH_3CN-d_3, 303K).

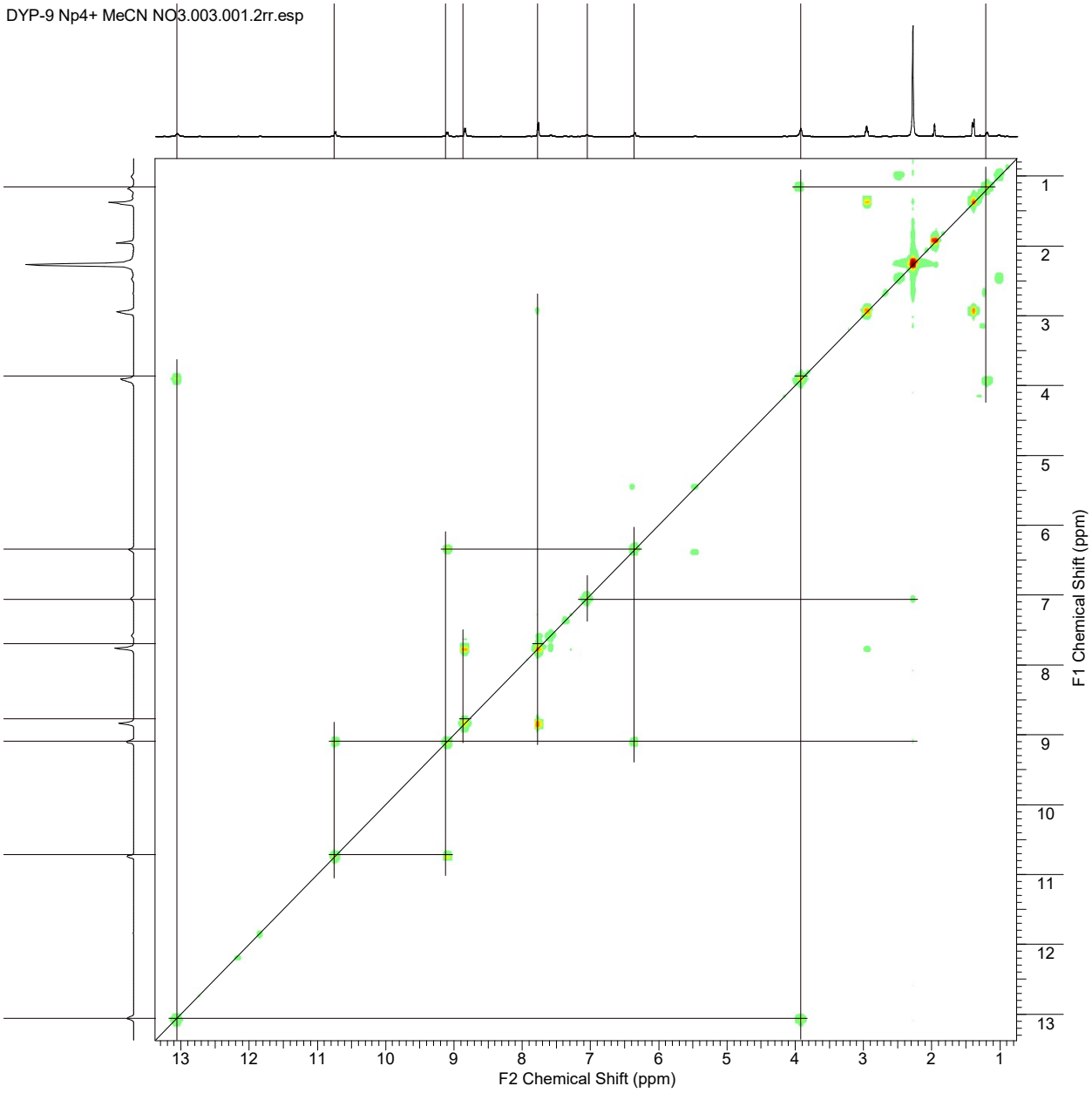

Figure S10. ^{1}H-^{1}H COSY Np^{4+} (600.13MHz for ^{1}H, CH_3CN-d_3, 303K).

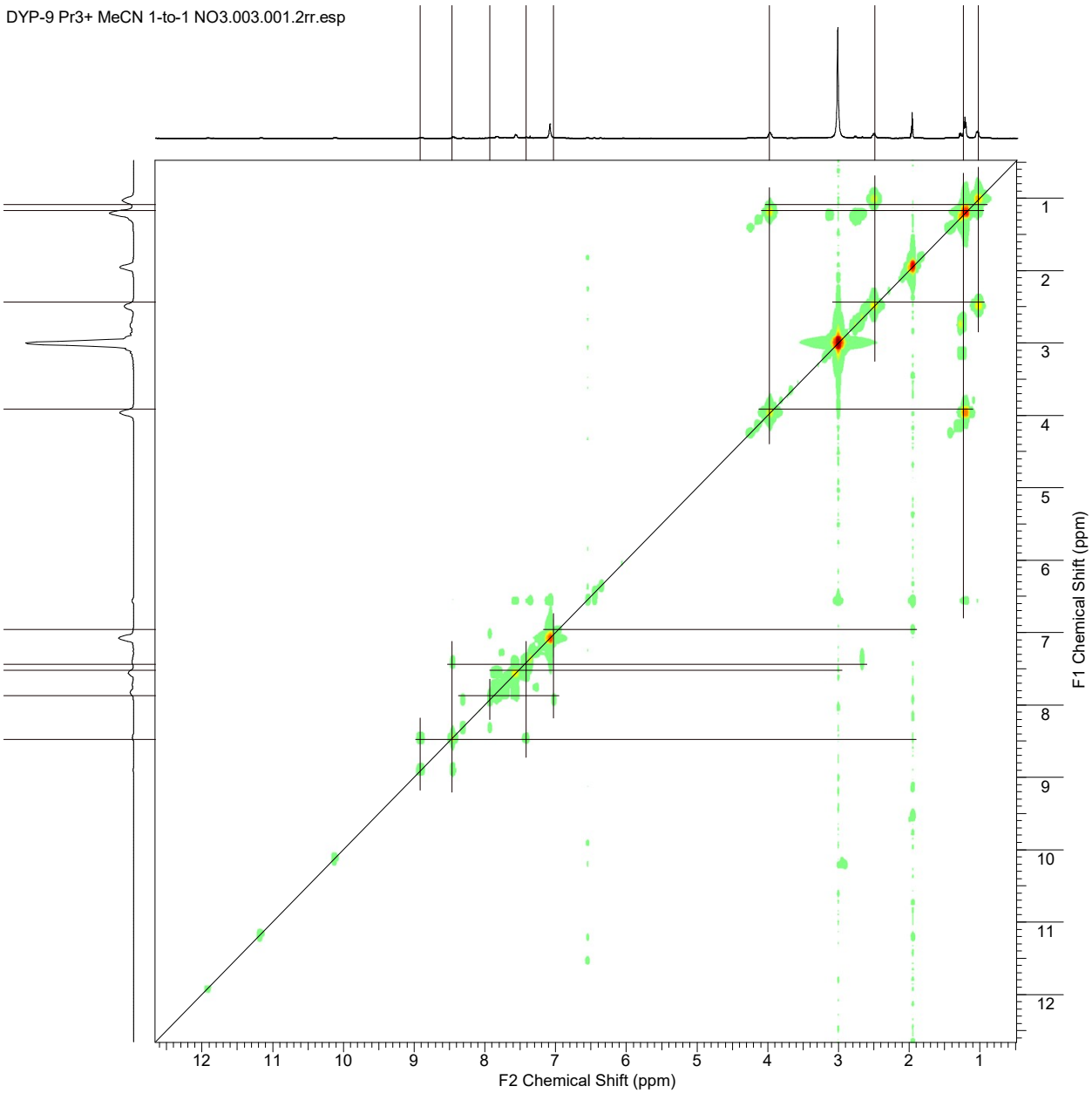

Figure S11. ^{1}H-^{1}H COSY Pu^{4+} (600.13MHz for ^{1}H, CH_3CN-d_3, 303K).

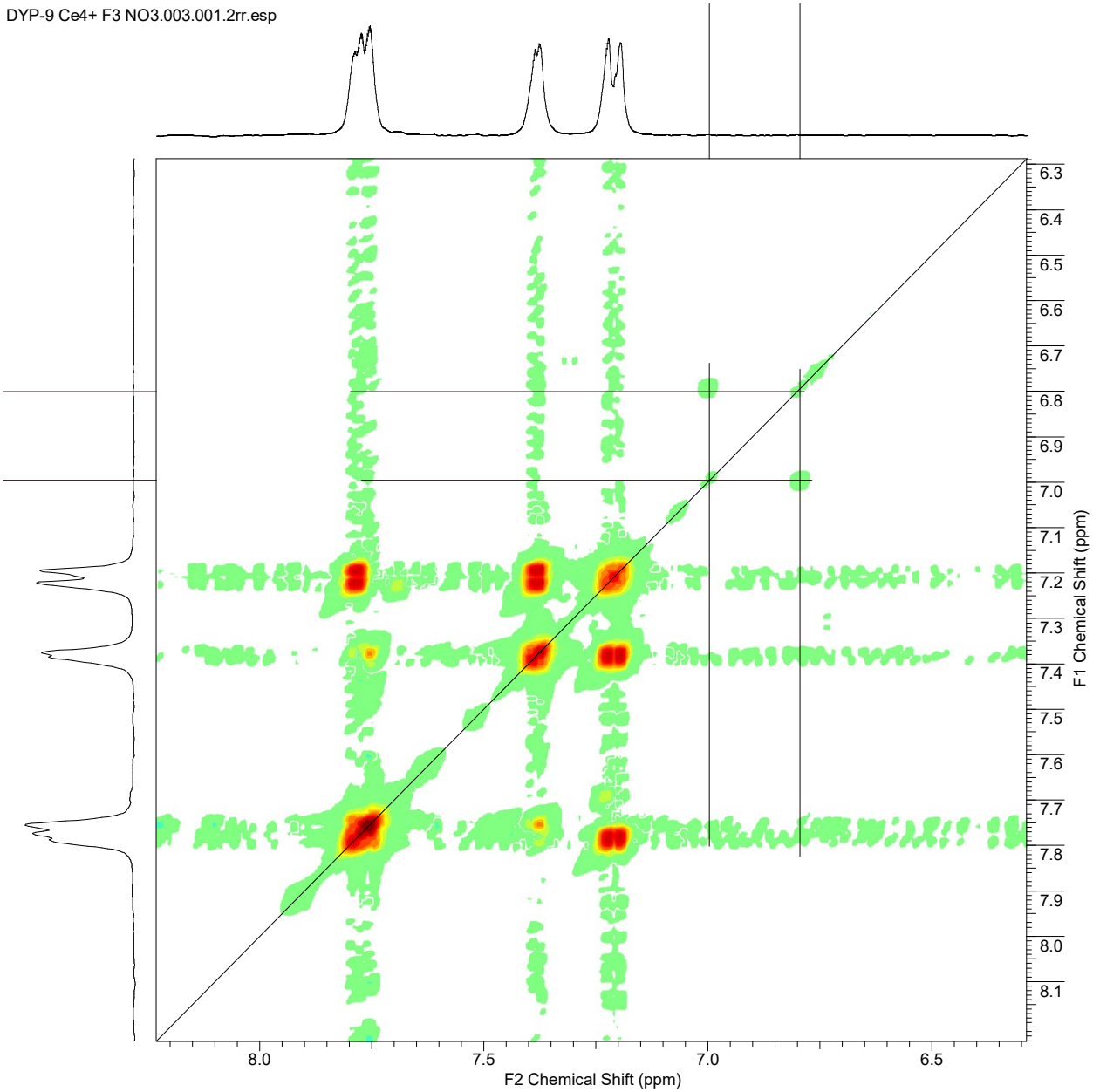

Figure S12. ^{1}H-^{1}H COSY Ce^{4+} (600.13MHz for ^{1}H, F-3 with DMSO-d_6, capillary, 303K).

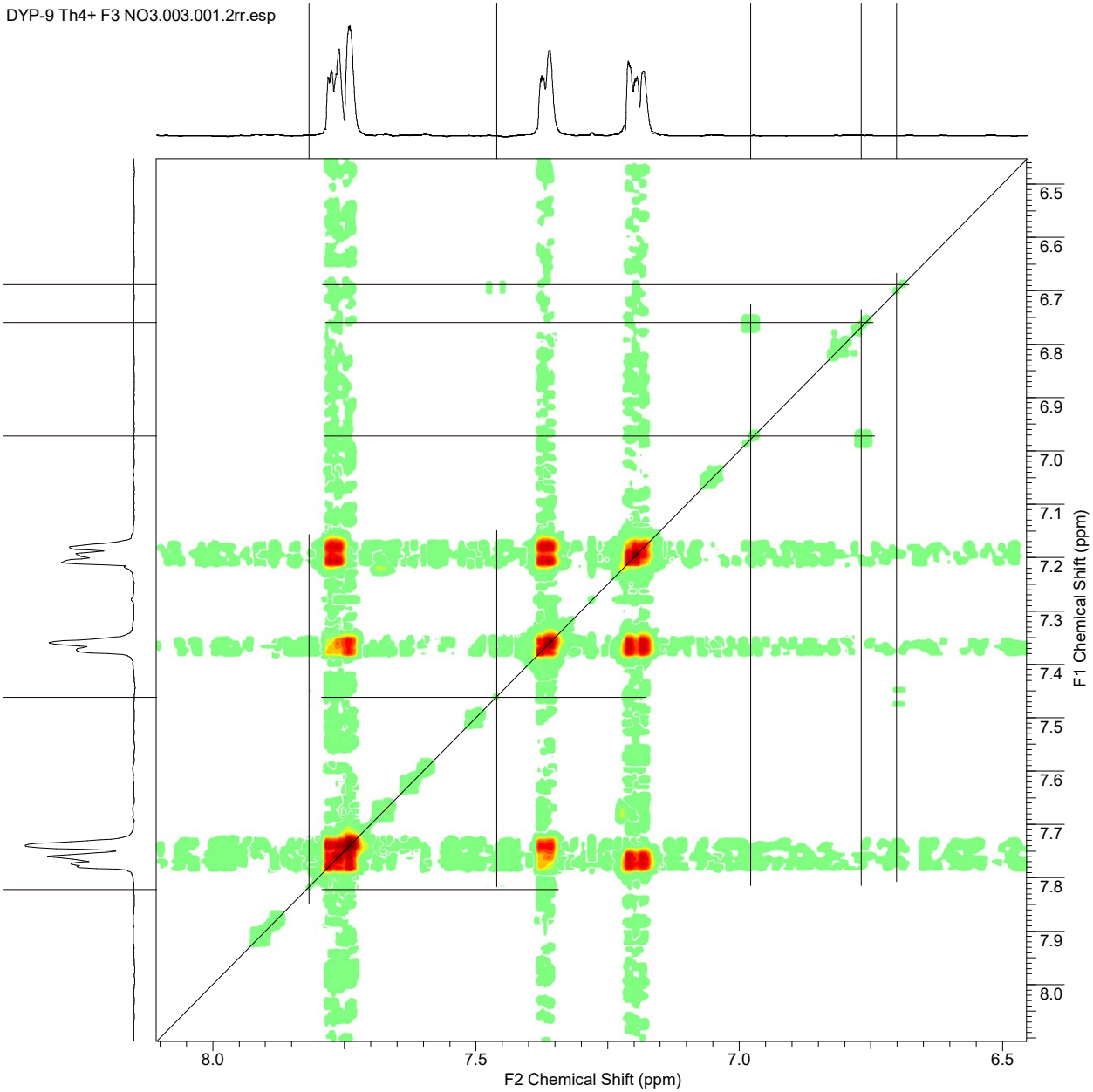

Figure S13. ^{1}H-^{1}H COSY Th^{4+} (600.13MHz for ^{1}H, F-3 with DMSO-d_6, capillary, 303K).

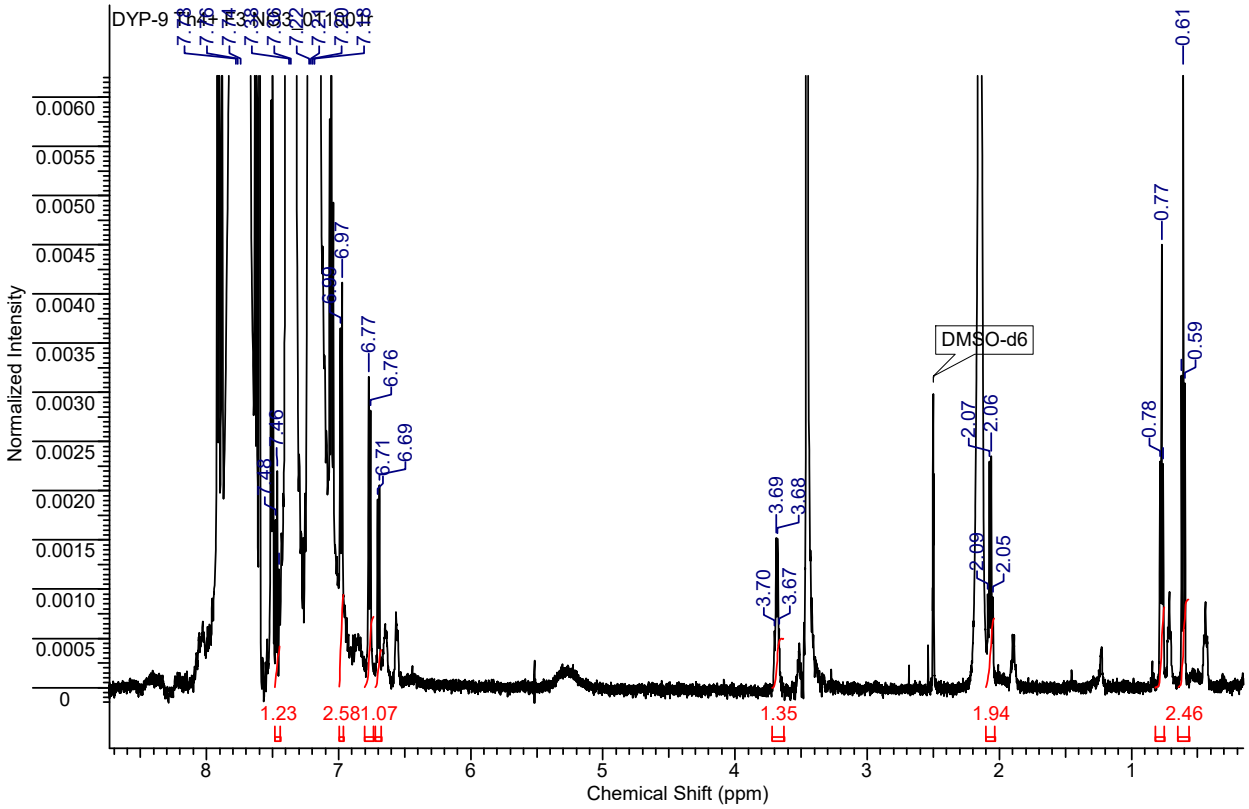

Figure S14. ^{1}H Th^{4+} (600.13MHz for ^{1}H, F-3 with DMSO-d_6, capillary, 303K).

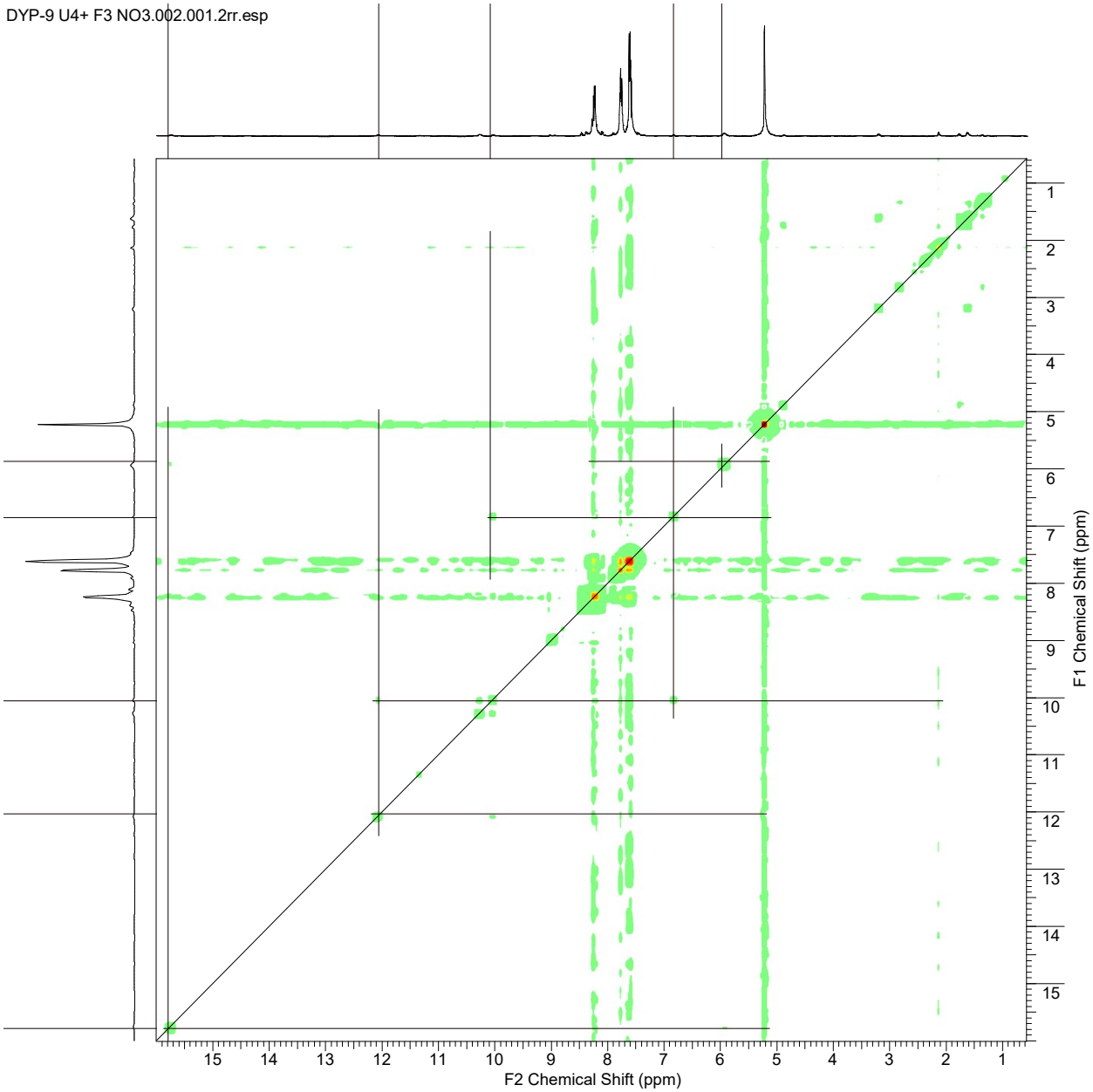

Figure S15. ^{1}H-^{1}H COSY U^{4+} (600.13MHz for ^{1}H, F-3 with DMSO-d_6, capillary, 303K).

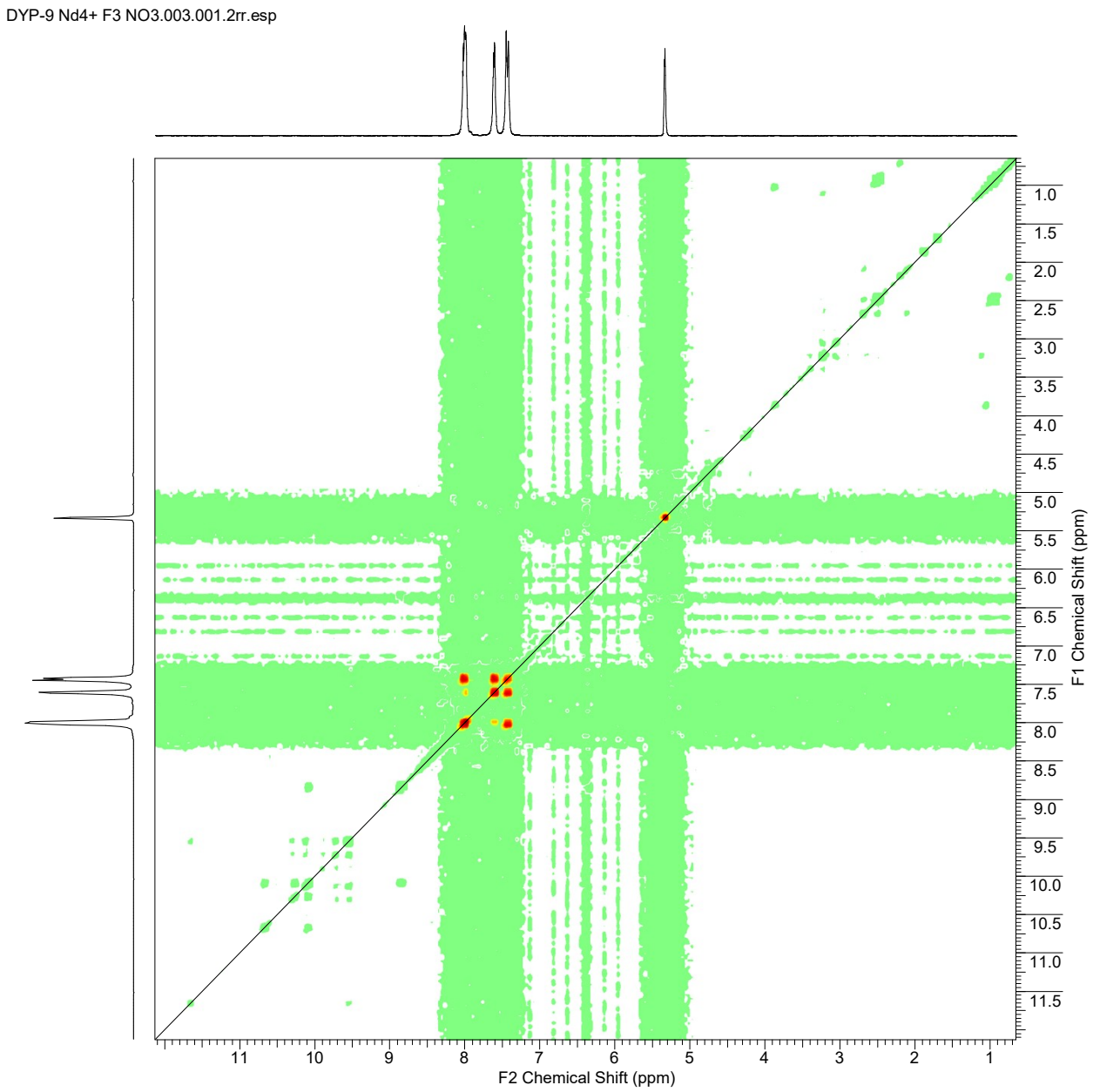

Figure S16. ^{1}H-^{1}H COSY Np^{4+} (600.13MHz for ^{1}H, F-3 with DMSO-d_6, capillary, 303K).

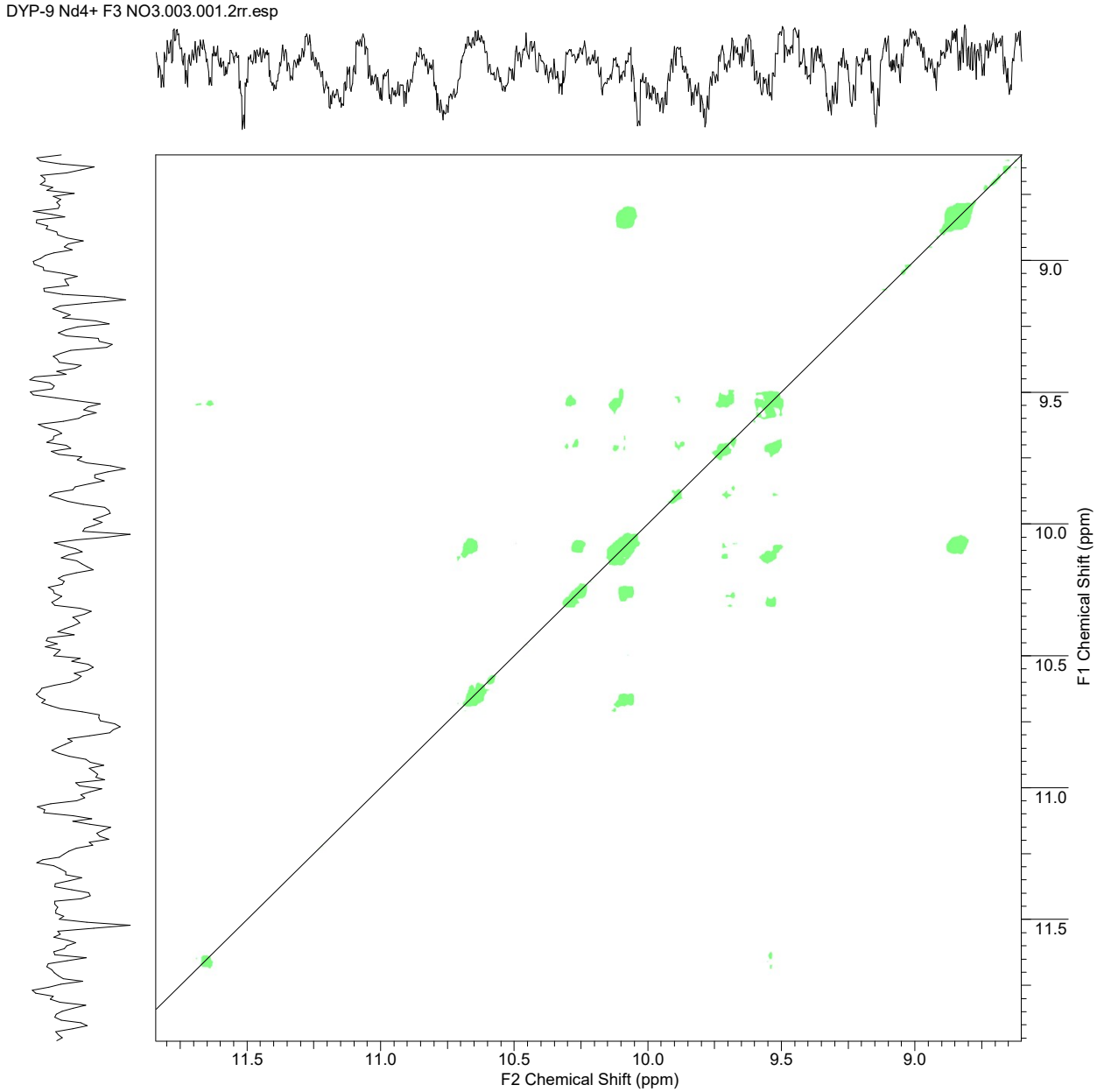

Figure S17. ^{1}H-^{1}H COSY Np^{4+} (600.13MHz for ^{1}H, F-3 with DMSO-d_6, capillary, 303K) 8 – 12 ppm region.

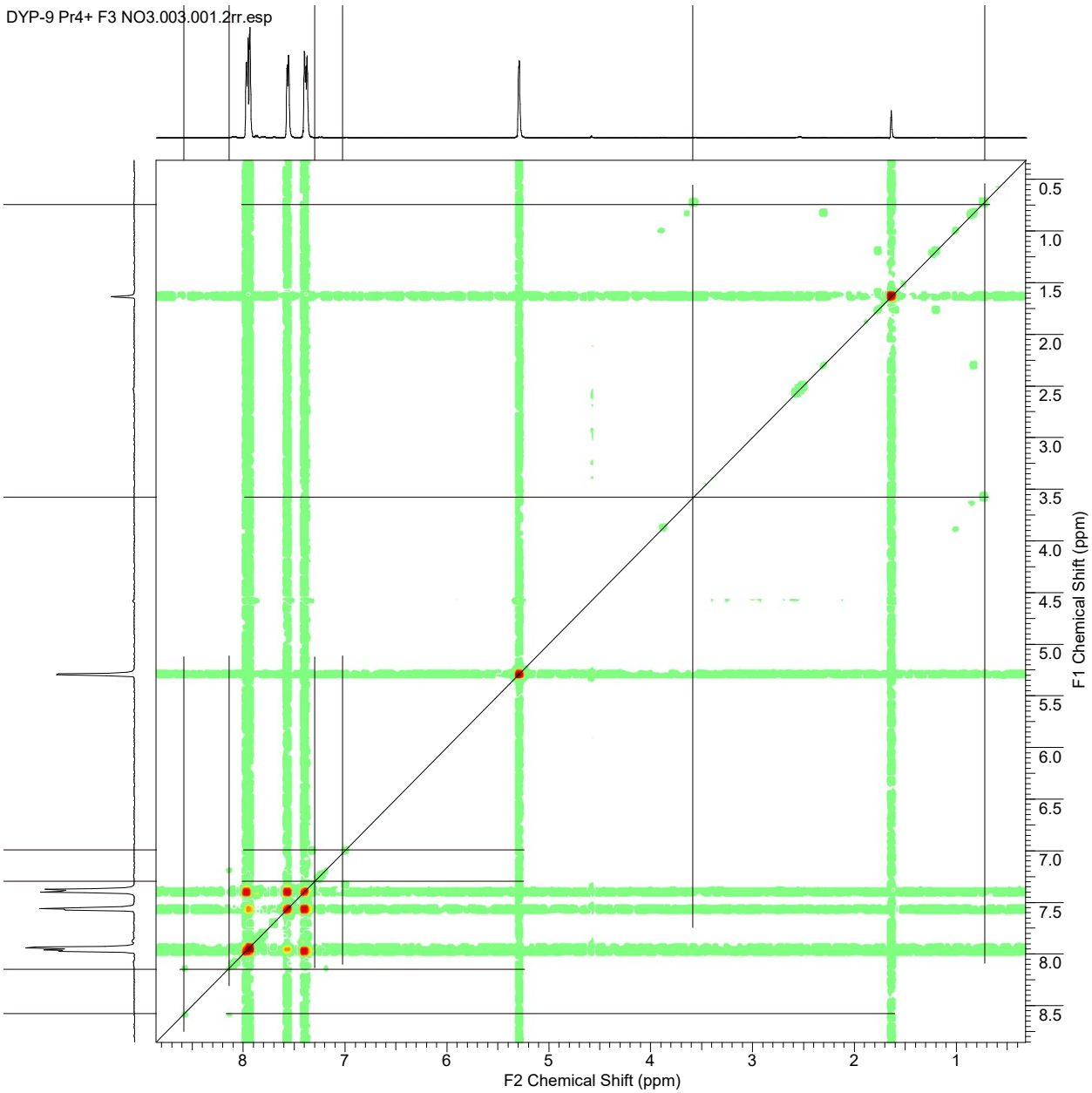

Figure S18. ^{1}H-^{1}H COSY Pu^{4+} (600.13MHz for ^{1}H, F-3 with DMSO-d_6, capillary, 303K).

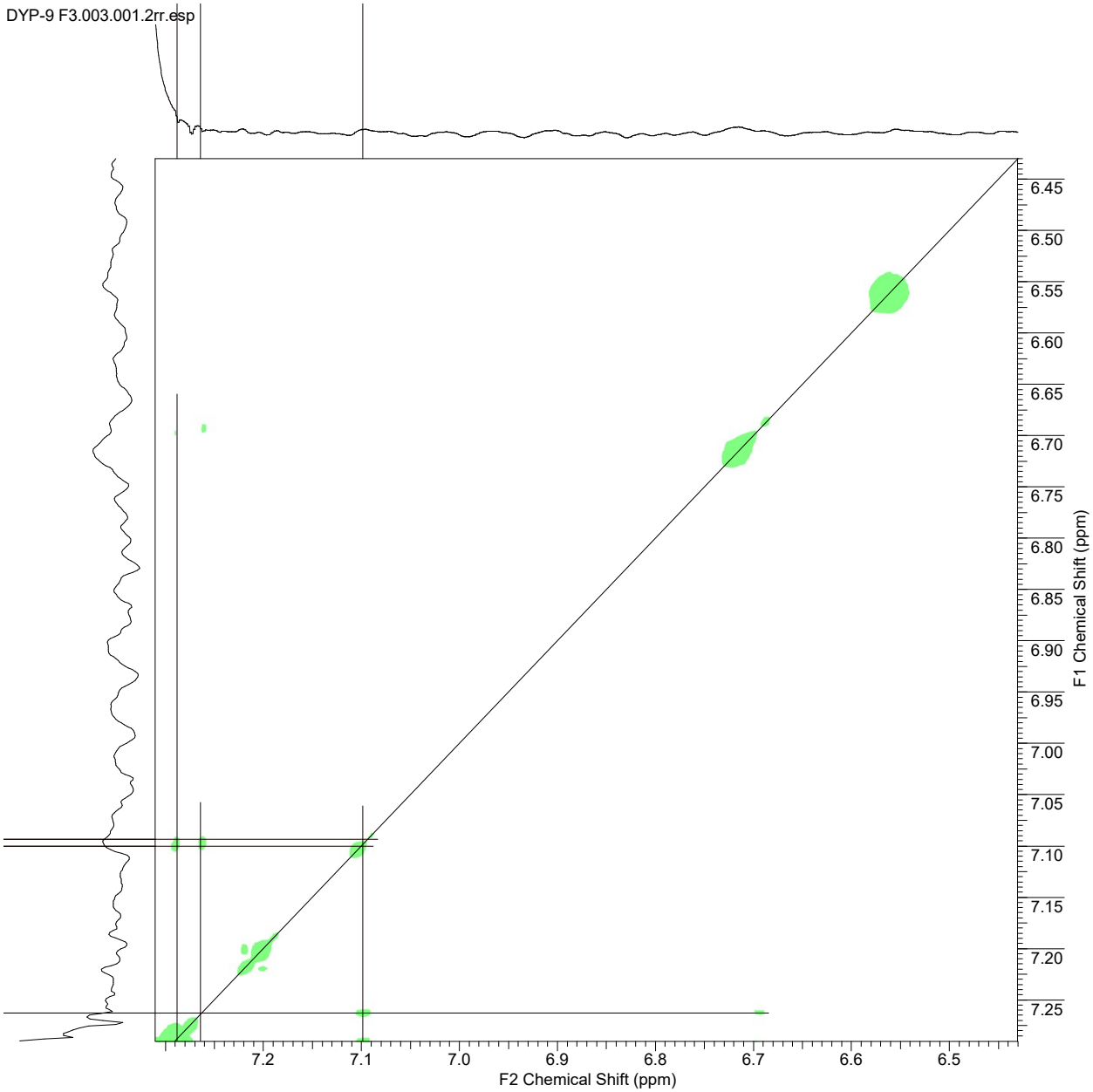

Figure S19. ^{1}H-^{1}H COSY ^{4Et}DABipy (600.13MHz for ^{1}H, F-3 with DMSO-d_6, capillary, 303K).

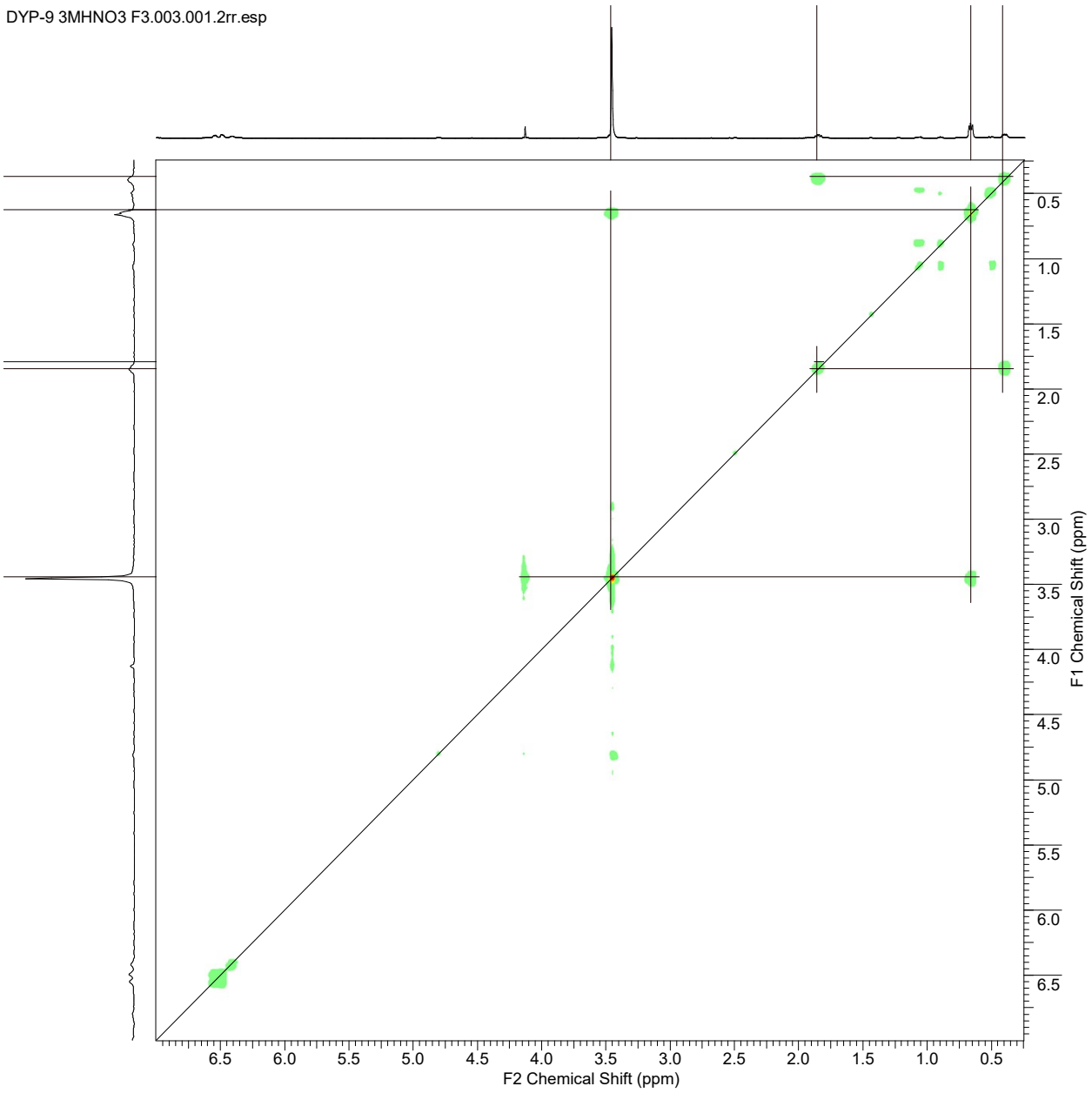

Figure S20. ^{1}H-^{1}H COSY ^{4Et}DABipy in F-3 after contact with 3 M HNO_3 (600.13MHz for ^{1}H, F-3 with DMSO-d_6, capillary, 303K).

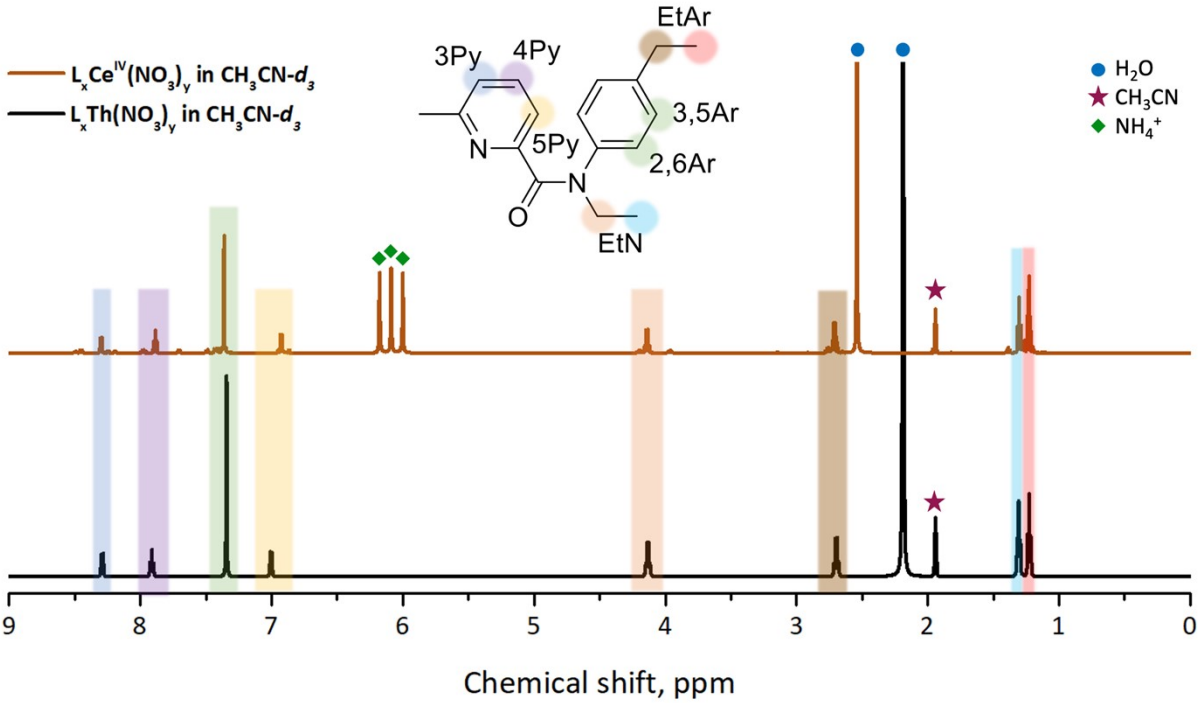

Figure S21. ^{1}H-NMR spectra of Th(IV) and Ce(IV) complexes with ^{4Et}DABipy (L) (600.13MHz for ^{1}H, CH_3CN-d_3, 303K). Insertion shows labelling of ^{4Et}DABipy protons.

6 Solvent extraction

Table S9. D of M(IV) (M = Ce, Th, U, Np, Pu), Ce(III) and U(VI) as a function of $C(HNO_3)$. $C(^{4Et}DABipy)$ = 0.05 M in F-3.

$C(HNO_3)$, M	Ce	Th	Th	U	Np	Pu	Ce(III)	U(VI)
0.5	0.02	2.1	2.1	4.1	3.4	0.1	0.04	2.3
0.7	0.02	3.6	3.6	8.8	7.1	0.3	0.30	–
1	0.06	18.7	18.7	17.9	19.4	0.5	0.09	7.3
2	0.09	254	254	662	88.9	9.2	0.23	54
3	0.42	1753	1753	4949	218.1	159	0.46	155
5	0.54	13145	13145	13992	540	164	0.45	4161

Table S10. D as a function of $C(^{4Et}DABipy)$ for An(IV). $C(HNO_3)$ = 3 M.

$C(^{4Et}DABipy)$, M	Ce	Th	U	Np	Pu
0.0025	< 0.01	187	317	28.8	42.4
0.005	0.02	338	685	38.7	68.5
0.0075	0.03	400	1081	57.3	75.9
0.01	0.04	740	1464	66.7	143
0.05	0.41	3270	5100	218.1	520

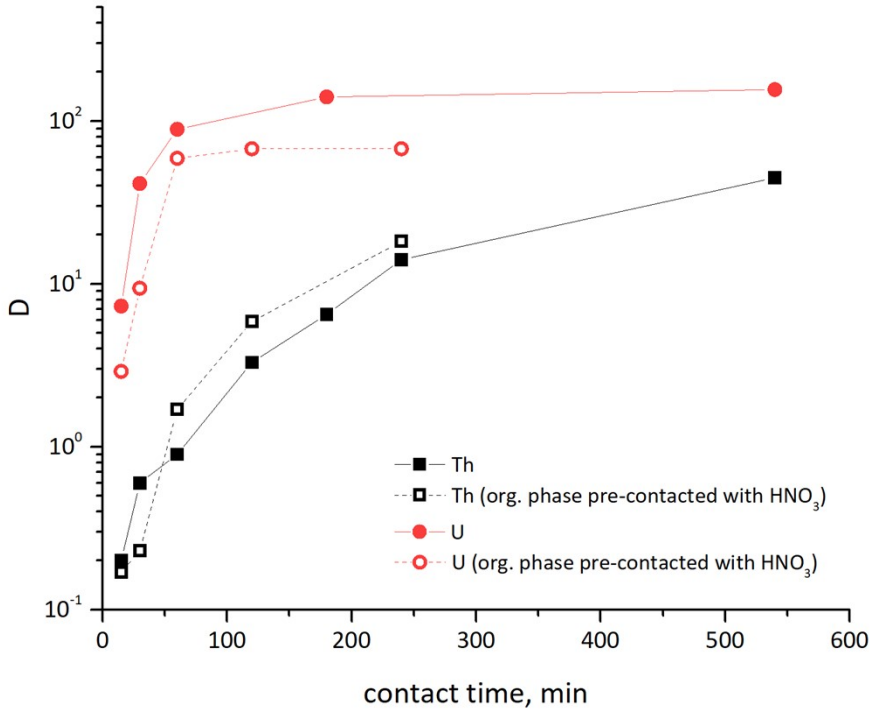

Figure S22. Contact times with pre-equilibrated organic phase.

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