Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information

Synthesis and Characterization of a Tetrathiafulvalene-Salphen Actinide Complex

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1. Synthetic Experimental

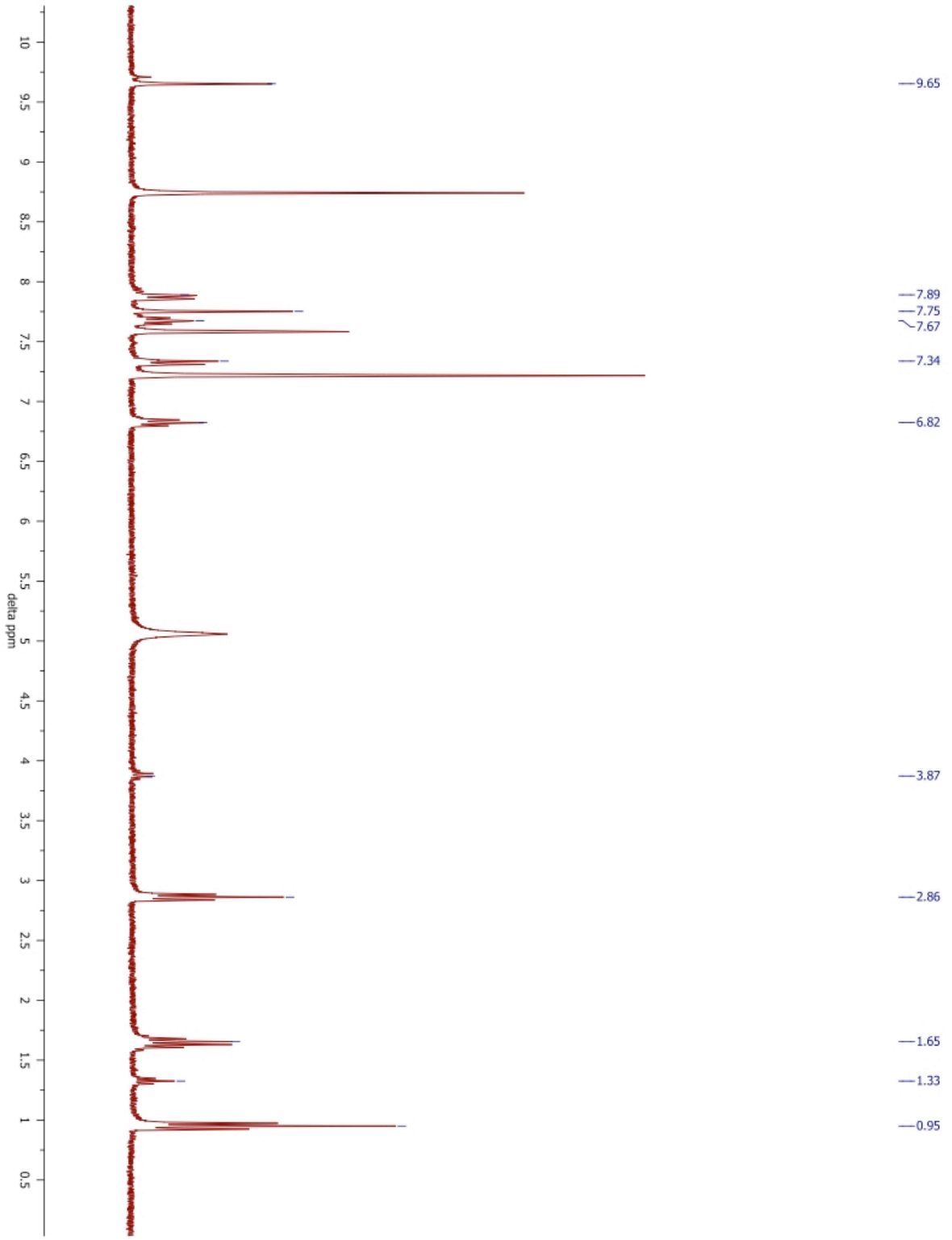
General Procedures

The ^{1}H NMR spectrum of **1** was measured at 25 °C using a 400 MHz Varian Unity Innova instrument. The ^{13}C NMR spectrum of **1** was measured at 25 °C using a 400 MHz Varian Unity Innova instrument. Electrochemistry was done on a CV-50W Voltammetric Analyzer. The measurements were performed using a glassy carbon working and a Pt counter electrode at a scan rate of 50 mV/s with TBA•PF_6 as the supporting electrolyte. Potentials are referenced to $(C_5H_5)_2Fe/(C_5H_5)_2Fe^{1+}$. Elemental Analyses were performed by the UC Berkeley Microanalytical Laboratory.

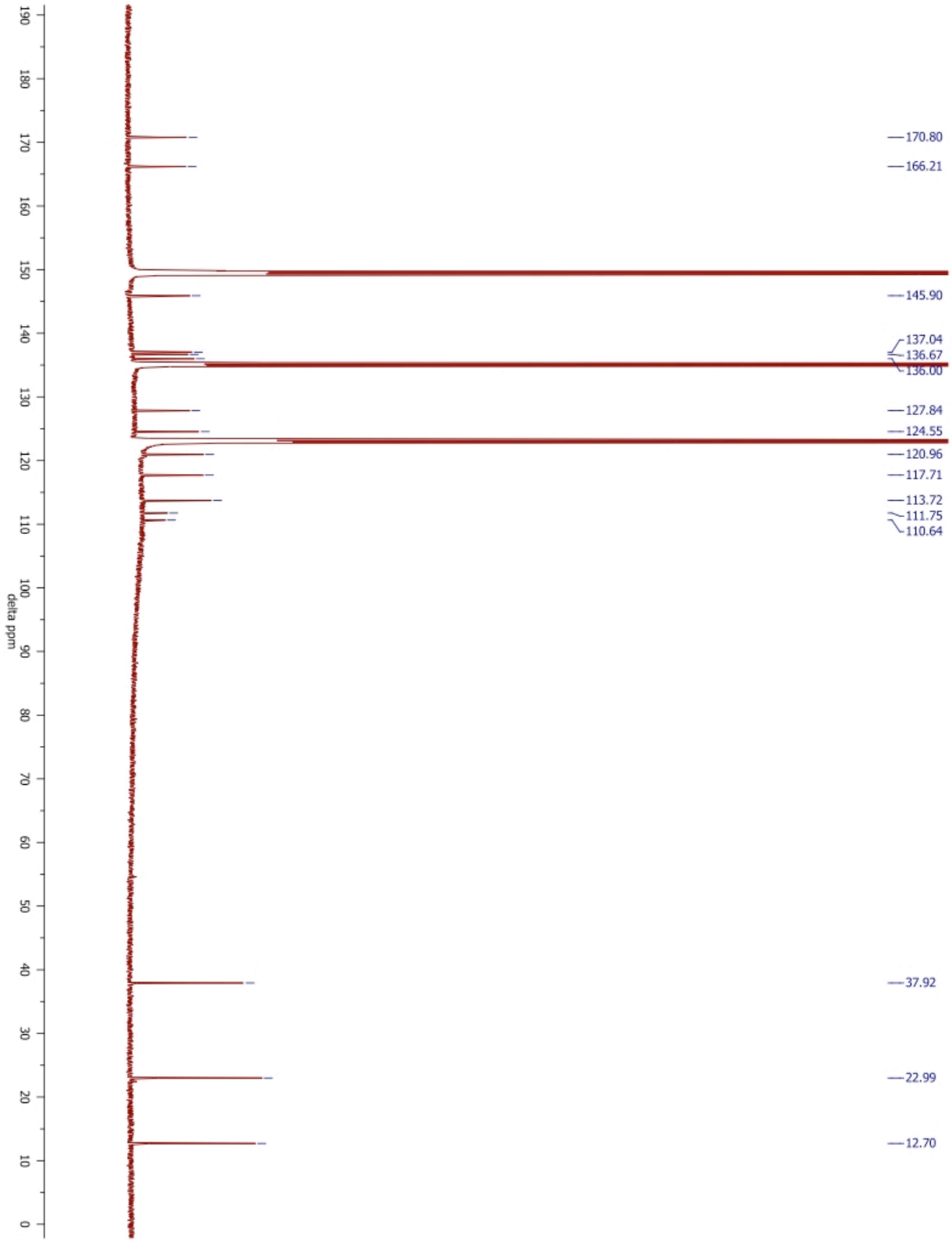
Preparation of 1

A stock solution (1 mL) of salicylaldehyde (0.12 mmol in ethanol) was added to a flask that contained **2** (25 mg, 0.06 mmol) and $UO_2(NO_3)_2$•$6H_2O$ (30 mg, 0.06 mmol) dissolved in ethanol (10 mL). The solution was stirred at room temperature (12 h), during which time a dark orange precipitate was formed. The precipitate was isolated via vacuum filtration, washed with cold ethanol (10 mL, 3x), and dried in vacuo to afford **1** without further purification in 73% yield. ^{1}H NMR (pyridine-d_5): δ 9.62 (s, NH, 2H), 7.84 (d, J = 8.6 Hz, 2H), 7.72 (s, Ar-H, 2H) 7.64 (t, J = 7.5, 7.59 Hz, 2H) 7.29 (d, J = 8.3 Hz, 2H) 6.79 (t, J = 7.3, 7.48 Hz, 2H) 2.82 (t, J = 7.1 Hz, -S-$CH_2CH_2CH_3$, 4H) 1.61 (m, J = 7.10, 7.47 Hz, -S-$CH_2CH_2CH_3$, 4H) 0.92 (t, J = 7.4 Hz, -S-$CH_2CH_2CH_3$, 6H) ppm; ^{13}C NMR (pyridine-d_5): δ 171.2, 166.6, 146.3, 137.1, 136.4, 128.3, 125.0, 121.4, 118.1, 114.1, 112.2, 111.1, 38.3, 23.4, 13.1 ppm. Anal. Calc. [$C_{59}H_{66}N_4O_7S_{12}U$ • CH_3OH]: C, 39.57; H, 3.21; N, 2.98; S, 20.45. Found C, 39.18; H, 3.34; N, 2.96; S, 20.01.

^{1}H NMR spectrum of **1**



^{13}C NMR spectrum of **1**



c. Elemental Analysis

	CERTIFICATE OF ANALYSES			
sampleID	**%C**	**%H**	**%N**	**%S**
TTF salphen (UO2)MeOH	39.18	3.34	2.96	20.01

d. Theory vs. Experimental Cyclic Voltammetry

Table S1. Comparison of the calculated and experimental reduction potentials for ^{TTF}salphenH_2, (salophen)UO_2(DMSO), and (^{TTF}salphen)UO_2(DMSO).

	$TTF^{\bullet+}$/TTF			UO_2^{2+}/UO_2^{1+}	
	DFT (vacuum)	DFT (CH_2Cl_2)	DFT (DSMO)	Exp.	Exp.
^{TTF}salphenH_2	5.981	4.847	4.703	0.085	–
(salophen)UO_2(DMSO)	–	–	–	–	-1.512
1(DMSO)	5.815	4.784	4.697	0.158	-1.496
Difference	0.166	0.063	0.006	–[a]	0.016

[a] Experimental comparisons between ^{TTF}salphenH_2 and **1•MeOH** cannot be made due to the differences associated with the experimental conditions.

3. X-ray Crystallography

Crystals of **1** grew as red blocks from slow evaporation of **1** dissolved in an equimolar solution of methylene chloride and methanol. Crystals of **1** were mounted in a nylon cryoloop from Paratone-N oil. The data were collected on a Brucker D8 diffractometer, with APEX II charge-coupled-device (CCD) detector, and Cryo Industries of America Cryocool G2 low temperature device (120 K). The instrument was equipped with graphite monochromatized MoKα X-ray source (λ = 0.71073 Å), and a 0.5 mm monocapillary. A hemisphere of data was collected using ω scans, with 10-second frame exposures and 0.5º frame widths. Data collection and initial indexing and cell refinement were handled using APEX II software.[1] Frame integration, including Lorentz-polarization corrections, and final cell parameter calculations were carried out using SAINT+ software.[2] The data were corrected for absorption using redundant reflections and the SADABS program.[3] No appreciable decay in the reflection intensity was observed as monitored *via* analysis of redundant frames. The structure was solved using direct methods and difference Fourier techniques. All hydrogen atom positions were idealized, and rode on the atom they were attached to. The final refinement included anisotropic temperature factors on all non-hydrogen atoms. Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXTL.[4]

Table 1. Crystal data and structure refinement for **1**.

Identification code	(^{TTF}Salphen)UO_2(MeOH)	
Empirical formula	$C_{31.50}$ H_{28} Cl N_2 O_5 S_6 U	
Formula weight	980.40	
Temperature	120(1) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.7141(6) Å	α= 82.010(1)°.
	b = 12.0383(7) Å	β= 75.098(1)°.
	c = 16.5610(10) Å	γ = 68.090(1)°.
Volume	1734.35(18) $Å^3$	
Z	2	
Density (calculated)	1.877 Mg/m^3	
Absorption coefficient	5.161 mm^{-1}	
F(000)	952	
Crystal size	0.20 x 0.16 x 0.06 mm^3	
Theta range for data collection	1.83 to 28.36°.	
Index ranges	-12<=h<=12, -15<=k<=15, -21<=l<=21	
Reflections collected	19573	
Independent reflections	7907 [R(int) = 0.0238]	
Completeness to theta = 25.00°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7471 and 0.4251	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7907 / 0 / 436	
Goodness-of-fit on F^2	1.089	
Final R indices [I>2sigma(I)]	R1 = 0.0248, wR2 = 0.0577	
R indices (all data)	R1 = 0.0289, wR2 = 0.0590	
Largest diff. peak and hole	1.058 and -0.765 e.$Å^{-3}$	
CCDC number	781609	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **1**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cl(1)	9441(2)	6600(2)	127(1)	35(1)
U(1)	5710(1)	-1284(1)	6559(1)	13(1)
S(1)	5242(1)	2671(1)	9607(1)	18(1)
S(2)	7839(1)	499(1)	9917(1)	16(1)
S(3)	5990(1)	4106(1)	10873(1)	20(1)
S(4)	8515(1)	1917(1)	11190(1)	19(1)
S(5)	6460(1)	5522(1)	12077(1)	22(1)
S(6)	9395(1)	3077(1)	12359(1)	21(1)
N(1)	4066(3)	121(2)	7730(2)	14(1)
N(2)	6467(3)	-1781(2)	7955(2)	14(1)
O(1)	6874(3)	-390(2)	6214(1)	18(1)
O(2)	4528(3)	-2154(2)	6941(1)	18(1)
O(3)	3727(2)	247(2)	6105(1)	17(1)
O(4)	7776(3)	-2956(2)	6487(1)	18(1)
O(5)	6108(3)	-1835(2)	5124(1)	19(1)
C(1)	2249(4)	488(3)	6447(2)	16(1)
C(2)	1225(4)	639(3)	5942(2)	18(1)
C(3)	-303(4)	846(3)	6297(2)	20(1)
C(4)	-866(4)	935(3)	7157(2)	22(1)
C(5)	109(4)	847(3)	7654(2)	17(1)
C(6)	1677(4)	627(3)	7318(2)	14(1)
C(7)	2605(4)	609(3)	7881(2)	16(1)
C(8)	8116(3)	-3954(3)	6957(2)	15(1)
C(9)	8955(4)	-5067(3)	6588(2)	19(1)
C(10)	9371(4)	-6108(3)	7078(2)	23(1)
C(11)	8962(4)	-6098(3)	7948(2)	24(1)
C(12)	8162(4)	-5025(3)	8322(2)	20(1)
C(13)	7713(4)	-3935(3)	7843(2)	17(1)
C(14)	7064(3)	-2837(3)	8284(2)	16(1)
C(15)	7055(6)	-2990(4)	4804(3)	41(1)
C(16)	4870(4)	240(3)	8297(2)	14(1)

C(17)	6133(4)	-775(3)	8424(2)	14(1)
C(18)	4527(4)	1302(3)	8679(2)	15(1)
C(19)	7028(4)	-730(3)	8941(2)	14(1)
C(20)	5451(4)	1341(3)	9182(2)	14(1)
C(21)	6685(4)	329(3)	9317(2)	14(1)
C(22)	6693(4)	1985(3)	10165(2)	17(1)
C(23)	6989(4)	2579(3)	10688(2)	17(1)
C(24)	6928(4)	4152(3)	11637(2)	17(1)
C(25)	8100(4)	3164(3)	11773(2)	17(1)
C(26)	4456(4)	5863(4)	12585(3)	32(1)
C(27)	4124(5)	6288(4)	13450(2)	35(1)
C(28)	4533(5)	7368(4)	13483(3)	37(1)
C(29)	8906(4)	2166(3)	13278(2)	26(1)
C(30)	7607(5)	2889(4)	13947(2)	36(1)
C(31)	7973(6)	3818(4)	14304(3)	51(1)
C(32)	9377(8)	5144(7)	457(5)	26(2)
Cl(2)	9093(2)	5943(2)	160(1)	37(1)

Table 3. Bond lengths [Å] and angles [°] for **1**.

Cl(1)-Cl(2)	0.959(3)
Cl(1)-C(32)	1.781(8)
Cl(1)-C(32)#1	2.203(9)
U(1)-O(2)	1.776(2)
U(1)-O(1)	1.780(2)
U(1)-O(4)	2.241(2)
U(1)-O(3)	2.321(2)
U(1)-O(5)	2.452(2)
U(1)-N(2)	2.531(3)
U(1)-N(1)	2.544(3)
S(1)-C(20)	1.760(3)
S(1)-C(22)	1.764(3)
S(2)-C(21)	1.758(3)
S(2)-C(22)	1.758(3)
S(3)-C(24)	1.757(3)
S(3)-C(23)	1.757(3)
S(4)-C(23)	1.758(3)
S(4)-C(25)	1.761(3)
S(5)-C(24)	1.749(3)
S(5)-C(26)	1.823(4)
S(6)-C(25)	1.742(3)
S(6)-C(29)	1.816(4)
N(1)-C(7)	1.288(4)
N(1)-C(16)	1.419(4)
N(2)-C(14)	1.292(4)
N(2)-C(17)	1.420(4)
O(3)-C(1)	1.336(4)
O(4)-C(8)	1.318(4)
O(5)-C(15)	1.436(4)
C(1)-C(2)	1.405(5)
C(1)-C(6)	1.414(4)
C(2)-C(3)	1.388(5)
C(3)-C(4)	1.392(5)
C(4)-C(5)	1.374(5)

C(5)-C(6)	1.416(4)
C(6)-C(7)	1.449(4)
C(8)-C(9)	1.410(4)
C(8)-C(13)	1.418(5)
C(9)-C(10)	1.378(5)
C(10)-C(11)	1.394(5)
C(11)-C(12)	1.371(5)
C(12)-C(13)	1.416(4)
C(13)-C(14)	1.445(4)
C(16)-C(18)	1.393(4)
C(16)-C(17)	1.409(4)
C(17)-C(19)	1.386(4)
C(18)-C(20)	1.390(4)
C(19)-C(21)	1.385(4)
C(20)-C(21)	1.394(4)
C(22)-C(23)	1.341(5)
C(24)-C(25)	1.345(5)
C(26)-C(27)	1.503(5)
C(27)-C(28)	1.505(5)
C(29)-C(30)	1.518(5)
C(30)-C(31)	1.522(6)
C(32)-Cl(2)	0.992(8)
C(32)-C(32)#1	1.664(15)
C(32)-Cl(2)#1	1.762(8)
C(32)-Cl(1)#1	2.203(9)
Cl(2)-C(32)#1	1.762(8)
Cl(2)-Cl(2)#1	2.326(4)

Cl(2)-Cl(1)-C(32)	24.5(3)
Cl(2)-Cl(1)-C(32)#1	50.8(2)
C(32)-Cl(1)-C(32)#1	47.9(4)
O(2)-U(1)-O(1)	177.91(10)
O(2)-U(1)-O(4)	89.90(9)
O(1)-U(1)-O(4)	90.83(9)
O(2)-U(1)-O(3)	90.71(9)
O(1)-U(1)-O(3)	89.36(9)

O(4)-U(1)-O(3)	157.61(8)
O(2)-U(1)-O(5)	90.86(9)
O(1)-U(1)-O(5)	91.19(9)
O(4)-U(1)-O(5)	79.03(8)
O(3)-U(1)-O(5)	78.58(7)
O(2)-U(1)-N(2)	86.71(9)
O(1)-U(1)-N(2)	91.70(9)
O(4)-U(1)-N(2)	70.02(8)
O(3)-U(1)-N(2)	132.36(8)
O(5)-U(1)-N(2)	148.95(8)
O(2)-U(1)-N(1)	87.22(9)
O(1)-U(1)-N(1)	90.86(9)
O(4)-U(1)-N(1)	133.09(8)
O(3)-U(1)-N(1)	69.28(8)
O(5)-U(1)-N(1)	147.77(8)
N(2)-U(1)-N(1)	63.07(8)
C(20)-S(1)-C(22)	95.10(15)
C(21)-S(2)-C(22)	95.21(15)
C(24)-S(3)-C(23)	95.43(16)
C(23)-S(4)-C(25)	95.72(16)
C(24)-S(5)-C(26)	102.27(17)
C(25)-S(6)-C(29)	102.81(16)
C(7)-N(1)-C(16)	119.7(3)
C(7)-N(1)-U(1)	125.6(2)
C(16)-N(1)-U(1)	114.35(18)
C(14)-N(2)-C(17)	118.1(3)
C(14)-N(2)-U(1)	126.9(2)
C(17)-N(2)-U(1)	114.97(19)
C(1)-O(3)-U(1)	125.25(19)
C(8)-O(4)-U(1)	133.5(2)
C(15)-O(5)-U(1)	124.7(2)
O(3)-C(1)-C(2)	120.3(3)
O(3)-C(1)-C(6)	121.0(3)
C(2)-C(1)-C(6)	118.7(3)
C(3)-C(2)-C(1)	120.6(3)
C(2)-C(3)-C(4)	121.0(3)

C(5)-C(4)-C(3)	119.0(3)
C(4)-C(5)-C(6)	121.7(3)
C(1)-C(6)-C(5)	118.8(3)
C(1)-C(6)-C(7)	123.1(3)
C(5)-C(6)-C(7)	118.0(3)
N(1)-C(7)-C(6)	124.5(3)
O(4)-C(8)-C(9)	120.4(3)
O(4)-C(8)-C(13)	121.2(3)
C(9)-C(8)-C(13)	118.4(3)
C(10)-C(9)-C(8)	120.6(3)
C(9)-C(10)-C(11)	121.3(3)
C(12)-C(11)-C(10)	119.2(3)
C(11)-C(12)-C(13)	121.3(3)
C(12)-C(13)-C(8)	119.2(3)
C(12)-C(13)-C(14)	117.3(3)
C(8)-C(13)-C(14)	122.8(3)
N(2)-C(14)-C(13)	125.0(3)
C(18)-C(16)-C(17)	120.3(3)
C(18)-C(16)-N(1)	123.7(3)
C(17)-C(16)-N(1)	115.9(3)
C(19)-C(17)-C(16)	120.2(3)
C(19)-C(17)-N(2)	123.6(3)
C(16)-C(17)-N(2)	116.1(3)
C(20)-C(18)-C(16)	118.9(3)
C(21)-C(19)-C(17)	119.3(3)
C(18)-C(20)-C(21)	120.6(3)
C(18)-C(20)-S(1)	122.7(2)
C(21)-C(20)-S(1)	116.5(2)
C(19)-C(21)-C(20)	120.7(3)
C(19)-C(21)-S(2)	122.3(2)
C(20)-C(21)-S(2)	116.9(2)
C(23)-C(22)-S(2)	122.0(3)
C(23)-C(22)-S(1)	122.6(3)
S(2)-C(22)-S(1)	115.16(18)
C(22)-C(23)-S(3)	123.4(3)
C(22)-C(23)-S(4)	122.4(3)

S(3)-C(23)-S(4)	113.99(19)
C(25)-C(24)-S(5)	123.4(3)
C(25)-C(24)-S(3)	117.5(2)
S(5)-C(24)-S(3)	118.55(19)
C(24)-C(25)-S(6)	125.6(3)
C(24)-C(25)-S(4)	116.7(3)
S(6)-C(25)-S(4)	117.04(19)
C(27)-C(26)-S(5)	110.9(3)
C(26)-C(27)-C(28)	114.5(3)
C(30)-C(29)-S(6)	113.1(3)
C(29)-C(30)-C(31)	113.5(3)
Cl(2)-C(32)-C(32)#1	78.7(6)
Cl(2)-C(32)-Cl(2)#1	112.2(6)
C(32)#1-C(32)-Cl(2)#1	33.5(4)
Cl(2)-C(32)-Cl(1)	23.7(3)
C(32)#1-C(32)-Cl(1)	79.4(5)
Cl(2)#1-C(32)-Cl(1)	110.0(4)
Cl(2)-C(32)-Cl(1)#1	126.3(6)
C(32)#1-C(32)-Cl(1)#1	52.6(5)
Cl(2)#1-C(32)-Cl(1)#1	24.95(15)
Cl(1)-C(32)-Cl(1)#1	132.1(4)
Cl(1)-Cl(2)-C(32)	131.8(5)
Cl(1)-Cl(2)-C(32)#1	104.2(3)
C(32)-Cl(2)-C(32)#1	67.8(6)
Cl(1)-Cl(2)-Cl(2)#1	118.1(2)
C(32)-Cl(2)-Cl(2)#1	44.5(4)
C(32)#1-Cl(2)-Cl(2)#1	23.3(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+1,-z

Table 4. Anisotropic displacement parameters ($Å^2$ x 10^3) for **1**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(1)	33(1)	36(1)	31(1)	12(1)	-8(1)	-10(1)
U(1)	13(1)	13(1)	11(1)	-2(1)	-1(1)	-3(1)
S(1)	21(1)	13(1)	19(1)	-4(1)	-8(1)	-2(1)
S(2)	18(1)	14(1)	16(1)	-3(1)	-5(1)	-3(1)
S(3)	22(1)	15(1)	22(1)	-6(1)	-9(1)	-3(1)
S(4)	21(1)	15(1)	21(1)	-4(1)	-8(1)	-3(1)
S(5)	18(1)	20(1)	28(1)	-12(1)	-1(1)	-5(1)
S(6)	19(1)	26(1)	21(1)	-4(1)	-5(1)	-10(1)
N(1)	15(1)	13(1)	11(1)	0(1)	-2(1)	-3(1)
N(2)	11(1)	14(1)	15(1)	-5(1)	0(1)	-3(1)
O(1)	17(1)	19(1)	19(1)	-3(1)	-3(1)	-7(1)
O(2)	19(1)	19(1)	16(1)	0(1)	-2(1)	-9(1)
O(3)	14(1)	20(1)	14(1)	-1(1)	-2(1)	-4(1)
O(4)	19(1)	14(1)	16(1)	-2(1)	-1(1)	-2(1)
O(5)	21(1)	18(1)	14(1)	-5(1)	-2(1)	-4(1)
C(1)	18(2)	13(2)	15(2)	2(1)	-3(1)	-6(1)
C(2)	18(2)	16(2)	17(2)	3(1)	-6(1)	-4(1)
C(3)	19(2)	21(2)	23(2)	3(1)	-10(1)	-7(1)
C(4)	14(2)	20(2)	28(2)	4(1)	-4(1)	-4(1)
C(5)	16(2)	14(2)	18(2)	4(1)	-1(1)	-4(1)
C(6)	15(2)	7(1)	17(2)	2(1)	-4(1)	-1(1)
C(7)	16(2)	11(2)	17(2)	4(1)	-4(1)	-4(1)
C(8)	12(2)	15(2)	20(2)	-2(1)	-4(1)	-6(1)
C(9)	18(2)	19(2)	19(2)	-6(1)	-2(1)	-5(1)
C(10)	20(2)	16(2)	28(2)	-7(1)	-3(1)	-1(1)
C(11)	29(2)	11(2)	28(2)	2(1)	-10(2)	-2(1)
C(12)	24(2)	16(2)	19(2)	1(1)	-9(1)	-4(1)
C(13)	15(2)	15(2)	22(2)	0(1)	-6(1)	-6(1)
C(14)	13(2)	16(2)	17(2)	0(1)	-4(1)	-3(1)
C(15)	62(3)	25(2)	29(2)	-11(2)	-17(2)	1(2)
C(16)	16(2)	14(2)	10(2)	-1(1)	-1(1)	-5(1)

C(17)	16(2)	15(2)	9(1)	-1(1)	1(1)	-5(1)
C(18)	17(2)	14(2)	13(2)	0(1)	-1(1)	-4(1)
C(19)	15(2)	13(2)	14(2)	0(1)	-4(1)	-4(1)
C(20)	19(2)	13(2)	9(1)	-3(1)	0(1)	-7(1)
C(21)	15(2)	15(2)	11(2)	-1(1)	-2(1)	-3(1)
C(22)	17(2)	16(2)	14(2)	-3(1)	-3(1)	-2(1)
C(23)	16(2)	15(2)	17(2)	0(1)	-3(1)	-2(1)
C(24)	18(2)	18(2)	18(2)	-4(1)	-2(1)	-8(1)
C(25)	18(2)	20(2)	13(2)	-3(1)	1(1)	-10(1)
C(26)	23(2)	36(2)	38(2)	-18(2)	6(2)	-13(2)
C(27)	31(2)	36(2)	31(2)	-5(2)	2(2)	-7(2)
C(28)	31(2)	43(2)	36(2)	-22(2)	-4(2)	-5(2)
C(29)	36(2)	19(2)	28(2)	6(1)	-17(2)	-13(2)
C(30)	49(3)	46(3)	22(2)	-4(2)	-1(2)	-31(2)
C(31)	67(3)	63(3)	31(2)	-23(2)	10(2)	-41(3)
C(32)	23(4)	29(4)	26(4)	12(3)	-5(3)	-14(3)
Cl(2)	34(1)	40(1)	31(1)	-3(1)	-5(1)	-8(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^{-3}) for **1**.

	x	y	z	U(eq)
H(2)	1574	599	5365	21
H(3)	-962	927	5954	24
H(4)	-1885	1052	7391	26
H(5)	-272	935	8226	21
H(9)	9230	-5099	6008	23
H(10)	9936	-6831	6822	27
H(11)	9228	-6809	8271	29
H(12)	7909	-5014	8903	24
H(15A)	8077	-3169	4859	62
H(15B)	7051	-2985	4225	62
H(15C)	6672	-3589	5114	62
H(18)	3693	1973	8597	18
H(19)	7850	-1404	9035	17
H(26A)	3833	6479	12253	38
H(26B)	4198	5151	12619	38
H(27A)	4680	5638	13790	42
H(27B)	3047	6479	13695	42
H(28A)	5614	7166	13295	56
H(28B)	4218	7619	14047	56
H(28C)	4027	8007	13127	56
H(29A)	8624	1554	13111	31
H(29B)	9795	1766	13513	31
H(30A)	7351	2344	14398	43
H(30B)	6720	3292	13710	43
H(31A)	8870	3430	14523	76
H(31B)	7134	4211	14744	76
H(31C)	8145	4401	13870	76

5. **Computational details**

All density functional theory (DFT) calculations were carried out with the Gaussian 09 package.[1] The geometry optimizations were carried out with Becke's three parameter (B3) hybrid exchange functionals combined with Lee-Yang-Parr (LYP) correlation functionals (B3LYP).[2] For the light main group elements, the basis set of 6-31G(d) was used for geometry optimization and for frequency calculations based on the optimized geometries of local minimum. A larger basis set of 6-311++g(2d,p) was used for single point (SP) energy calculations. For uranium, the Stuttgart RSC ECP (effective core potential) was used. The free energies of reactive species were obtained based on the SP electronic energies and thermal correction calculated by the smaller basis sets. The universal solvation model[3], SMD developed by Truhlar et al, was used to account for the solvation effect. DMSO and dichloromethane (DCE) was used, respectively to compare with the gas phase calculations. The absolute redox potentials were estimated by Nernst equation.

$$V_{ox} = \Delta G^{ox}/nF = (G(A) - (G(A^-))/nF$$

where V_{ox} denotes oxidization potential, F is Faraday constant, n is to the number of electrons involved in the redox processes, A^-/A are general designations of oxidation couples, ΔG^{ox} refers to the free energy change associated with the redox couples.

As discussed in the text, the easier oxidation of **1**(DMSO) than ^{TTF}salophenH2 is due to the more delocalized SOMO (singly occupied orbitals of TTF^{1+}), as shown in Figure S4

1 Gaussian 09, Revision A.1, Frisch, M. J. et al. Gaussian, Inc., Wallingford CT, 2009
2 (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
3 Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B* **2009**, *113*, 6378-6396.

4. References for Supporting Information

1. APEX II 1.08, **2004**, Bruker AXS, Inc., Madison, Wisconsin 53719 USA.
2. SAINT+ 7.06, **2003**, Bruker AXS, Inc., Madison, Wisconsin 53719 USA.
3. SADABS 2.03, **2001**, George Sheldrick, University of Göttingen, Germany.
4. SHELXTL 5.10, **1997**, Bruker AXS, Inc., Madison, Wisconsin 53719 USA.