Electronic Supplementary Material (ESI) for ChemComm.

Organosoluble Tetravalent Actinide Di- and Trifluorides

Garret Gotthelf, Matthew A. Stuber, Anna Y. Kornienko, Thomas J. Emge and John G. Brennan*

Department of Chemistry and Chemical Biology, Rutgers, the State University of New Jersey, 610 Taylor Road, Piscataway NJ 08854-8087, United States
*Email: bren@rci.rutgers.edu

Supporting Information (SI)

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1. Experimental Section

General Methods. All syntheses were carried out under ultrapure nitrogen (Welco Praxair), using conventional drybox or Schlenk techniques. Pyridine (Aldrich) and hexane (Aldrich) were purified with a dual column Solv-Tek solvent purification system and collected immediately prior to use. Iodine (Fisher), silver fluride (Sigma), silved diflouride (Sigma), PhSSPh (Acros), thorium chips (International Bioanalytical Industries Inc., 3495 North Dixie Hwy, Unit #8, Boca Raton, FL 33431), and mercury (Strem Chemicals) were purchased and used as received. Melting points were recorded in sealed capillaries and are uncorrected. IR spectra were recorded on a Thermo Nicolet Avatar 360 FTIR spectrometer from 4000 to 450 cm^{-1} as Nujol mulls on CsI plates. UV−vis absorption spectra were recorded on a Varian DMS 100S spectrometer with the samples dissolved in pyridine, placed in either a 1.0 mm × 1.0 cm Spectrosil quartz cell or a 1.0 cm^2 special optical glass cuvette, and scanned from 200 to 1000 nm. NMR data were collected on a Varian VNMRS 500 spectrometer at 25 °C with the compounds dissolved in NC_5D_5. ^1H and ^{19}F NMR spectra were obtained at 499 and 476 MHz, respectively. Elemental analyses were performed by Quantitative Technologies, Inc. (Whitehouse, NJ).

X-ray Structure Determination. Data for **1** – **4** were collected on a Bruker Smart APEX CCD diffractometer with graphite monochromatized Mo Kα radiation (λ = 0.71073 Å).[4] Crystals were immersed in Paratone oil and examined at low temperatures. The data were corrected for

Lorenz effects and polarization, and absorption, the latter by a multi-scan method or by a numerical method when the multi-scan method appeared insufficient.[4] The structures were solved by direct methods.[5] All non-hydrogen atoms were refined[5] based upon F_{obs}^2. All hydrogen atom coordinates were calculated with idealized geometries. Crystallographic data and final R indices for **1 - 4** are given in Table 1. The crystals used for **1**, **2**, and **4** had inversion twinning and that for **3** did not. Thermal ellipsoid diagrams for **1-4** are shown in Figures 1-4, respectively.[6] Complete crystallographic details and fully-labeled thermal ellipsoid diagrams are given in the Supporting Information.

Synthesis of $(py)_4UI_2F_2 \cdot 2py$ (1).

Pyridine (20 mL) was added to a flask containing Uranium metal (0.119 g, 0.500 mmol), I_2 (0.127 g, 0.500 mmol), and AgF_2 (0.0776 g, 0.500 mmol). The mixture was stirred for 48 h at 25°C in which it went from yellow to orange quickly. It then transitioned to green after 24 hours stirring, and the then the flask was subsequently placed in oil bath at 65°C to stir for additional 48 h. After heating the reaction was brought to 25°C and stirred for 6 hours to normalize. In this time the reaction transitioned from orange to a dark green solution with. The resulting green solution (25 mL) was filtered to remove away from metallic silver and a brown precipitate and the volume was reduced in vacuo to 15 mL. Layering the green solution with hexane (15 mL) cooling to 2°C gave blue-green cubic shaped crystals (0.48, 47%) that melt at 124°C and decompose into a dark red product at 208°C, with condensation of a colorless slight yellow volatile product at the top of the tube. Anal. Calcd for $C_{20}H_{20}F_2I_2N_4U$: C, 28.4; H, 2.38; N, 6.62 Found C, 27.7; H, 2.41; N, 6.03. IR: 2923 (w), 2853 (w), 1597 (s), 1579 (s), 1460 (m), 1376 (m), 1261 (s), 1220 (s), 1093 (w), 1029 (w), 800 (m), 756 (s), 722 (s), 700 (s), 620 (s), 482 (s). ^{1}H

NMR: 8.46 (s, J= 2, 2H, py), 7.46 (m, J= 1, 1H, py), 7.08 (m, 2H, py). UV/Vis (Pyridine, 1.18 x 10^{-2} M): 469 nm (ε = 24), 511 nm (ε = 20), 579 nm (ε = 29), 589 nm (ε = 28), 622 nm (ε = 19).

Synthesis of $(py)_7Th_2F_5(SC_6F_5)_3 \cdot 2py$ (2)

Th (0.232 g, 1.00 mmol), $(SPh)_2$ (0.330 g, 1.51 mmol), $(SC_6F_5)_2$ (0.200 g, 0.503 mmol), and Hg (0.019 g, 0.095 mmol) were combined in pyridine (20 mL) and the solution was stirred for 5 d at 25°C. AgF (0.190 g, 1.50 mmol) was added to the cloudy gray solution and stirred for additional 24 h. The resulting red solution (15 mL) was filtered and layered with hexane (20 mL) to form colorless crystals (0.219 g, 23%), that melt at 155 °C and decompose at 275 °C. Anal. Calcd for $C_{63}H_{45}F_{20}N_9S_3Th_2$: C, 40.5; H, 2.43; N, 6.75. Found: C, 39.8; H, 2.56; N, 6.64. IR: 2926 (s), 1620 (w), 1505 (m), 1463 (s), 1377 (s), 1260 (w), 1225 (w), 1153 (w), 1071 (w), 1039 (w), 1008 (w), 968 (w), 861 (w), 810 (w), 754 (w), 744 (w), 700 (m), 623 (w) cm^{-1}. ^1H NMR (toluene-d8): 8.33 (m, 2H), 6.88 (m, 1H), 6.56 (m, 2H). ^{19}F NMR (toluene-d_8): -137 (d, 2F), -159 (t, 1F), -162 (td, 2F).

2. X-ray powder diffraction patterns and calculated profiles for compounds 1and 2.

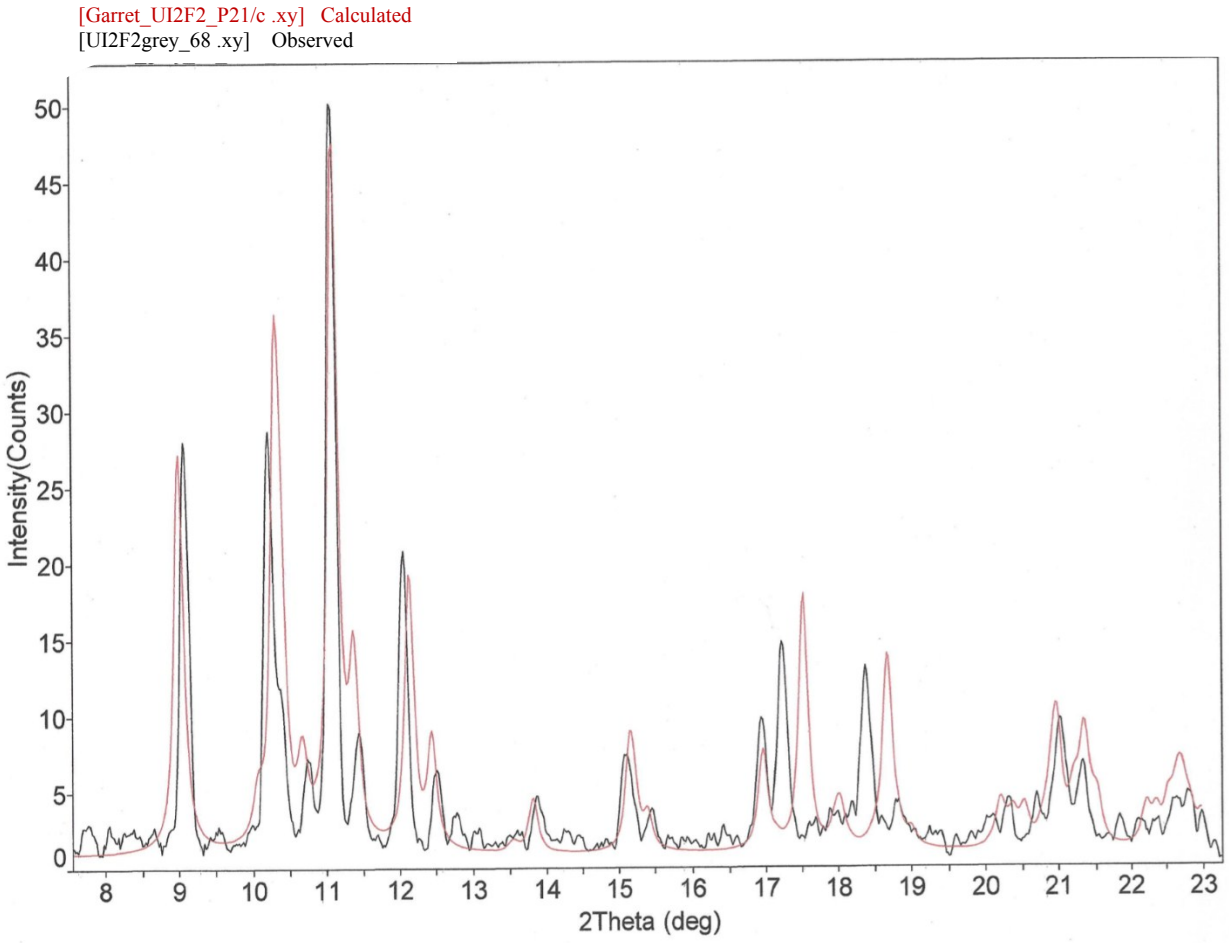

Figure *S*1. PXRD and calculated pattern from single crystal (in red) for $(py)_4UF_2I_2 \cdot 2py$ **(1).**

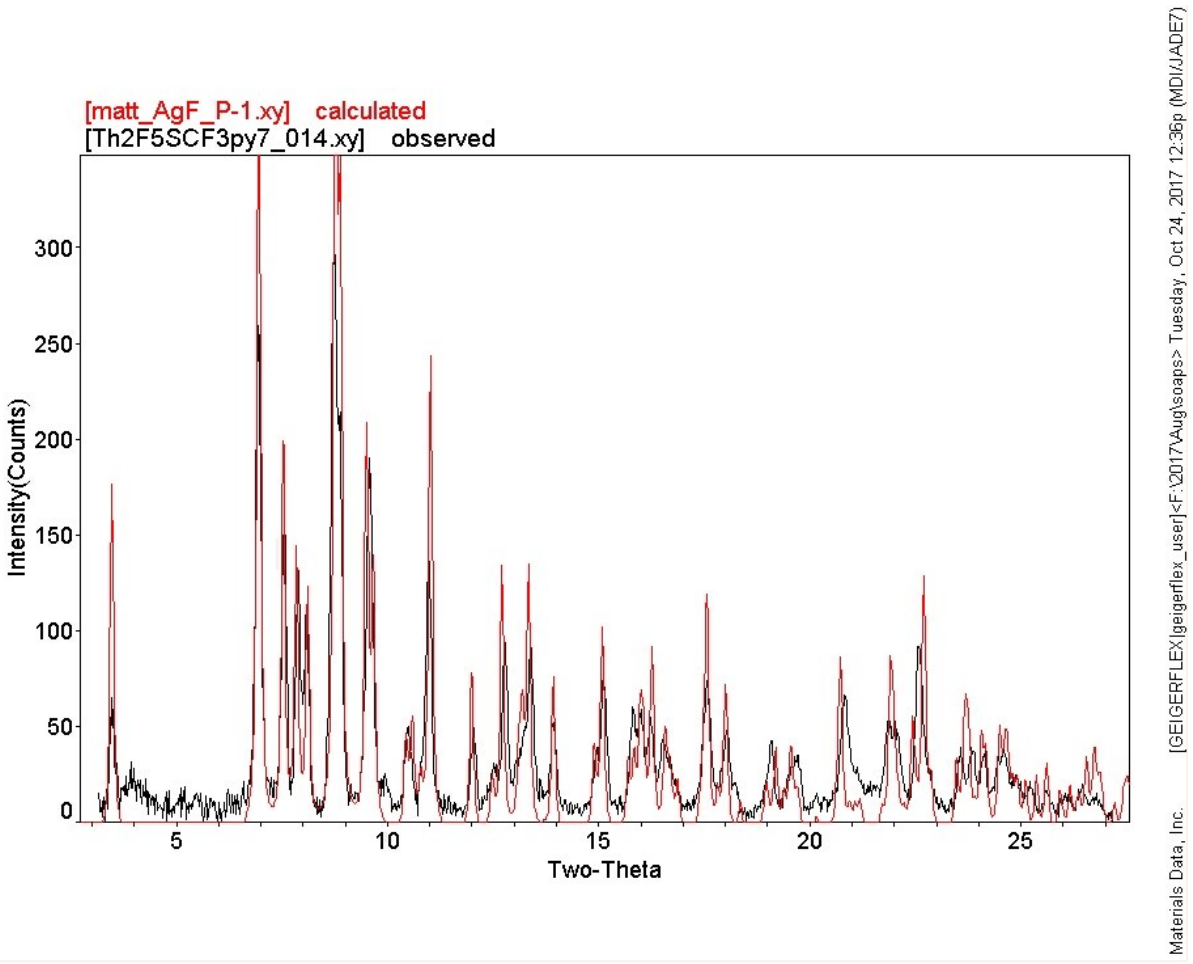

Figure *S*2. PXRD and calculated pattern from single crystal (in red) for $(py)_7Th_2F_5(SC_6F_5)_3 \cdot 2py$**(2).**

3. ^{1}H NMR data for compounds 1 and 2.

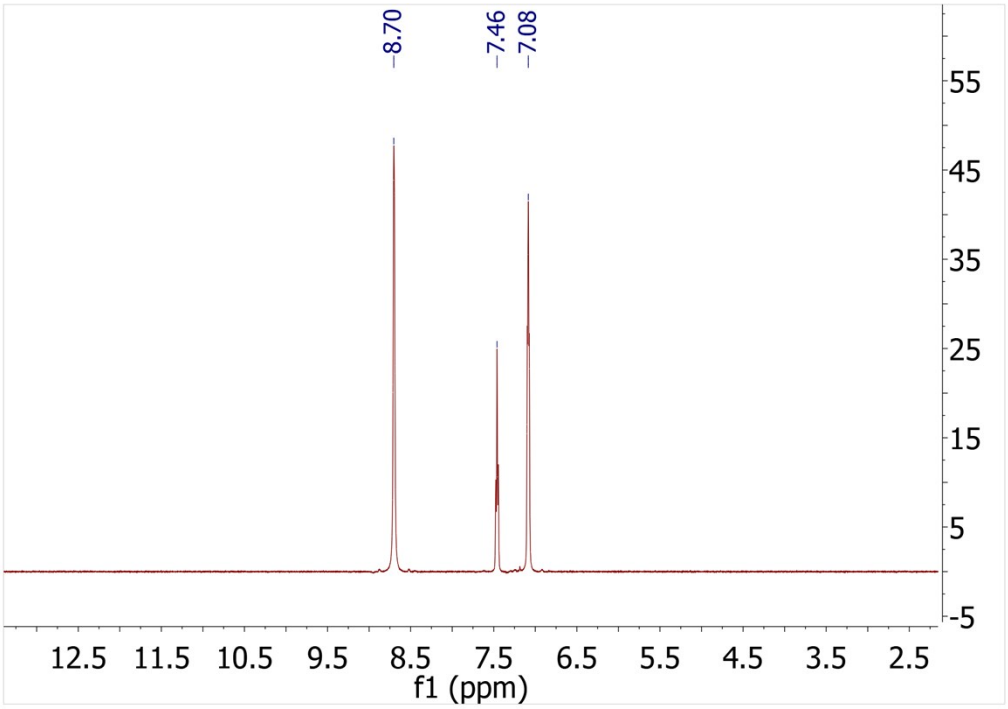

Figure *S*3. ^{1}H NMR spectrum of $(py)_4UI_2F_2 \cdot 2py$ **(1)** in pyridine-*d5*.

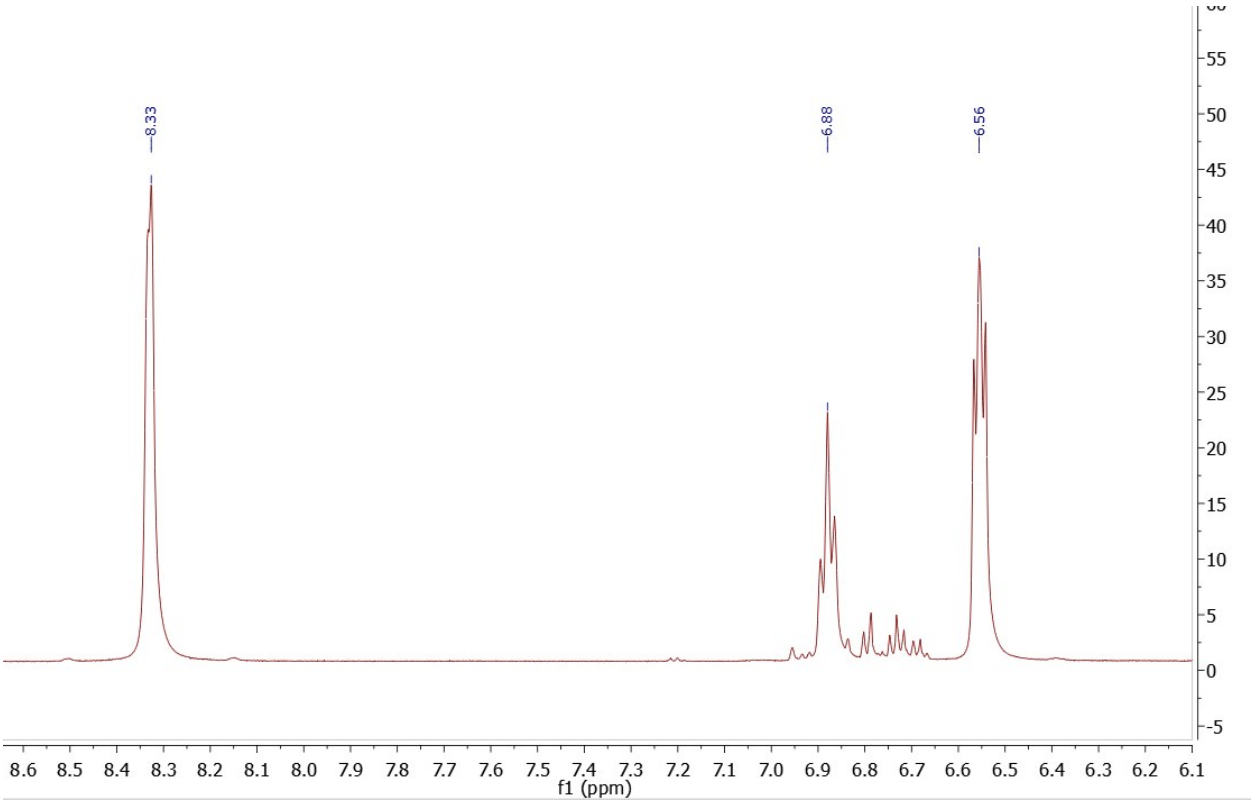

Figure *S*4. ^{1}H NMR spectrum of $(py)_7Th_2F_5(SC_6F_5)_3 \cdot 2py$ **(2)** in toluene-*d8*.

4. ^{19}F NMR data for compounds 1 and 2.

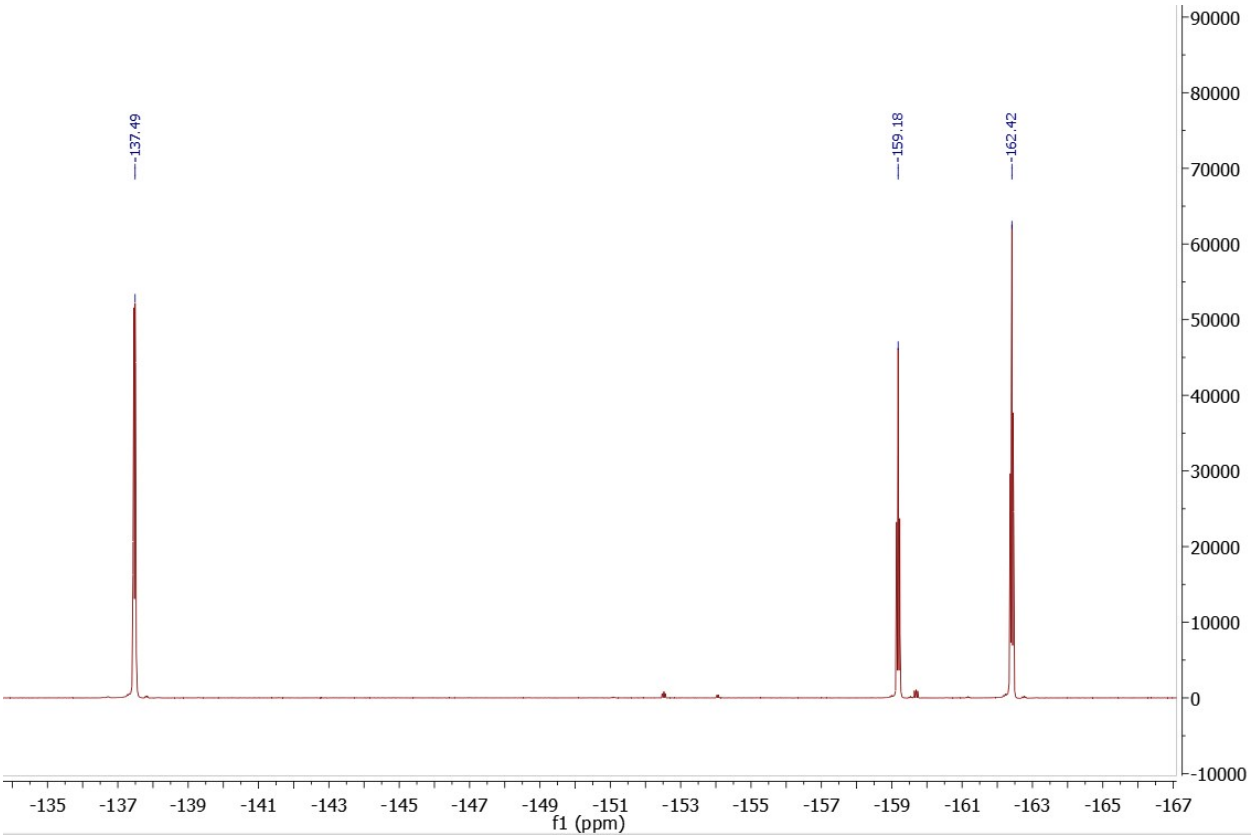

Figure *S*5. ^{19}F NMR spectrum of $(py)_7Th_2F_5(SC_6F_5)_3 \cdot 2py$**(2)** in toluene-*d8*.

5. UV-Vis profile for compound 1.

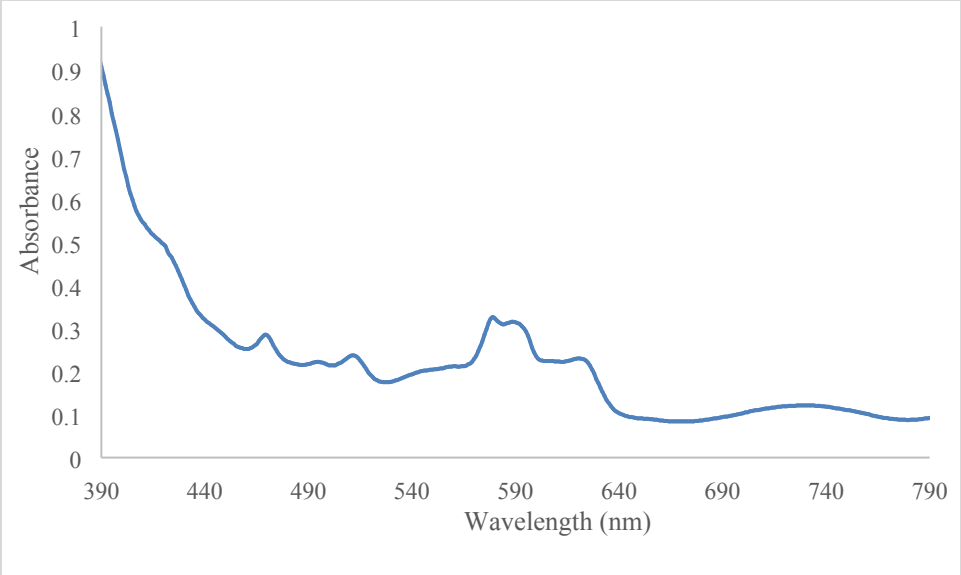

Figure *S6*. UV-vis profile of $(py)_4UF_2I_2 \cdot 2py$

6. IR profiles for compounds 1 and 2.

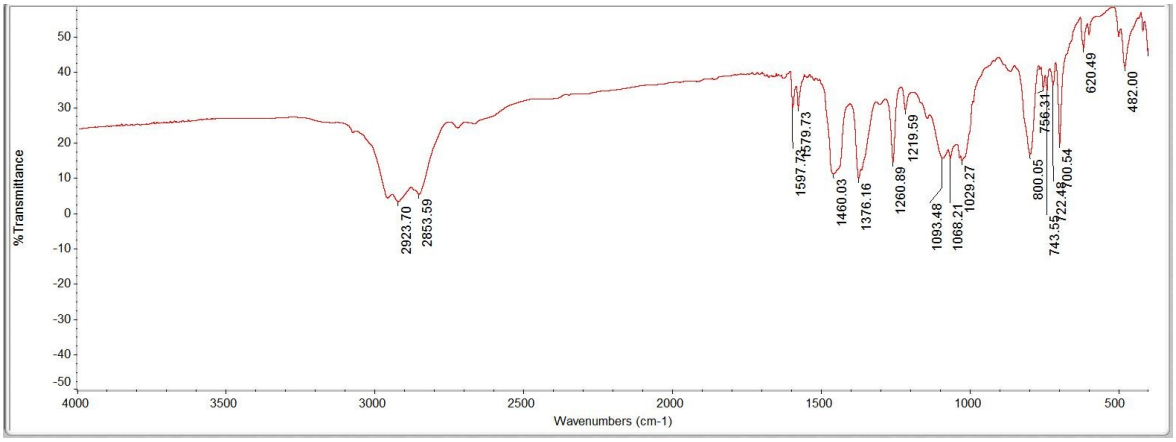

Figure *S7*. IR profile of $(py)_4UF_2I_2 \cdot 2py$ **(1)**.

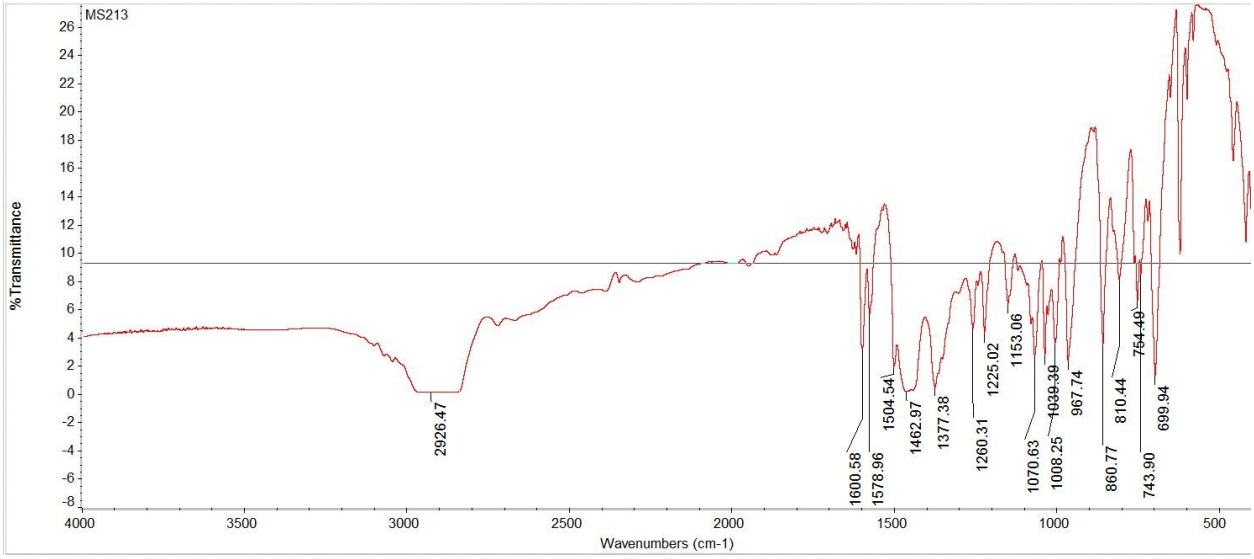

Figure *S8*. IR profile of $(py)_7Th_2F_5(SC_6F_5)_3 \cdot 2py$ **(2)**.

7. Summary of Crystallographic Details for compounds 1 and 2, Table S1.

Table S1. Summary of Crystallographic Details for **1** and **2**.

	1	**2**
empirical formula	$C_{30}H_{30}F_2I_2N_6U$	$C_{63}H_{45}F_{20}N_9S_3Th_2$
fw	1004.43	1868.34
crystal system	Monoclinic	Triclinic
space group	$P2_1/n$	P-1
a (Å)	9.809(2)	11.1776(10)
b (Å)	38.747(9)	12.1625(11)
c (Å)	9.755(2)	25.368(2)
α (deg)	90	81.4051(15)
β (deg)	117.859(3)	86.7035(15)
γ (deg)	90	74.0481(15)
V (Å^3)	3277.5(13)	3278.2(5)
Z	4	2
D(calcd) (Mg/cm^3)	2.036	1.893
T (K)	120(2)	120(2)
abs	6.876	4.732

coeff(mm^{-1})		
R(F)[b] [I > 2σ(I)]	0.0586	0.0360
$R_w(F^2)$[c] [I > 2σ(I)]	0.0675	0.0438

Definitions: [a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; [b] $R_w(F^2) = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

8. Crystallographic tables for compounds 1 (Tables S2-S8), 2 (Tables S9-S15),

Table S2. Crystal data and structure refinement for ui2f2bm_0m.

Identification code	ui2f2bm_0m	
Empirical formula	C30 H30 F2 I2 N6 U	
Formula weight	1004.43	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 9.809(2) Å	α= 90°.
	b = 38.747(9) Å	β= 117.859(3)°.
	c = 9.755(2) Å	γ = 90°.
Volume	3277.5(13) $Å^3$	
Z	4	
Density (calculated)	2.036 Mg/m^3	
Absorption coefficient	6.876 mm^{-1}	
F(000)	1872	
Crystal size	0.200 x 0.160 x 0.060 mm^3	
Theta range for data collection	2.102 to 27.484°.	
Index ranges	-12<=h<=12, -50<=k<=47, -12<=l<=12	
Reflections collected	26307	
Independent reflections	7447 [R(int) = 0.0414]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Numerical	
Max. and min. transmission	0.5075 and 0.1599	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7447 / 0 / 372	

Goodness-of-fit on F^2	1.215
Final R indices [I>2sigma(I)]	R1 = 0.0586, wR2 = 0.1280
R indices (all data)	R1 = 0.0675, wR2 = 0.1360
Extinction coefficient	0.00016(5)
Largest diff. peak and hole	1.732 and -2.017 e.$Å^{-3}$

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $(py)_4UF_2I_2 \cdot 2py$ **(1)**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
U(1)	3029(1)	3780(1)	6678(1)	20(1)
I(1)	1350(1)	3362(1)	8199(1)	28(1)
I(2)	3862(1)	4478(1)	5597(1)	24(1)
F(1)	1301(8)	3654(2)	4451(8)	25(2)
F(2)	5225(9)	3691(2)	8471(9)	30(2)
N(1)	3419(13)	3114(3)	6408(13)	26(2)
N(2)	4590(13)	3631(3)	5189(14)	27(2)
N(3)	3522(13)	4183(3)	9133(13)	25(2)
N(4)	505(13)	4180(3)	5963(13)	23(2)
C(1)	2614(16)	2945(3)	5053(16)	26(3)
C(2)	2876(18)	2608(4)	4833(19)	35(3)
C(3)	4064(18)	2434(3)	6098(17)	32(3)
C(4)	4882(19)	2599(3)	7466(18)	35(3)
C(5)	4524(16)	2938(3)	7610(15)	26(3)
C(6)	3902(16)	3634(4)	3638(17)	29(3)
C(7)	4590(17)	3490(4)	2796(17)	36(3)
C(8)	6016(17)	3344(3)	3560(20)	35(3)
C(9)	6742(19)	3347(4)	5160(20)	40(4)
C(10)	6022(16)	3495(3)	5932(17)	28(3)
C(11)	4832(15)	4365(3)	9787(16)	27(3)
C(12)	5217(16)	4585(4)	11025(16)	30(3)
C(13)	4179(15)	4628(4)	11616(16)	31(3)
C(14)	2837(16)	4439(4)	10970(16)	31(3)
C(15)	2543(14)	4227(3)	9732(15)	23(3)
C(16)	505(15)	4516(3)	6296(16)	24(3)
C(17)	-787(17)	4717(3)	5864(16)	28(3)
C(18)	-2202(16)	4555(4)	5051(15)	25(3)
C(19)	-2265(15)	4209(3)	4689(16)	26(3)
C(20)	-903(15)	4036(3)	5152(16)	25(3)
N(5)	7659(18)	2903(3)	11696(19)	47(4)
C(21)	8200(20)	2583(4)	11610(20)	44(4)

C(22)	9188(19)	2528(4)	11045(19)	40(4)
C(23)	9690(20)	2806(4)	10520(20)	44(4)
C(24)	9220(20)	3132(5)	10640(20)	50(4)
C(25)	8220(20)	3162(5)	11260(30)	56(5)
N(6)	-1157(19)	4020(4)	-96(19)	54(4)
C(26)	-677(18)	4116(5)	1390(20)	50(5)
C(27)	-703(18)	4451(5)	1776(19)	46(4)
C(28)	-1170(20)	4707(4)	700(20)	42(4)
C(29)	-1654(18)	4612(4)	-840(20)	40(4)
C(30)	-1663(19)	4280(5)	-1179(18)	39(4)

Table S4. Bond lengths [Å] and angles [°] $(py)_4UF_2I_2 \cdot 2py$ **(1)**..

U(1)-F(2)	2.073(8)	C(11)-C(12)	1.378(19)
U(1)-F(1)	2.095(7)	C(11)-H(11)	0.9500
U(1)-N(2)	2.620(11)	C(12)-C(13)	1.40(2)
U(1)-N(1)	2.640(11)	C(12)-H(12)	0.9500
U(1)-N(3)	2.707(11)	C(13)-C(14)	1.374(19)
U(1)-N(4)	2.720(11)	C(13)-H(13)	0.9500
U(1)-I(1)	3.1346(10)	C(14)-C(15)	1.374(19)
U(1)-I(2)	3.1475(11)	C(14)-H(14)	0.9500
N(1)-C(1)	1.350(17)	C(15)-H(15)	0.9500
N(1)-C(5)	1.352(17)	C(16)-C(17)	1.374(18)
N(2)-C(6)	1.337(18)	C(16)-H(16)	0.9500
N(2)-C(10)	1.351(18)	C(17)-C(18)	1.386(19)
N(3)-C(11)	1.338(17)	C(17)-H(17)	0.9500
N(3)-C(15)	1.347(16)	C(18)-C(19)	1.380(19)
N(4)-C(16)	1.342(16)	C(18)-H(18)	0.9500
N(4)-C(20)	1.349(16)	C(19)-C(20)	1.368(17)
C(1)-C(2)	1.370(19)	C(19)-H(19)	0.9500
C(1)-H(1)	0.9500	C(20)-H(20)	0.9500
C(2)-C(3)	1.41(2)	N(5)-C(25)	1.31(2)
C(2)-H(2)	0.9500	N(5)-C(21)	1.36(2)
C(3)-C(4)	1.35(2)	C(21)-C(22)	1.34(2)
C(3)-H(3)	0.9500	C(21)-H(21)	0.9500
C(4)-C(5)	1.384(19)	C(22)-C(23)	1.38(2)
C(4)-H(4)	0.9500	C(22)-H(22)	0.9500
C(5)-H(5)	0.9500	C(23)-C(24)	1.37(2)
C(6)-C(7)	1.40(2)	C(23)-H(23)	0.9500
C(6)-H(6)	0.9500	C(24)-C(25)	1.37(2)
C(7)-C(8)	1.36(2)	C(24)-H(24)	0.9500
C(7)-H(7)	0.9500	C(25)-H(25)	0.9500
C(8)-C(9)	1.38(2)	N(6)-C(26)	1.34(2)
C(8)-H(8)	0.9500	N(6)-C(30)	1.37(2)
C(9)-C(10)	1.37(2)	C(26)-C(27)	1.36(3)
C(9)-H(9)	0.9500	C(26)-H(26)	0.9500
C(10)-H(10)	0.9500	C(27)-C(28)	1.36(2)

C(27)-H(27)	0.9500	C(29)-C(30)	1.32(2)
C(28)-C(29)	1.40(2)	C(29)-H(29)	0.9500
C(28)-H(28)	0.9500	C(30)-H(30)	0.9500

F(2)-U(1)-F(1)	148.6(3)	C(6)-N(2)-U(1)	120.5(9)
F(2)-U(1)-N(2)	77.6(4)	C(10)-N(2)-U(1)	121.3(9)
F(1)-U(1)-N(2)	76.9(3)	C(11)-N(3)-C(15)	116.5(12)
F(2)-U(1)-N(1)	77.2(3)	C(11)-N(3)-U(1)	117.4(9)
F(1)-U(1)-N(1)	75.7(3)	C(15)-N(3)-U(1)	126.1(9)
N(2)-U(1)-N(1)	65.2(3)	C(16)-N(4)-C(20)	115.2(11)
F(2)-U(1)-N(3)	70.4(3)	C(16)-N(4)-U(1)	126.4(8)
F(1)-U(1)-N(3)	140.9(3)	C(20)-N(4)-U(1)	118.4(8)
N(2)-U(1)-N(3)	135.1(3)	N(1)-C(1)-C(2)	123.3(13)
N(1)-U(1)-N(3)	132.6(3)	N(1)-C(1)-H(1)	118.3
F(2)-U(1)-N(4)	140.7(3)	C(2)-C(1)-H(1)	118.3
F(1)-U(1)-N(4)	70.6(3)	C(1)-C(2)-C(3)	117.2(14)
N(2)-U(1)-N(4)	132.9(3)	C(1)-C(2)-H(2)	121.4
N(1)-U(1)-N(4)	133.5(3)	C(3)-C(2)-H(2)	121.4
N(3)-U(1)-N(4)	70.3(3)	C(4)-C(3)-C(2)	120.4(13)
F(2)-U(1)-I(1)	94.7(2)	C(4)-C(3)-H(3)	119.8
F(1)-U(1)-I(1)	91.2(2)	C(2)-C(3)-H(3)	119.8
N(2)-U(1)-I(1)	136.1(2)	C(3)-C(4)-C(5)	119.0(14)
N(1)-U(1)-I(1)	71.0(2)	C(3)-C(4)-H(4)	120.5
N(3)-U(1)-I(1)	78.2(2)	C(5)-C(4)-H(4)	120.5
N(4)-U(1)-I(1)	78.4(2)	N(1)-C(5)-C(4)	122.0(13)
F(2)-U(1)-I(2)	95.5(2)	N(1)-C(5)-H(5)	119.0
F(1)-U(1)-I(2)	93.7(2)	C(4)-C(5)-H(5)	119.0
N(2)-U(1)-I(2)	72.1(2)	N(2)-C(6)-C(7)	122.2(13)
N(1)-U(1)-I(2)	137.3(2)	N(2)-C(6)-H(6)	118.9
N(3)-U(1)-I(2)	80.4(2)	C(7)-C(6)-H(6)	118.9
N(4)-U(1)-I(2)	76.9(2)	C(8)-C(7)-C(6)	119.8(14)
I(1)-U(1)-I(2)	151.57(3)	C(8)-C(7)-H(7)	120.1
C(1)-N(1)-C(5)	118.0(11)	C(6)-C(7)-H(7)	120.1
C(1)-N(1)-U(1)	121.7(9)	C(7)-C(8)-C(9)	118.2(14)
C(5)-N(1)-U(1)	120.2(9)	C(7)-C(8)-H(8)	120.9
C(6)-N(2)-C(10)	117.3(12)	C(9)-C(8)-H(8)	120.9

C(10)-C(9)-C(8)	119.7(15)	N(4)-C(20)-H(20)	117.7
C(10)-C(9)-H(9)	120.1	C(19)-C(20)-H(20)	117.7
C(8)-C(9)-H(9)	120.1	C(25)-N(5)-C(21)	116.2(14)
N(2)-C(10)-C(9)	122.7(14)	C(22)-C(21)-N(5)	123.3(15)
N(2)-C(10)-H(10)	118.6	C(22)-C(21)-H(21)	118.4
C(9)-C(10)-H(10)	118.6	N(5)-C(21)-H(21)	118.4
N(3)-C(11)-C(12)	123.5(12)	C(21)-C(22)-C(23)	118.9(14)
N(3)-C(11)-H(11)	118.2	C(21)-C(22)-H(22)	120.6
C(12)-C(11)-H(11)	118.2	C(23)-C(22)-H(22)	120.6
C(11)-C(12)-C(13)	118.8(13)	C(24)-C(23)-C(22)	119.3(14)
C(11)-C(12)-H(12)	120.6	C(24)-C(23)-H(23)	120.3
C(13)-C(12)-H(12)	120.6	C(22)-C(23)-H(23)	120.3
C(14)-C(13)-C(12)	118.3(13)	C(23)-C(24)-C(25)	117.4(16)
C(14)-C(13)-H(13)	120.8	C(23)-C(24)-H(24)	121.3
C(12)-C(13)-H(13)	120.8	C(25)-C(24)-H(24)	121.3
C(13)-C(14)-C(15)	118.9(13)	N(5)-C(25)-C(24)	124.8(16)
C(13)-C(14)-H(14)	120.5	N(5)-C(25)-H(25)	117.6
C(15)-C(14)-H(14)	120.5	C(24)-C(25)-H(25)	117.6
N(3)-C(15)-C(14)	123.9(13)	C(26)-N(6)-C(30)	116.4(16)
N(3)-C(15)-H(15)	118.1	N(6)-C(26)-C(27)	121.4(15)
C(14)-C(15)-H(15)	118.1	N(6)-C(26)-H(26)	119.3
N(4)-C(16)-C(17)	125.4(13)	C(27)-C(26)-H(26)	119.3
N(4)-C(16)-H(16)	117.3	C(26)-C(27)-C(28)	121.7(16)
C(17)-C(16)-H(16)	117.3	C(26)-C(27)-H(27)	119.2
C(16)-C(17)-C(18)	116.9(12)	C(28)-C(27)-H(27)	119.2
C(16)-C(17)-H(17)	121.6	C(27)-C(28)-C(29)	117.4(15)
C(18)-C(17)-H(17)	121.6	C(27)-C(28)-H(28)	121.3
C(19)-C(18)-C(17)	119.9(12)	C(29)-C(28)-H(28)	121.3
C(19)-C(18)-H(18)	120.0	C(30)-C(29)-C(28)	118.8(15)
C(17)-C(18)-H(18)	120.0	C(30)-C(29)-H(29)	120.6
C(20)-C(19)-C(18)	118.0(12)	C(28)-C(29)-H(29)	120.6
C(20)-C(19)-H(19)	121.0	C(29)-C(30)-N(6)	124.2(15)
C(18)-C(19)-H(19)	121.0	C(29)-C(30)-H(30)	117.9
N(4)-C(20)-C(19)	124.5(12)	N(6)-C(30)-H(30)	117.9

Table S5. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $(py)_4UF_2I_2 \cdot 2py$ **(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}
U(1)	21(1)	18(1)	21(1)	0(1)	9(1)	1(1)
I(1)	34(1)	23(1)	29(1)	2(1)	16(1)	-4(1)
I(2)	27(1)	21(1)	28(1)	1(1)	16(1)	0(1)
F(1)	20(4)	25(4)	25(4)	0(3)	7(3)	3(3)
F(2)	32(4)	30(4)	22(4)	-3(3)	7(3)	1(3)
N(1)	22(6)	22(5)	29(6)	2(4)	6(5)	-1(4)
N(2)	26(6)	19(5)	39(7)	-5(5)	18(5)	-2(4)
N(3)	24(6)	24(6)	31(6)	-1(5)	15(5)	1(4)
N(4)	25(6)	24(5)	23(5)	1(4)	11(5)	-2(4)
C(1)	26(7)	23(6)	30(7)	2(5)	13(6)	-1(5)
C(2)	37(8)	26(7)	42(9)	-1(6)	17(7)	2(6)
C(3)	43(9)	18(6)	35(8)	0(6)	19(7)	7(6)
C(4)	43(9)	16(6)	40(8)	5(6)	15(7)	4(6)
C(5)	30(7)	29(7)	20(6)	0(5)	12(5)	4(5)
C(6)	21(7)	27(7)	34(7)	-10(6)	8(6)	-2(5)
C(7)	26(7)	54(10)	27(7)	-4(7)	12(6)	-10(7)
C(8)	35(8)	17(6)	68(11)	-13(7)	36(8)	-11(6)
C(9)	38(9)	26(7)	67(11)	3(7)	35(8)	-5(6)
C(10)	30(7)	18(6)	36(8)	1(5)	16(6)	1(5)
C(11)	17(6)	34(7)	33(7)	2(6)	13(5)	0(5)
C(12)	23(7)	34(7)	22(6)	-3(6)	2(5)	-4(6)
C(13)	18(6)	34(7)	28(7)	-12(6)	1(5)	-4(5)
C(14)	29(7)	39(8)	23(6)	0(6)	11(6)	3(6)
C(15)	17(6)	28(7)	24(6)	2(5)	10(5)	-1(5)
C(16)	22(6)	17(6)	34(7)	-1(5)	14(6)	-1(5)
C(17)	43(8)	23(6)	25(7)	-1(5)	22(6)	-1(6)
C(18)	24(7)	30(7)	21(6)	1(5)	10(5)	4(5)
C(19)	16(6)	23(6)	35(7)	5(5)	8(5)	-1(5)
C(20)	25(7)	12(5)	36(7)	1(5)	13(6)	1(5)
N(5)	58(10)	37(7)	69(10)	-5(7)	48(9)	-7(7)
C(21)	44(10)	36(8)	58(11)	9(8)	28(8)	0(7)

C(22)	41(9)	35(8)	44(9)	12(7)	21(7)	14(7)
C(23)	54(10)	42(9)	58(11)	4(8)	45(9)	12(8)
C(24)	44(10)	43(9)	76(14)	-3(9)	39(10)	-7(8)
C(25)	69(13)	38(9)	97(16)	-11(10)	69(13)	-8(9)
N(6)	55(10)	47(9)	57(10)	10(7)	23(8)	-1(7)
C(26)	31(9)	72(13)	36(9)	30(9)	6(7)	8(8)
C(27)	35(9)	85(14)	33(8)	-5(8)	28(7)	-15(8)
C(28)	44(9)	29(8)	63(11)	-6(7)	32(8)	-8(7)
C(29)	34(8)	44(9)	47(9)	20(7)	24(8)	5(7)
C(30)	40(9)	58(11)	25(7)	-4(7)	19(7)	-8(8)

Table S6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for $(py)_4UF_2I_2 \cdot 2py$ **(1)**..

	x	y	z	U(eq)
H(1)	1826	3067	4210	32
H(2)	2282	2495	3868	42
H(3)	4291	2201	5989	38
H(4)	5691	2483	8316	41
H(5)	5072	3050	8583	31
H(6)	2915	3739	3090	35
H(7)	4064	3493	1695	43
H(8)	6497	3244	3010	42
H(9)	7734	3246	5729	48
H(10)	6555	3503	7033	33
H(11)	5535	4341	9376	33
H(12)	6173	4705	11468	36
H(13)	4394	4784	12444	37
H(14)	2124	4455	11371	37
H(15)	1594	4105	9271	28
H(16)	1478	4624	6877	29
H(17)	-713	4955	6111	33
H(18)	-3128	4682	4743	30
H(19)	-3225	4094	4135	32
H(20)	-952	3799	4884	30
H(21)	7856	2391	11967	53
H(22)	9538	2301	11007	48
H(23)	10361	2772	10070	52
H(24)	9576	3329	10322	60
H(25)	7908	3388	11367	67
H(26)	-312	3944	2174	60
H(27)	-384	4508	2830	55
H(28)	-1177	4942	981	51
H(29)	-1968	4782	-1633	48
H(30)	-2044	4218	-2237	47

Table S7. Torsion angles [°]

for $(py)_4UF_2I_2 \cdot 2py$ **(1)**..

C(5)-N(1)-C(1)-C(2)	-1(2)	C(21)-C(22)-C(23)-C(24)	3(3)
U(1)-N(1)-C(1)-C(2)	174.3(11)	C(22)-C(23)-C(24)-C(25)	-2(3)
N(1)-C(1)-C(2)-C(3)	-1(2)	C(21)-N(5)-C(25)-C(24)	4(3)
C(1)-C(2)-C(3)-C(4)	1(2)	C(23)-C(24)-C(25)-N(5)	-1(3)
C(2)-C(3)-C(4)-C(5)	1(2)	C(30)-N(6)-C(26)-C(27)	0(3)
C(1)-N(1)-C(5)-C(4)	3(2)	N(6)-C(26)-C(27)-C(28)	-2(3)
U(1)-N(1)-C(5)-C(4)	-172.7(11)	C(26)-C(27)-C(28)-C(29)	1(2)
C(3)-C(4)-C(5)-N(1)	-2(2)	C(27)-C(28)-C(29)-C(30)	2(2)
C(10)-N(2)-C(6)-C(7)	3(2)	C(28)-C(29)-C(30)-N(6)	-3(3)
U(1)-N(2)-C(6)-C(7)	-166.5(11)	C(26)-N(6)-C(30)-C(29)	2(3)
N(2)-C(6)-C(7)-C(8)	-1(2)		
C(6)-C(7)-C(8)-C(9)	0(2)		
C(7)-C(8)-C(9)-C(10)	0(2)		
C(6)-N(2)-C(10)-C(9)	-3.7(19)		
U(1)-N(2)-C(10)-C(9)	165.7(10)		
C(8)-C(9)-C(10)-N(2)	2(2)		
C(15)-N(3)-C(11)-C(12)	1(2)		
U(1)-N(3)-C(11)-C(12)	178.8(11)		
N(3)-C(11)-C(12)-C(13)	-2(2)		
C(11)-C(12)-C(13)-C(14)	2(2)		
C(12)-C(13)-C(14)-C(15)	-3(2)		
C(11)-N(3)-C(15)-C(14)	-1(2)		
U(1)-N(3)-C(15)-C(14)	-179.0(10)		
C(13)-C(14)-C(15)-N(3)	2(2)		
C(20)-N(4)-C(16)-C(17)	-1(2)		
U(1)-N(4)-C(16)-C(17)	177.0(10)		
N(4)-C(16)-C(17)-C(18)	2(2)		
C(16)-C(17)-C(18)-C(19)	-1.1(19)		
C(17)-C(18)-C(19)-C(20)	0(2)		
C(16)-N(4)-C(20)-C(19)	-1(2)		
U(1)-N(4)-C(20)-C(19)	-178.6(11)		
C(18)-C(19)-C(20)-N(4)	1(2)		
C(25)-N(5)-C(21)-C(22)	-3(3)		
N(5)-C(21)-C(22)-C(23)	0(3)		

Table S8. Hydrogen bonds for $(py)_4UF_2I_2 \cdot 2py$ **(1)**. [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(1)-H(1)...F(1)	0.95	2.37	2.972(15)	121.2
C(6)-H(6)...F(1)	0.95	2.52	3.005(16)	112.0
C(20)-H(20)...F(1)	0.95	2.50	2.953(15)	109.2
C(26)-H(26)...F(1)	0.95	2.33	3.237(17)	160.3
C(5)-H(5)...F(2)	0.95	2.49	3.024(16)	115.5
C(10)-H(10)...F(2)	0.95	2.43	3.021(17)	120.1
C(11)-H(11)...F(2)	0.95	2.64	3.014(16)	103.9
C(15)-H(15)...I(1)	0.95	3.04	3.636(13)	122.6
C(16)-H(16)...I(2)	0.95	3.17	3.665(13)	114.0
C(7)-H(7)...I(1)#1	0.95	3.24	4.140(15)	159.0
C(9)-H(9)...I(1)#2	0.95	3.26	4.086(17)	147.2
C(22)-H(22)...I(1)#3	0.95	3.28	4.078(15)	142.5
C(24)-H(24)...I(1)#2	0.95	3.27	3.935(17)	128.7
C(5)-H(5)...N(5)	0.95	2.96	3.73(2)	138.5
C(11)-H(11)...I(2)	0.95	3.30	3.765(14)	112.1
C(20)-H(20)...I(1)	0.95	3.41	3.796(13)	107.1

Symmetry transformations used to generate equivalent atoms:

#1 x,y,z-1 #2 x+1,y,z #3 x+1,-y+1/2,z+1/2

Table S9. Crystal data and structure refinement for th2f5scf3_multiscan.

Identification code	th2f5scf3_multiscan	
Empirical formula	C63 H45 F20 N9 S3 Th2	
Formula weight	1868.34	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.1776(10) Å	α= 81.4051(15)°.
	b = 12.1625(11) Å	β= 86.7035(15)°.
	c = 25.368(2) Å	γ = 74.0481(15)°.
Volume	3278.2(5) $Å^3$	
Z	2	
Density (calculated)	1.893 Mg/m^3	
Absorption coefficient	4.732 mm^{-1}	
F(000)	1788	
Crystal size	0.21 x 0.17 x 0.06 mm^3	
Theta range for data collection	1.895 to 28.912°.	
Index ranges	-15<=h<=15, -16<=k<=16, -34<=l<=34	
Reflections collected	38001	
Independent reflections	17263 [R(int) = 0.0247]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.0526 and 0.0212	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	17263 / 1635 / 905	
Goodness-of-fit on F^2	1.144	
Final R indices [I>2sigma(I)]	R1 = 0.0360, wR2 = 0.0794	
R indices (all data)	R1 = 0.0438, wR2 = 0.0820	
Extinction coefficient	n/a	
Largest diff. peak and hole	3.295 and -1.248 e.$Å^{-3}$	

Table S10. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $(py)_7Th_2F_5(SC_6F_5)_3$ ·2py**(2)**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Th(1)	6701(1)	7782(1)	2593(1)	28(1)
Th(2)	7092(1)	10691(1)	2025(1)	25(1)
S(1)	8121(1)	7598(1)	3563(1)	34(1)
S(2)	9018(1)	9686(1)	1274(1)	32(1)
S(3)	4434(1)	11897(1)	2190(1)	34(1)
F(1)	8240(2)	8769(2)	2370(1)	30(1)
F(2)	6094(2)	9725(2)	2743(1)	32(1)
F(3)	6288(2)	9185(2)	1821(1)	29(1)
F(4)	6462(2)	6085(2)	2879(1)	36(1)
F(5)	7402(2)	12349(2)	1732(1)	34(1)
F(6)	6519(3)	9021(2)	4348(1)	55(1)
F(7)	5349(3)	8298(3)	5218(1)	70(1)
F(8)	5501(3)	6005(3)	5496(1)	63(1)
F(9)	6861(3)	4471(3)	4879(1)	57(1)
F(10)	8054(3)	5155(2)	4005(1)	49(1)
F(11)	7856(3)	9379(2)	286(1)	40(1)
F(12)	7639(3)	10691(3)	-661(1)	51(1)
F(13)	8557(3)	12582(2)	-837(1)	51(1)
F(14)	9705(3)	13117(2)	-29(1)	51(1)
F(15)	9923(3)	11826(3)	926(1)	46(1)
F(16)	2686(3)	11909(3)	1338(1)	47(1)
F(17)	1935(3)	13506(3)	491(1)	52(1)
F(18)	2754(3)	15433(3)	321(1)	53(1)
F(19)	4256(3)	15801(2)	1048(1)	53(1)
F(20)	4978(3)	14241(2)	1911(1)	46(1)
C(1)	7342(4)	7127(4)	4136(2)	33(1)
C(2)	6646(5)	7874(4)	4467(2)	40(1)
C(3)	6026(5)	7514(5)	4923(2)	46(1)
C(4)	6098(5)	6373(5)	5057(2)	45(1)
C(5)	6789(5)	5593(4)	4745(2)	43(1)
C(6)	7396(4)	5967(4)	4293(2)	37(1)
C(7)	8890(4)	10545(4)	650(2)	30(1)

C(8)	8333(4)	10300(3)	224(2)	31(1)
C(9)	8216(4)	10965(4)	-270(2)	37(1)
C(10)	8679(4)	11921(4)	-357(2)	38(1)
C(11)	9252(4)	12188(4)	51(2)	38(1)
C(12)	9352(4)	11508(4)	542(2)	34(1)
C(13)	3901(4)	12977(4)	1654(2)	31(1)
C(14)	3085(4)	12859(4)	1281(2)	34(1)
C(15)	2683(4)	13683(4)	844(2)	38(1)
C(16)	3083(4)	14669(4)	765(2)	39(1)
C(17)	3862(4)	14836(4)	1128(2)	37(1)
C(18)	4233(4)	14013(4)	1561(2)	34(1)
N(1)	6985(3)	6766(3)	1695(1)	33(1)
C(19)	7060(5)	5636(4)	1732(2)	40(1)
C(20)	7501(5)	4990(4)	1329(2)	48(1)
C(21)	7898(5)	5513(4)	859(2)	45(1)
C(22)	7808(5)	6678(4)	802(2)	40(1)
C(23)	7357(4)	7269(4)	1228(2)	34(1)
N(2)	8931(3)	6292(3)	2462(1)	32(1)
C(24)	9239(4)	5267(4)	2779(2)	36(1)
C(25)	10274(5)	4398(4)	2685(2)	42(1)
C(26)	11028(5)	4561(4)	2249(2)	49(1)
C(27)	10720(4)	5612(4)	1925(2)	43(1)
C(28)	9678(4)	6448(4)	2047(2)	36(1)
N(3)	4975(3)	8054(3)	3399(2)	39(1)
C(29)	4586(5)	7149(5)	3643(2)	47(1)
C(30)	3716(5)	7222(5)	4052(2)	53(1)
C(31)	3218(5)	8268(6)	4229(2)	61(2)
C(32)	3593(5)	9226(5)	3981(3)	61(2)
C(33)	4478(4)	9065(5)	3573(2)	48(1)
N(4)	4437(3)	7992(3)	2270(1)	34(1)
C(34)	3960(5)	7080(4)	2349(2)	45(1)
C(35)	2763(5)	7147(5)	2200(2)	55(1)
C(36)	2051(4)	8168(4)	1947(2)	44(1)
C(37)	2525(4)	9105(4)	1861(2)	37(1)
C(38)	3712(4)	8989(4)	2031(2)	34(1)
N(5)	9288(3)	10638(3)	2445(1)	32(1)

C(39)	9908(4)	11403(4)	2239(2)	35(1)
C(40)	11000(4)	11463(4)	2457(2)	40(1)
C(41)	11461(5)	10720(5)	2903(2)	48(1)
C(42)	10826(5)	9934(5)	3121(2)	51(1)
C(43)	9757(4)	9906(4)	2878(2)	39(1)
N(6)	6932(3)	11683(3)	2921(1)	31(1)
C(44)	6893(4)	12800(4)	2875(2)	38(1)
C(45)	6808(5)	13380(4)	3312(2)	44(1)
C(46)	6757(5)	12778(4)	3813(2)	49(1)
C(47)	6818(5)	11620(4)	3863(2)	46(1)
C(48)	6899(4)	11105(4)	3412(2)	37(1)
N(7)	6040(3)	11356(3)	1058(1)	30(1)
C(49)	6179(4)	12323(4)	748(2)	33(1)
C(50)	5635(4)	12723(4)	254(2)	39(1)
C(51)	4920(5)	12125(4)	68(2)	44(1)
C(52)	4744(4)	11150(4)	380(2)	40(1)
C(53)	5321(4)	10794(4)	865(2)	35(1)
N(8)	929(8)	10773(7)	4450(3)	109(2)
C(61)	1286(9)	10643(8)	4943(3)	101(3)
C(62)	746(8)	11329(9)	5297(3)	94(2)
C(63)	-209(8)	12268(8)	5143(4)	96(3)
C(64)	-624(8)	12429(8)	4622(4)	102(3)
C(65)	-10(7)	11620(8)	4303(3)	88(2)
N(9A)	3024(9)	4894(9)	3212(3)	57(3)
C(71A)	2027(9)	5525(5)	3491(5)	64(3)
C(72A)	1404(8)	4959(12)	3884(4)	72(3)
C(73A)	1777(12)	3762(13)	3998(4)	76(4)
C(74A)	2774(13)	3131(6)	3719(5)	70(3)
C(75A)	3398(8)	3697(9)	3326(4)	61(3)
N(9B)	1469(10)	4321(16)	4007(5)	75(4)
C(71B)	1696(14)	5300(9)	3708(7)	76(4)
C(72B)	2639(17)	5191(11)	3322(6)	65(4)
C(73B)	3356(12)	4101(16)	3235(5)	54(4)
C(74B)	3129(12)	3121(9)	3533(7)	68(4)
C(75B)	2186(14)	3231(11)	3919(5)	70(4)

Table S11. Bond lengths [Å] and angles [°] for $(py)_7Th_2F_5(SC_6F_5)_3 \cdot 2py$**(2)**.

Th(1)-F(4)	2.165(2)	F(18)-C(16)	1.347(5)
Th(1)-F(1)	2.354(2)	F(19)-C(17)	1.347(5)
Th(1)-F(2)	2.355(2)	F(20)-C(18)	1.358(5)
Th(1)-F(3)	2.373(2)	C(1)-C(2)	1.380(6)
Th(1)-N(4)	2.639(4)	C(1)-C(6)	1.393(6)
Th(1)-N(2)	2.685(4)	C(2)-C(3)	1.389(7)
Th(1)-N(1)	2.712(4)	C(3)-C(4)	1.360(7)
Th(1)-N(3)	2.722(4)	C(4)-C(5)	1.369(7)
Th(1)-S(1)	2.9529(11)	C(5)-C(6)	1.381(6)
Th(1)-Th(2)	3.7473(3)	C(7)-C(8)	1.387(6)
Th(2)-F(5)	2.155(2)	C(7)-C(12)	1.390(6)
Th(2)-F(3)	2.382(2)	C(8)-C(9)	1.378(6)
Th(2)-F(1)	2.397(2)	C(9)-C(10)	1.381(7)
Th(2)-F(2)	2.407(2)	C(10)-C(11)	1.372(7)
Th(2)-N(7)	2.697(3)	C(11)-C(12)	1.379(6)
Th(2)-N(6)	2.703(4)	C(13)-C(18)	1.392(6)
Th(2)-N(5)	2.713(3)	C(13)-C(14)	1.400(6)
Th(2)-S(2)	2.9206(11)	C(14)-C(15)	1.384(6)
Th(2)-S(3)	2.9669(11)	C(15)-C(16)	1.376(7)
S(1)-C(1)	1.754(4)	C(16)-C(17)	1.376(7)
S(2)-C(7)	1.752(4)	C(17)-C(18)	1.370(6)
S(3)-C(13)	1.748(4)	N(1)-C(19)	1.344(5)
F(6)-C(2)	1.352(5)	N(1)-C(23)	1.349(5)
F(7)-C(3)	1.340(6)	C(19)-C(20)	1.369(7)
F(8)-C(4)	1.347(5)	C(19)-H(19)	0.9500
F(9)-C(5)	1.337(5)	C(20)-C(21)	1.373(7)
F(10)-C(6)	1.344(5)	C(20)-H(20)	0.9500
F(11)-C(8)	1.354(5)	C(21)-C(22)	1.379(7)
F(12)-C(9)	1.342(5)	C(21)-H(21)	0.9500
F(13)-C(10)	1.347(5)	C(22)-C(23)	1.382(6)
F(14)-C(11)	1.344(5)	C(22)-H(22)	0.9500
F(15)-C(12)	1.351(5)	C(23)-H(23)	0.9500
F(16)-C(14)	1.335(5)	N(2)-C(28)	1.330(6)
F(17)-C(15)	1.337(5)	N(2)-C(24)	1.348(6)

C(24)-C(25)	1.373(6)	C(40)-H(40)	0.9500
C(24)-H(24)	0.9500	C(41)-C(42)	1.377(7)
C(25)-C(26)	1.376(7)	C(41)-H(41)	0.9500
C(25)-H(25)	0.9500	C(42)-C(43)	1.386(6)
C(26)-C(27)	1.380(7)	C(42)-H(42)	0.9500
C(26)-H(26)	0.9500	C(43)-H(43)	0.9500
C(27)-C(28)	1.374(7)	N(6)-C(44)	1.335(5)
C(27)-H(27)	0.9500	N(6)-C(48)	1.340(6)
C(28)-H(28)	0.9500	C(44)-C(45)	1.384(7)
N(3)-C(33)	1.332(7)	C(44)-H(44)	0.9500
N(3)-C(29)	1.346(6)	C(45)-C(46)	1.375(7)
C(29)-C(30)	1.377(7)	C(45)-H(45)	0.9500
C(29)-H(29)	0.9500	C(46)-C(47)	1.378(7)
C(30)-C(31)	1.372(9)	C(46)-H(46)	0.9500
C(30)-H(30)	0.9500	C(47)-C(48)	1.371(7)
C(31)-C(32)	1.397(8)	C(47)-H(47)	0.9500
C(31)-H(31)	0.9500	C(48)-H(48)	0.9500
C(32)-C(33)	1.387(7)	N(7)-C(53)	1.341(6)
C(32)-H(32)	0.9500	N(7)-C(49)	1.355(5)
C(33)-H(33)	0.9500	C(49)-C(50)	1.386(6)
N(4)-C(38)	1.339(6)	C(49)-H(49)	0.9500
N(4)-C(34)	1.342(6)	C(50)-C(51)	1.362(7)
C(34)-C(35)	1.389(7)	C(50)-H(50)	0.9500
C(34)-H(34)	0.9500	C(51)-C(52)	1.379(7)
C(35)-C(36)	1.367(7)	C(51)-H(51)	0.9500
C(35)-H(35)	0.9500	C(52)-C(53)	1.376(6)
C(36)-C(37)	1.368(7)	C(52)-H(52)	0.9500
C(36)-H(36)	0.9500	C(53)-H(53)	0.9500
C(37)-C(38)	1.382(6)	N(8)-C(65)	1.280(10)
C(37)-H(37)	0.9500	N(8)-C(61)	1.310(10)
C(38)-H(38)	0.9500	C(61)-C(62)	1.324(11)
N(5)-C(43)	1.338(6)	C(61)-H(61)	0.9500
N(5)-C(39)	1.337(5)	C(62)-C(63)	1.357(12)
C(39)-C(40)	1.393(6)	C(62)-H(62)	0.9500
C(39)-H(39)	0.9500	C(63)-C(64)	1.396(13)
C(40)-C(41)	1.367(7)	C(63)-H(63)	0.9500

C(64)-C(65)	1.376(12)	C(75A)-H(75A)	0.9500
C(64)-H(64)	0.9500	N(9B)-C(71B)	1.3900
C(65)-H(65)	0.9500	N(9B)-C(75B)	1.3900
N(9A)-C(71A)	1.3900	C(71B)-C(72B)	1.3900
N(9A)-C(75A)	1.3900	C(71B)-H(71B)	0.9500
C(71A)-C(72A)	1.3900	C(72B)-C(73B)	1.3900
C(71A)-H(71A)	0.9500	C(72B)-H(72B)	0.9500
C(72A)-C(73A)	1.3900	C(73B)-C(74B)	1.3900
C(72A)-H(72A)	0.9500	C(73B)-H(73B)	0.9500
C(73A)-C(74A)	1.3900	C(74B)-C(75B)	1.3900
C(73A)-H(73A)	0.9500	C(74B)-H(74B)	0.9500
C(74A)-C(75A)	1.3900	C(75B)-H(75B)	0.9500
C(74A)-H(74A)	0.9500		

F(4)-Th(1)-F(1)	142.17(9)	F(1)-Th(1)-N(3)	128.09(10)
F(4)-Th(1)-F(2)	143.55(9)	F(2)-Th(1)-N(3)	70.19(10)
F(1)-Th(1)-F(2)	65.74(8)	F(3)-Th(1)-N(3)	116.78(10)
F(4)-Th(1)-F(3)	139.06(9)	N(4)-Th(1)-N(3)	67.46(11)
F(1)-Th(1)-F(3)	65.23(8)	N(2)-Th(1)-N(3)	134.69(11)
F(2)-Th(1)-F(3)	64.00(8)	N(1)-Th(1)-N(3)	134.72(11)
F(4)-Th(1)-N(4)	78.30(10)	F(4)-Th(1)-S(1)	88.33(7)
F(1)-Th(1)-N(4)	135.97(9)	F(1)-Th(1)-S(1)	72.05(6)
F(2)-Th(1)-N(4)	89.86(10)	F(2)-Th(1)-S(1)	80.06(6)
F(3)-Th(1)-N(4)	71.24(9)	F(3)-Th(1)-S(1)	132.29(6)
F(4)-Th(1)-N(2)	74.36(10)	N(4)-Th(1)-S(1)	141.98(8)
F(1)-Th(1)-N(2)	69.20(9)	N(2)-Th(1)-S(1)	73.40(8)
F(2)-Th(1)-N(2)	132.80(9)	N(1)-Th(1)-S(1)	137.70(8)
F(3)-Th(1)-N(2)	108.45(9)	N(3)-Th(1)-S(1)	74.66(8)
N(4)-Th(1)-N(2)	133.98(11)	F(4)-Th(1)-Th(2)	176.98(7)
F(4)-Th(1)-N(1)	76.82(10)	F(1)-Th(1)-Th(2)	38.35(5)
F(1)-Th(1)-N(1)	96.02(9)	F(2)-Th(1)-Th(2)	38.61(5)
F(2)-Th(1)-N(1)	132.88(9)	F(3)-Th(1)-Th(2)	38.09(5)
F(3)-Th(1)-N(1)	68.90(9)	N(4)-Th(1)-Th(2)	100.20(8)
N(4)-Th(1)-N(1)	73.68(11)	N(2)-Th(1)-Th(2)	105.20(7)
N(2)-Th(1)-N(1)	64.52(11)	N(1)-Th(1)-Th(2)	100.27(7)
F(4)-Th(1)-N(3)	73.43(11)	N(3)-Th(1)-Th(2)	108.51(8)

S(1)-Th(1)-Th(2)	94.41(2)	S(2)-Th(2)-S(3)	146.65(3)
F(5)-Th(2)-F(3)	145.31(8)	F(5)-Th(2)-Th(1)	176.58(7)
F(5)-Th(2)-F(1)	139.79(8)	F(3)-Th(2)-Th(1)	37.92(5)
F(3)-Th(2)-F(1)	64.43(8)	F(1)-Th(2)-Th(1)	37.53(5)
F(5)-Th(2)-F(2)	141.75(9)	F(2)-Th(2)-Th(1)	37.62(6)
F(3)-Th(2)-F(2)	63.08(8)	N(7)-Th(2)-Th(1)	109.67(7)
F(1)-Th(2)-F(2)	64.28(8)	N(6)-Th(2)-Th(1)	100.80(7)
F(5)-Th(2)-N(7)	73.62(10)	N(5)-Th(2)-Th(1)	101.84(7)
F(3)-Th(2)-N(7)	71.78(9)	S(2)-Th(2)-Th(1)	91.76(2)
F(1)-Th(2)-N(7)	125.86(9)	S(3)-Th(2)-Th(1)	93.80(2)
F(2)-Th(2)-N(7)	120.49(9)	C(1)-S(1)-Th(1)	111.20(15)
F(5)-Th(2)-N(6)	77.04(10)	C(7)-S(2)-Th(2)	111.88(14)
F(3)-Th(2)-N(6)	131.43(9)	C(13)-S(3)-Th(2)	110.50(14)
F(1)-Th(2)-N(6)	98.81(9)	Th(1)-F(1)-Th(2)	104.12(8)
F(2)-Th(2)-N(6)	68.57(9)	Th(1)-F(2)-Th(2)	103.77(9)
N(7)-Th(2)-N(6)	134.58(10)	Th(1)-F(3)-Th(2)	104.00(9)
F(5)-Th(2)-N(5)	74.85(10)	C(2)-C(1)-C(6)	115.0(4)
F(3)-Th(2)-N(5)	131.41(9)	C(2)-C(1)-S(1)	122.6(3)
F(1)-Th(2)-N(5)	67.79(9)	C(6)-C(1)-S(1)	122.4(4)
F(2)-Th(2)-N(5)	103.32(9)	F(6)-C(2)-C(1)	120.0(4)
N(7)-Th(2)-N(5)	135.93(10)	F(6)-C(2)-C(3)	116.8(4)
N(6)-Th(2)-N(5)	64.08(11)	C(1)-C(2)-C(3)	123.2(4)
F(5)-Th(2)-S(2)	88.20(7)	F(7)-C(3)-C(4)	120.9(5)
F(3)-Th(2)-S(2)	80.42(6)	F(7)-C(3)-C(2)	119.6(5)
F(1)-Th(2)-S(2)	68.11(6)	C(4)-C(3)-C(2)	119.5(5)
F(2)-Th(2)-S(2)	128.79(6)	F(8)-C(4)-C(3)	120.5(5)
N(7)-Th(2)-S(2)	74.79(7)	F(8)-C(4)-C(5)	119.9(5)
N(6)-Th(2)-S(2)	138.03(8)	C(3)-C(4)-C(5)	119.6(4)
N(5)-Th(2)-S(2)	74.21(8)	F(9)-C(5)-C(4)	119.6(4)
F(5)-Th(2)-S(3)	88.11(7)	F(9)-C(5)-C(6)	120.4(5)
F(3)-Th(2)-S(3)	84.00(6)	C(4)-C(5)-C(6)	120.0(4)
F(1)-Th(2)-S(3)	129.47(6)	F(10)-C(6)-C(5)	116.8(4)
F(2)-Th(2)-S(3)	66.47(6)	F(10)-C(6)-C(1)	120.6(4)
N(7)-Th(2)-S(3)	72.37(7)	C(5)-C(6)-C(1)	122.5(4)
N(6)-Th(2)-S(3)	72.77(8)	C(8)-C(7)-C(12)	115.0(4)
N(5)-Th(2)-S(3)	136.03(8)	C(8)-C(7)-S(2)	122.1(3)

C(12)-C(7)-S(2)	122.9(3)	C(23)-N(1)-Th(1)	121.7(3)
F(11)-C(8)-C(9)	117.0(4)	N(1)-C(19)-C(20)	123.7(4)
F(11)-C(8)-C(7)	119.8(4)	N(1)-C(19)-H(19)	118.2
C(9)-C(8)-C(7)	123.2(4)	C(20)-C(19)-H(19)	118.2
F(12)-C(9)-C(8)	119.9(4)	C(19)-C(20)-C(21)	118.9(4)
F(12)-C(9)-C(10)	120.4(4)	C(19)-C(20)-H(20)	120.5
C(8)-C(9)-C(10)	119.7(4)	C(21)-C(20)-H(20)	120.5
F(13)-C(10)-C(11)	120.8(4)	C(20)-C(21)-C(22)	119.2(5)
F(13)-C(10)-C(9)	120.1(4)	C(20)-C(21)-H(21)	120.4
C(11)-C(10)-C(9)	119.1(4)	C(22)-C(21)-H(21)	120.4
F(14)-C(11)-C(10)	119.6(4)	C(21)-C(22)-C(23)	118.4(4)
F(14)-C(11)-C(12)	120.5(4)	C(21)-C(22)-H(22)	120.8
C(10)-C(11)-C(12)	119.9(4)	C(23)-C(22)-H(22)	120.8
F(15)-C(12)-C(11)	116.6(4)	N(1)-C(23)-C(22)	123.3(4)
F(15)-C(12)-C(7)	120.3(4)	N(1)-C(23)-H(23)	118.4
C(11)-C(12)-C(7)	123.1(4)	C(22)-C(23)-H(23)	118.4
C(18)-C(13)-C(14)	114.5(4)	C(28)-N(2)-C(24)	117.6(4)
C(18)-C(13)-S(3)	124.0(3)	C(28)-N(2)-Th(1)	122.4(3)
C(14)-C(13)-S(3)	121.6(3)	C(24)-N(2)-Th(1)	119.4(3)
F(16)-C(14)-C(15)	117.7(4)	N(2)-C(24)-C(25)	122.5(4)
F(16)-C(14)-C(13)	119.6(4)	N(2)-C(24)-H(24)	118.8
C(15)-C(14)-C(13)	122.7(4)	C(25)-C(24)-H(24)	118.8
F(17)-C(15)-C(16)	120.1(4)	C(24)-C(25)-C(26)	119.5(5)
F(17)-C(15)-C(14)	120.0(4)	C(24)-C(25)-H(25)	120.2
C(16)-C(15)-C(14)	119.8(4)	C(26)-C(25)-H(25)	120.2
F(18)-C(16)-C(17)	120.8(4)	C(25)-C(26)-C(27)	118.2(5)
F(18)-C(16)-C(15)	119.5(4)	C(25)-C(26)-H(26)	120.9
C(17)-C(16)-C(15)	119.6(4)	C(27)-C(26)-H(26)	120.9
F(19)-C(17)-C(18)	121.3(4)	C(28)-C(27)-C(26)	119.2(5)
F(19)-C(17)-C(16)	119.3(4)	C(28)-C(27)-H(27)	120.4
C(18)-C(17)-C(16)	119.4(4)	C(26)-C(27)-H(27)	120.4
F(20)-C(18)-C(17)	116.5(4)	N(2)-C(28)-C(27)	123.1(4)
F(20)-C(18)-C(13)	119.5(4)	N(2)-C(28)-H(28)	118.5
C(17)-C(18)-C(13)	124.0(4)	C(27)-C(28)-H(28)	118.5
C(19)-N(1)-C(23)	116.6(4)	C(33)-N(3)-C(29)	116.8(4)
C(19)-N(1)-Th(1)	119.8(3)	C(33)-N(3)-Th(1)	122.7(3)

C(29)-N(3)-Th(1)	120.5(3)	C(39)-N(5)-Th(2)	120.1(3)
N(3)-C(29)-C(30)	123.6(6)	N(5)-C(39)-C(40)	122.7(4)
N(3)-C(29)-H(29)	118.2	N(5)-C(39)-H(39)	118.7
C(30)-C(29)-H(29)	118.2	C(40)-C(39)-H(39)	118.7
C(31)-C(30)-C(29)	118.9(5)	C(41)-C(40)-C(39)	119.3(4)
C(31)-C(30)-H(30)	120.5	C(41)-C(40)-H(40)	120.4
C(29)-C(30)-H(30)	120.5	C(39)-C(40)-H(40)	120.4
C(30)-C(31)-C(32)	118.8(5)	C(40)-C(41)-C(42)	118.5(5)
C(30)-C(31)-H(31)	120.6	C(40)-C(41)-H(41)	120.8
C(32)-C(31)-H(31)	120.6	C(42)-C(41)-H(41)	120.8
C(33)-C(32)-C(31)	118.0(6)	C(41)-C(42)-C(43)	119.4(5)
C(33)-C(32)-H(32)	121.0	C(41)-C(42)-H(42)	120.3
C(31)-C(32)-H(32)	121.0	C(43)-C(42)-H(42)	120.3
N(3)-C(33)-C(32)	123.8(5)	N(5)-C(43)-C(42)	122.7(5)
N(3)-C(33)-H(33)	118.1	N(5)-C(43)-H(43)	118.7
C(32)-C(33)-H(33)	118.1	C(42)-C(43)-H(43)	118.7
C(38)-N(4)-C(34)	117.2(4)	C(44)-N(6)-C(48)	118.0(4)
C(38)-N(4)-Th(1)	122.7(3)	C(44)-N(6)-Th(2)	118.8(3)
C(34)-N(4)-Th(1)	120.1(3)	C(48)-N(6)-Th(2)	123.1(3)
N(4)-C(34)-C(35)	122.6(5)	N(6)-C(44)-C(45)	122.8(4)
N(4)-C(34)-H(34)	118.7	N(6)-C(44)-H(44)	118.6
C(35)-C(34)-H(34)	118.7	C(45)-C(44)-H(44)	118.6
C(36)-C(35)-C(34)	119.1(5)	C(46)-C(45)-C(44)	118.4(4)
C(36)-C(35)-H(35)	120.5	C(46)-C(45)-H(45)	120.8
C(34)-C(35)-H(35)	120.5	C(44)-C(45)-H(45)	120.8
C(37)-C(36)-C(35)	119.0(4)	C(45)-C(46)-C(47)	119.0(5)
C(37)-C(36)-H(36)	120.5	C(45)-C(46)-H(46)	120.5
C(35)-C(36)-H(36)	120.5	C(47)-C(46)-H(46)	120.5
C(36)-C(37)-C(38)	119.0(4)	C(48)-C(47)-C(46)	119.2(5)
C(36)-C(37)-H(37)	120.5	C(48)-C(47)-H(47)	120.4
C(38)-C(37)-H(37)	120.5	C(46)-C(47)-H(47)	120.4
N(4)-C(38)-C(37)	123.0(4)	N(6)-C(48)-C(47)	122.4(4)
N(4)-C(38)-H(38)	118.5	N(6)-C(48)-H(48)	118.8
C(37)-C(38)-H(38)	118.5	C(47)-C(48)-H(48)	118.8
C(43)-N(5)-C(39)	117.5(4)	C(53)-N(7)-C(49)	116.4(4)
C(43)-N(5)-Th(2)	122.3(3)	C(53)-N(7)-Th(2)	123.0(3)

C(49)-N(7)-Th(2)	120.5(3)	C(71A)-N(9A)-C(75A)	120.0
N(7)-C(49)-C(50)	123.1(4)	C(72A)-C(71A)-N(9A)	120.0
N(7)-C(49)-H(49)	118.4	C(72A)-C(71A)-H(71A)	120.0
C(50)-C(49)-H(49)	118.4	N(9A)-C(71A)-H(71A)	120.0
C(51)-C(50)-C(49)	118.9(4)	C(71A)-C(72A)-C(73A)	120.0
C(51)-C(50)-H(50)	120.5	C(71A)-C(72A)-H(72A)	120.0
C(49)-C(50)-H(50)	120.5	C(73A)-C(72A)-H(72A)	120.0
C(50)-C(51)-C(52)	119.0(4)	C(74A)-C(73A)-C(72A)	120.0
C(50)-C(51)-H(51)	120.5	C(74A)-C(73A)-H(73A)	120.0
C(52)-C(51)-H(51)	120.5	C(72A)-C(73A)-H(73A)	120.0
C(53)-C(52)-C(51)	119.0(5)	C(73A)-C(74A)-C(75A)	120.0
C(53)-C(52)-H(52)	120.5	C(73A)-C(74A)-H(74A)	120.0
C(51)-C(52)-H(52)	120.5	C(75A)-C(74A)-H(74A)	120.0
N(7)-C(53)-C(52)	123.4(4)	C(74A)-C(75A)-N(9A)	120.0
N(7)-C(53)-H(53)	118.3	C(74A)-C(75A)-H(75A)	120.0
C(52)-C(53)-H(53)	118.3	N(9A)-C(75A)-H(75A)	120.0
C(65)-N(8)-C(61)	117.4(8)	C(71B)-N(9B)-C(75B)	120.0
N(8)-C(61)-C(62)	124.5(9)	N(9B)-C(71B)-C(72B)	120.0
N(8)-C(61)-H(61)	117.8	N(9B)-C(71B)-H(71B)	120.0
C(62)-C(61)-H(61)	117.8	C(72B)-C(71B)-H(71B)	120.0
C(61)-C(62)-C(63)	119.1(9)	C(73B)-C(72B)-C(71B)	120.0
C(61)-C(62)-H(62)	120.4	C(73B)-C(72B)-H(72B)	120.0
C(63)-C(62)-H(62)	120.4	C(71B)-C(72B)-H(72B)	120.0
C(62)-C(63)-C(64)	118.0(8)	C(72B)-C(73B)-C(74B)	120.0
C(62)-C(63)-H(63)	121.0	C(72B)-C(73B)-H(73B)	120.0
C(64)-C(63)-H(63)	121.0	C(74B)-C(73B)-H(73B)	120.0
C(65)-C(64)-C(63)	116.6(9)	C(73B)-C(74B)-C(75B)	120.0
C(65)-C(64)-H(64)	121.7	C(73B)-C(74B)-H(74B)	120.0
C(63)-C(64)-H(64)	121.7	C(75B)-C(74B)-H(74B)	120.0
N(8)-C(65)-C(64)	124.3(9)	C(74B)-C(75B)-N(9B)	120.0
N(8)-C(65)-H(65)	117.9	C(74B)-C(75B)-H(75B)	120.0
C(64)-C(65)-H(65)	117.9	N(9B)-C(75B)-H(75B)	120.0

Table S12. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $(py)_7Th_2F_5(SC_6F_5)_3 \cdot 2py$**(2)**. 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}
Th(1)	29(1)	24(1)	30(1)	4(1)	-3(1)	-11(1)
Th(2)	28(1)	23(1)	26(1)	2(1)	-1(1)	-10(1)
S(1)	37(1)	37(1)	29(1)	3(1)	-3(1)	-14(1)
S(2)	32(1)	31(1)	29(1)	2(1)	0(1)	-6(1)
S(3)	30(1)	36(1)	33(1)	1(1)	2(1)	-10(1)
F(1)	28(1)	28(1)	34(1)	4(1)	-4(1)	-10(1)
F(2)	38(1)	28(1)	29(1)	2(1)	3(1)	-13(1)
F(3)	32(1)	26(1)	29(1)	2(1)	-3(1)	-11(1)
F(4)	36(1)	30(1)	43(1)	7(1)	-4(1)	-15(1)
F(5)	38(1)	28(1)	36(1)	4(1)	-2(1)	-14(1)
F(6)	64(2)	34(2)	62(2)	-4(1)	11(2)	-8(1)
F(7)	75(2)	62(2)	64(2)	-13(2)	27(2)	-7(2)
F(8)	73(2)	72(2)	44(2)	1(2)	19(2)	-28(2)
F(9)	86(2)	42(2)	45(2)	5(1)	6(2)	-28(2)
F(10)	75(2)	36(1)	34(1)	-4(1)	8(1)	-14(1)
F(11)	50(2)	38(1)	36(1)	-5(1)	-1(1)	-17(1)
F(12)	66(2)	56(2)	31(1)	-7(1)	-7(1)	-14(2)
F(13)	63(2)	44(2)	34(1)	9(1)	8(1)	-2(1)
F(14)	55(2)	41(2)	58(2)	7(1)	9(1)	-22(1)
F(15)	48(2)	50(2)	47(2)	-4(1)	-4(1)	-26(1)
F(16)	48(2)	49(2)	49(2)	-4(1)	-3(1)	-22(1)
F(17)	53(2)	59(2)	46(2)	-5(1)	-13(1)	-17(2)
F(18)	63(2)	42(2)	45(2)	4(1)	-13(1)	-1(1)
F(19)	64(2)	35(2)	60(2)	1(1)	-8(2)	-18(1)
F(20)	49(2)	45(2)	48(2)	-6(1)	-10(1)	-20(1)
C(1)	36(2)	36(2)	26(2)	3(2)	-6(2)	-10(2)
C(2)	44(2)	34(2)	38(2)	1(2)	-1(2)	-7(2)
C(3)	45(3)	49(3)	42(3)	-8(2)	7(2)	-7(2)
C(4)	47(3)	58(3)	31(2)	2(2)	6(2)	-19(2)
C(5)	55(3)	42(3)	34(2)	6(2)	-3(2)	-20(2)
C(6)	48(3)	36(2)	26(2)	0(2)	0(2)	-12(2)
C(7)	28(2)	31(2)	27(2)	0(2)	3(2)	-4(2)

C(8)	32(2)	26(2)	33(2)	-3(2)	2(2)	-7(2)
C(9)	37(2)	39(2)	29(2)	-4(2)	1(2)	-3(2)
C(10)	41(2)	34(2)	30(2)	5(2)	9(2)	-1(2)
C(11)	36(2)	30(2)	44(2)	0(2)	7(2)	-9(2)
C(12)	31(2)	33(2)	35(2)	-1(2)	2(2)	-9(2)
C(13)	26(2)	33(2)	32(2)	-5(2)	3(2)	-6(2)
C(14)	32(2)	36(2)	35(2)	-7(2)	5(2)	-11(2)
C(15)	34(2)	44(2)	33(2)	-5(2)	-2(2)	-7(2)
C(16)	40(2)	35(2)	34(2)	1(2)	-1(2)	-1(2)
C(17)	38(2)	29(2)	41(2)	-3(2)	4(2)	-7(2)
C(18)	30(2)	33(2)	37(2)	-8(2)	-1(2)	-8(2)
N(1)	38(2)	29(2)	34(2)	1(1)	-6(2)	-14(2)
C(19)	55(3)	31(2)	38(2)	0(2)	-5(2)	-21(2)
C(20)	74(4)	33(2)	45(3)	-4(2)	-8(2)	-26(2)
C(21)	59(3)	38(2)	41(3)	-9(2)	-4(2)	-13(2)
C(22)	50(3)	38(2)	33(2)	1(2)	-3(2)	-15(2)
C(23)	38(2)	29(2)	35(2)	1(2)	-6(2)	-13(2)
N(2)	32(2)	30(2)	35(2)	-3(1)	-2(1)	-11(1)
C(24)	40(2)	36(2)	34(2)	-4(2)	-1(2)	-12(2)
C(25)	47(3)	31(2)	48(3)	-5(2)	0(2)	-8(2)
C(26)	44(3)	39(3)	64(3)	-16(2)	10(2)	-12(2)
C(27)	40(2)	43(3)	48(3)	-11(2)	10(2)	-16(2)
C(28)	38(2)	40(2)	37(2)	-4(2)	-4(2)	-20(2)
N(3)	33(2)	42(2)	39(2)	9(2)	-4(2)	-14(2)
C(29)	48(3)	58(3)	39(3)	9(2)	-3(2)	-28(2)
C(30)	49(3)	67(3)	45(3)	18(3)	-1(2)	-29(3)
C(31)	39(3)	81(4)	53(3)	17(3)	10(2)	-14(3)
C(32)	42(3)	59(3)	68(4)	12(3)	17(3)	-3(3)
C(33)	37(2)	45(3)	52(3)	10(2)	7(2)	-7(2)
N(4)	33(2)	37(2)	33(2)	3(2)	-3(1)	-16(2)
C(34)	49(3)	41(3)	50(3)	9(2)	-15(2)	-24(2)
C(35)	48(3)	54(3)	71(4)	9(3)	-20(3)	-31(2)
C(36)	36(2)	52(3)	49(3)	-5(2)	-11(2)	-18(2)
C(37)	35(2)	43(2)	31(2)	-5(2)	-3(2)	-7(2)
C(38)	33(2)	34(2)	38(2)	-3(2)	1(2)	-12(2)
N(5)	32(2)	32(2)	31(2)	-4(1)	-1(1)	-10(1)

C(39)	36(2)	33(2)	39(2)	-7(2)	1(2)	-13(2)
C(40)	38(2)	41(2)	49(3)	-15(2)	5(2)	-20(2)
C(41)	39(2)	60(3)	51(3)	-15(2)	-5(2)	-20(2)
C(42)	53(3)	66(3)	38(3)	1(2)	-17(2)	-23(3)
C(43)	43(2)	43(2)	35(2)	-4(2)	-4(2)	-17(2)
N(6)	32(2)	27(2)	34(2)	-2(1)	0(1)	-8(1)
C(44)	42(2)	32(2)	39(2)	-1(2)	-5(2)	-10(2)
C(45)	55(3)	32(2)	46(3)	-10(2)	-3(2)	-12(2)
C(46)	62(3)	40(3)	44(3)	-17(2)	6(2)	-9(2)
C(47)	64(3)	41(3)	35(2)	-7(2)	10(2)	-17(2)
C(48)	42(2)	30(2)	37(2)	-5(2)	5(2)	-10(2)
N(7)	29(2)	30(2)	30(2)	-2(1)	3(1)	-6(1)
C(49)	30(2)	31(2)	33(2)	1(2)	6(2)	-5(2)
C(50)	38(2)	38(2)	31(2)	5(2)	4(2)	-2(2)
C(51)	45(3)	48(3)	29(2)	-5(2)	-5(2)	3(2)
C(52)	38(2)	40(2)	38(2)	-11(2)	-6(2)	-3(2)
C(53)	33(2)	33(2)	37(2)	-5(2)	1(2)	-6(2)
N(8)	110(5)	106(5)	100(5)	-34(4)	-28(4)	8(4)
C(61)	98(6)	114(6)	77(5)	-29(5)	-24(4)	8(5)
C(62)	77(5)	139(7)	74(5)	-39(5)	5(4)	-30(5)
C(63)	84(5)	108(6)	122(6)	-64(5)	43(5)	-50(4)
C(64)	76(5)	87(5)	134(7)	-10(5)	8(5)	-13(4)
C(65)	73(5)	106(6)	83(5)	-18(4)	-6(4)	-14(4)
N(9A)	51(5)	57(6)	66(5)	-11(5)	10(4)	-18(5)
C(71A)	57(6)	78(7)	65(7)	-26(6)	2(5)	-22(5)
C(72A)	75(6)	77(8)	72(7)	-12(6)	10(6)	-36(6)
C(73A)	76(7)	84(8)	65(6)	-11(6)	10(6)	-20(7)
C(74A)	70(7)	74(6)	68(7)	5(5)	-7(6)	-29(5)
C(75A)	59(6)	65(7)	62(6)	-1(6)	-9(5)	-24(5)
N(9B)	85(8)	67(8)	73(7)	-1(7)	-9(6)	-21(7)
C(71B)	86(8)	73(7)	74(9)	-7(7)	-2(7)	-30(7)
C(72B)	73(9)	60(7)	66(8)	-13(7)	-7(7)	-23(7)
C(73B)	53(6)	51(8)	58(7)	-10(6)	-5(6)	-12(6)
C(74B)	56(7)	78(8)	74(9)	2(7)	2(6)	-34(6)
C(75B)	61(9)	84(8)	64(8)	-4(8)	-8(7)	-17(8)

Table S13. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for $(py)_7Th_2F_5(SC_6F_5)_3 \cdot 2py$**(2)**.

	x	y	z	U(eq)
H(19)	6791	5264	2055	48
H(20)	7533	4193	1373	58
H(21)	8229	5078	578	55
H(22)	8051	7065	477	48
H(23)	7307	8070	1190	40
H(24)	8721	5142	3080	44
H(25)	10469	3689	2919	51
H(26)	11741	3967	2173	58
H(27)	11223	5756	1622	52
H(28)	9482	7172	1824	44
H(29)	4931	6418	3526	57
H(30)	3464	6560	4209	64
H(31)	2629	8339	4516	73
H(32)	3252	9967	4088	74
H(33)	4745	9713	3408	57
H(34)	4461	6361	2514	54
H(35)	2444	6491	2274	66
H(36)	1238	8227	1833	53
H(37)	2046	9825	1686	45
H(38)	4029	9648	1975	41
H(39)	9590	11928	1931	42
H(40)	11419	12015	2298	48
H(41)	12204	10746	3059	57
H(42)	11117	9415	3434	62
H(43)	9339	9345	3025	47
H(44)	6925	13215	2529	45
H(45)	6786	14175	3266	52
H(46)	6680	13155	4120	59
H(47)	6804	11184	4205	55
H(48)	6932	10308	3449	44

H(49)	6672	12747	876	40
H(50)	5760	13403	48	46
H(51)	4548	12377	-272	52
H(52)	4232	10731	262	47
H(53)	5204	10114	1074	42
H(61)	1981	10013	5055	121
H(62)	1024	11167	5655	113
H(63)	-584	12800	5383	116
H(64)	-1296	13065	4493	122
H(65)	-303	11696	3952	106
H(71A)	1772	6343	3412	77
H(72A)	722	5390	4074	86
H(73A)	1351	3375	4267	91
H(74A)	3030	2312	3798	84
H(75A)	4079	3265	3136	74
H(71B)	1206	6045	3768	91
H(72B)	2794	5860	3118	77
H(73B)	4001	4026	2971	65
H(74B)	3619	2376	3473	81
H(75B)	2031	2561	4123	85

Table S14. Torsion angles [°] for $(py)_7Th_2F_5(SC_6F_5)_3 \cdot 2py$**(2)**.

Th(1)-S(1)-C(1)-C(2)	-100.0(4)	F(11)-C(8)-C(9)-C(10)	179.7(4)
Th(1)-S(1)-C(1)-C(6)	81.0(4)	C(7)-C(8)-C(9)-C(10)	0.6(7)
C(6)-C(1)-C(2)-F(6)	-179.3(4)	F(12)-C(9)-C(10)-F(13)	-0.3(7)
S(1)-C(1)-C(2)-F(6)	1.7(6)	C(8)-C(9)-C(10)-F(13)	-179.3(4)
C(6)-C(1)-C(2)-C(3)	-0.7(7)	F(12)-C(9)-C(10)-C(11)	179.3(4)
S(1)-C(1)-C(2)-C(3)	-179.8(4)	C(8)-C(9)-C(10)-C(11)	0.2(7)
F(6)-C(2)-C(3)-F(7)	-0.1(7)	F(13)-C(10)-C(11)-F(14)	-0.4(7)
C(1)-C(2)-C(3)-F(7)	-178.7(5)	C(9)-C(10)-C(11)-F(14)	-180.0(4)
F(6)-C(2)-C(3)-C(4)	178.7(5)	F(13)-C(10)-C(11)-C(12)	179.1(4)
C(1)-C(2)-C(3)-C(4)	0.1(8)	C(9)-C(10)-C(11)-C(12)	-0.4(7)
F(7)-C(3)-C(4)-F(8)	-1.0(8)	F(14)-C(11)-C(12)-F(15)	-0.2(6)
C(2)-C(3)-C(4)-F(8)	-179.8(5)	C(10)-C(11)-C(12)-F(15)	-179.8(4)
F(7)-C(3)-C(4)-C(5)	179.4(5)	F(14)-C(11)-C(12)-C(7)	179.3(4)
C(2)-C(3)-C(4)-C(5)	0.6(8)	C(10)-C(11)-C(12)-C(7)	-0.2(7)
F(8)-C(4)-C(5)-F(9)	0.2(8)	C(8)-C(7)-C(12)-F(15)	-179.5(4)
C(3)-C(4)-C(5)-F(9)	179.8(5)	S(2)-C(7)-C(12)-F(15)	-0.4(6)
F(8)-C(4)-C(5)-C(6)	179.7(5)	C(8)-C(7)-C(12)-C(11)	0.9(6)
C(3)-C(4)-C(5)-C(6)	-0.7(8)	S(2)-C(7)-C(12)-C(11)	-179.9(3)
F(9)-C(5)-C(6)-F(10)	-0.3(7)	Th(2)-S(3)-C(13)-C(18)	-72.5(4)
C(4)-C(5)-C(6)-F(10)	-179.8(4)	Th(2)-S(3)-C(13)-C(14)	107.8(3)
F(9)-C(5)-C(6)-C(1)	179.6(4)	C(18)-C(13)-C(14)-F(16)	-178.7(4)
C(4)-C(5)-C(6)-C(1)	0.1(8)	S(3)-C(13)-C(14)-F(16)	1.1(6)
C(2)-C(1)-C(6)-F(10)	-179.5(4)	C(18)-C(13)-C(14)-C(15)	2.5(6)
S(1)-C(1)-C(6)-F(10)	-0.5(6)	S(3)-C(13)-C(14)-C(15)	-177.8(3)
C(2)-C(1)-C(6)-C(5)	0.6(7)	F(16)-C(14)-C(15)-F(17)	-1.0(6)
S(1)-C(1)-C(6)-C(5)	179.7(4)	C(13)-C(14)-C(15)-F(17)	177.9(4)
Th(2)-S(2)-C(7)-C(8)	-99.6(3)	F(16)-C(14)-C(15)-C(16)	-179.2(4)
Th(2)-S(2)-C(7)-C(12)	81.3(4)	C(13)-C(14)-C(15)-C(16)	-0.3(7)
C(12)-C(7)-C(8)-F(11)	179.8(4)	F(17)-C(15)-C(16)-F(18)	-2.5(7)
S(2)-C(7)-C(8)-F(11)	0.6(6)	C(14)-C(15)-C(16)-F(18)	175.7(4)
C(12)-C(7)-C(8)-C(9)	-1.1(6)	F(17)-C(15)-C(16)-C(17)	-179.4(4)
S(2)-C(7)-C(8)-C(9)	179.7(3)	C(14)-C(15)-C(16)-C(17)	-1.2(7)
F(11)-C(8)-C(9)-F(12)	0.6(6)	F(18)-C(16)-C(17)-F(19)	2.8(7)
C(7)-C(8)-C(9)-F(12)	-178.5(4)	C(15)-C(16)-C(17)-F(19)	179.7(4)

F(18)-C(16)-C(17)-C(18)	-176.5(4)	N(4)-C(34)-C(35)-C(36)	2.1(9)
C(15)-C(16)-C(17)-C(18)	0.3(7)	C(34)-C(35)-C(36)-C(37)	-1.8(9)
F(19)-C(17)-C(18)-F(20)	2.2(6)	C(35)-C(36)-C(37)-C(38)	0.2(8)
C(16)-C(17)-C(18)-F(20)	-178.5(4)	C(34)-N(4)-C(38)-C(37)	-0.9(7)
F(19)-C(17)-C(18)-C(13)	-177.2(4)	Th(1)-N(4)-C(38)-C(37)	-180.0(3)
C(16)-C(17)-C(18)-C(13)	2.1(7)	C(36)-C(37)-C(38)-N(4)	1.2(7)
C(14)-C(13)-C(18)-F(20)	177.2(4)	C(43)-N(5)-C(39)-C(40)	-0.2(6)
S(3)-C(13)-C(18)-F(20)	-2.5(6)	Th(2)-N(5)-C(39)-C(40)	176.0(3)
C(14)-C(13)-C(18)-C(17)	-3.5(6)	N(5)-C(39)-C(40)-C(41)	-0.5(7)
S(3)-C(13)-C(18)-C(17)	176.8(4)	C(39)-C(40)-C(41)-C(42)	0.1(8)
C(23)-N(1)-C(19)-C(20)	0.9(7)	C(40)-C(41)-C(42)-C(43)	1.0(8)
Th(1)-N(1)-C(19)-C(20)	-163.3(4)	C(39)-N(5)-C(43)-C(42)	1.4(7)
N(1)-C(19)-C(20)-C(21)	0.2(8)	Th(2)-N(5)-C(43)-C(42)	-174.7(4)
C(19)-C(20)-C(21)-C(22)	-1.8(8)	C(41)-C(42)-C(43)-N(5)	-1.9(8)
C(20)-C(21)-C(22)-C(23)	2.1(8)	C(48)-N(6)-C(44)-C(45)	-0.6(7)
C(19)-N(1)-C(23)-C(22)	-0.6(6)	Th(2)-N(6)-C(44)-C(45)	179.8(4)
Th(1)-N(1)-C(23)-C(22)	163.3(3)	N(6)-C(44)-C(45)-C(46)	-0.3(8)
C(21)-C(22)-C(23)-N(1)	-0.9(7)	C(44)-C(45)-C(46)-C(47)	1.4(8)
C(28)-N(2)-C(24)-C(25)	-0.6(6)	C(45)-C(46)-C(47)-C(48)	-1.5(8)
Th(1)-N(2)-C(24)-C(25)	170.0(4)	C(44)-N(6)-C(48)-C(47)	0.4(7)
N(2)-C(24)-C(25)-C(26)	-0.6(7)	Th(2)-N(6)-C(48)-C(47)	180.0(4)
C(24)-C(25)-C(26)-C(27)	1.1(8)	C(46)-C(47)-C(48)-N(6)	0.6(8)
C(25)-C(26)-C(27)-C(28)	-0.4(8)	C(53)-N(7)-C(49)-C(50)	-0.9(6)
C(24)-N(2)-C(28)-C(27)	1.3(6)	Th(2)-N(7)-C(49)-C(50)	-178.4(3)
Th(1)-N(2)-C(28)-C(27)	-169.0(3)	N(7)-C(49)-C(50)-C(51)	0.4(7)
C(26)-C(27)-C(28)-N(2)	-0.9(7)	C(49)-C(50)-C(51)-C(52)	0.9(7)
C(33)-N(3)-C(29)-C(30)	0.2(7)	C(50)-C(51)-C(52)-C(53)	-1.6(7)
Th(1)-N(3)-C(29)-C(30)	-179.9(4)	C(49)-N(7)-C(53)-C(52)	0.2(6)
N(3)-C(29)-C(30)-C(31)	-0.7(8)	Th(2)-N(7)-C(53)-C(52)	177.6(3)
C(29)-C(30)-C(31)-C(32)	1.3(9)	C(51)-C(52)-C(53)-N(7)	1.0(7)
C(30)-C(31)-C(32)-C(33)	-1.5(9)	C(65)-N(8)-C(61)-C(62)	-0.3(17)
C(29)-N(3)-C(33)-C(32)	-0.5(8)	N(8)-C(61)-C(62)-C(63)	-3.2(17)
Th(1)-N(3)-C(33)-C(32)	179.6(4)	C(61)-C(62)-C(63)-C(64)	3.6(14)
C(31)-C(32)-C(33)-N(3)	1.1(9)	C(62)-C(63)-C(64)-C(65)	-0.8(13)
C(38)-N(4)-C(34)-C(35)	-0.8(8)	C(61)-N(8)-C(65)-C(64)	3.3(16)
Th(1)-N(4)-C(34)-C(35)	178.3(4)	C(63)-C(64)-C(65)-N(8)	-2.7(14)

C(75A)-N(9A)-C(71A)-C(72A)	0.0
N(9A)-C(71A)-C(72A)-C(73A)	0.0
C(71A)-C(72A)-C(73A)-C(74A)	0.0
C(72A)-C(73A)-C(74A)-C(75A)	0.0
C(73A)-C(74A)-C(75A)-N(9A)	0.0
C(71A)-N(9A)-C(75A)-C(74A)	0.0
C(75B)-N(9B)-C(71B)-C(72B)	0.0
N(9B)-C(71B)-C(72B)-C(73B)	0.0
C(71B)-C(72B)-C(73B)-C(74B)	0.0
C(72B)-C(73B)-C(74B)-C(75B)	0.0
C(73B)-C(74B)-C(75B)-N(9B)	0.0
C(71B)-N(9B)-C(75B)-C(74B)	0.0

Table S15. Hydrogen bonds for $(py)_7Th_2F_5(SC_6F_5)_3 \cdot 2py$**(2)** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(43)-H(43)...F(1)	0.95	2.41	2.919(5)	113.1
C(33)-H(33)...F(2)	0.95	2.20	2.863(5)	126.1
C(48)-H(48)...F(2)	0.95	2.35	2.891(5)	115.6
C(23)-H(23)...F(3)	0.95	2.30	2.903(5)	120.8
C(38)-H(38)...F(3)	0.95	2.45	2.965(5)	113.6
C(53)-H(53)...F(3)	0.95	2.28	2.932(5)	125.1
C(19)-H(19)...F(4)	0.95	2.42	3.045(6)	123.4
C(24)-H(24)...F(4)	0.95	2.52	2.996(5)	111.4
C(29)-H(29)...F(4)	0.95	2.30	2.935(6)	123.8
C(34)-H(34)...F(4)	0.95	2.39	3.030(6)	124.5
C(39)-H(39)...F(5)	0.95	2.42	3.003(5)	119.2
C(44)-H(44)...F(5)	0.95	2.38	3.024(5)	124.5
C(49)-H(49)...F(5)	0.95	2.30	2.924(5)	122.5
C(24)-H(24)...F(10)	0.95	2.42	3.307(5)	154.9
C(39)-H(39)...F(15)	0.95	2.57	3.294(5)	133.0
C(43)-H(43)...S(1)	0.95	2.96	3.904(5)	175.6
C(38)-H(38)...S(3)	0.95	3.02	3.919(5)	157.6
C(45)-H(45)...F(4)#1	0.95	2.32	3.233(5)	160.4
C(20)-H(20)...F(5)#2	0.95	2.33	3.252(5)	163.1
C(30)-H(30)...F(9)#3	0.95	2.52	3.297(6)	139.3
C(64)-H(64)...F(9)#4	0.95	2.54	3.306(10)	137.7
C(64)-H(64)...F(10)#4	0.95	2.58	3.413(10)	146.1
C(50)-H(50)...F(18)#5	0.95	2.52	3.366(6)	148.4
C(62)-H(62)...S(1)#6	0.95	3.00	3.757(8)	137.6
C(32)-H(32)...N(8)	0.95	2.67	3.317(10)	125.6

Symmetry transformations used to generate equivalent atoms:

#1 x,y+1,z #2 x,y-1,z #3 -x+1,-y+1,-z+1 #4 x-1,y+1,z

#5 -x+1,-y+3,-z #6 -x+1,-y+2,-z+1

8. Fully labeled thermal ellipsoid diagrams for compounds 1and 2.

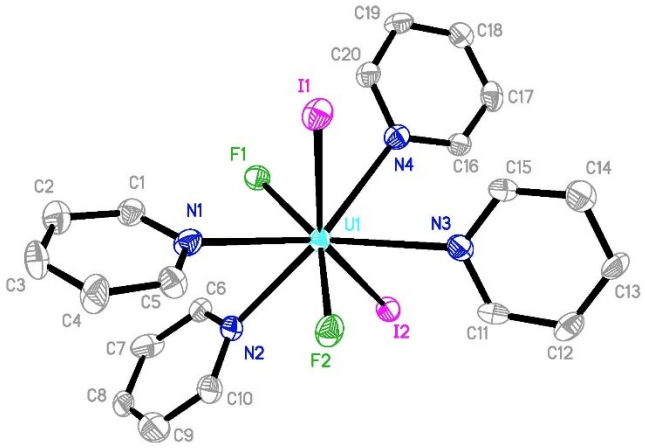

Figure *S8.* Fully labeled thermal ellipsoid plot for $(py)_4UF_2I_2 \cdot 2py$ (**1**)

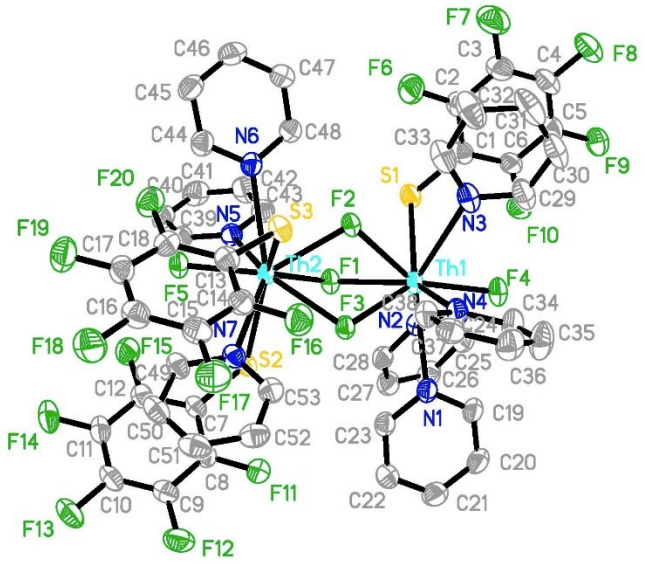

Figure *S9.* Fully labeled thermal ellipsoid plot for $(py)_7Th_2F_5(SC_6F_5)_3 \cdot 2py$ (**2**)

9. Unit cell packing diagrams common to compounds 1 and 2.

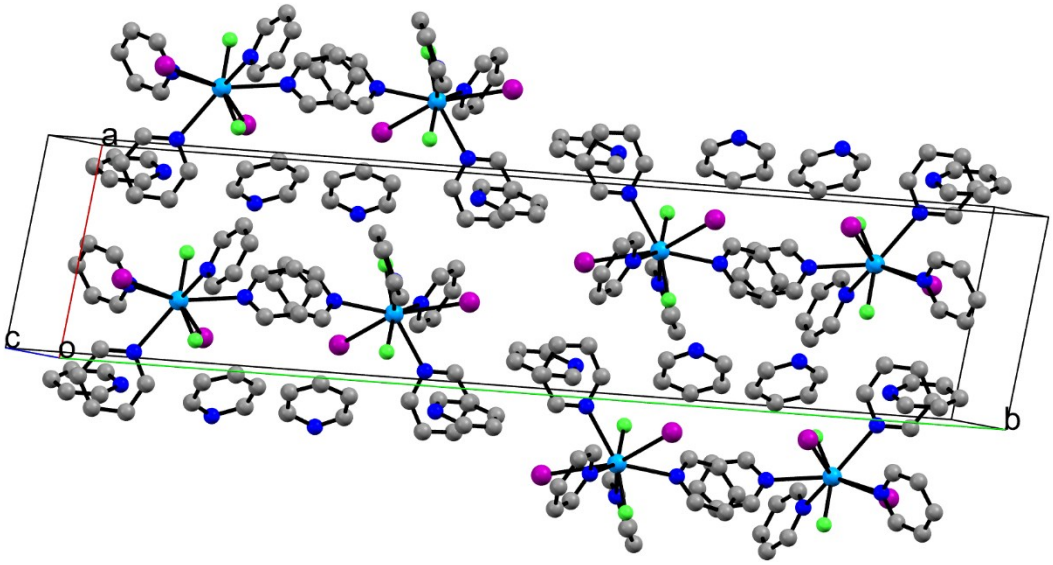

Figure *S10*. Unit cell packing for $(py)_4UF_2I_2 \cdot 2py$ (**1**)

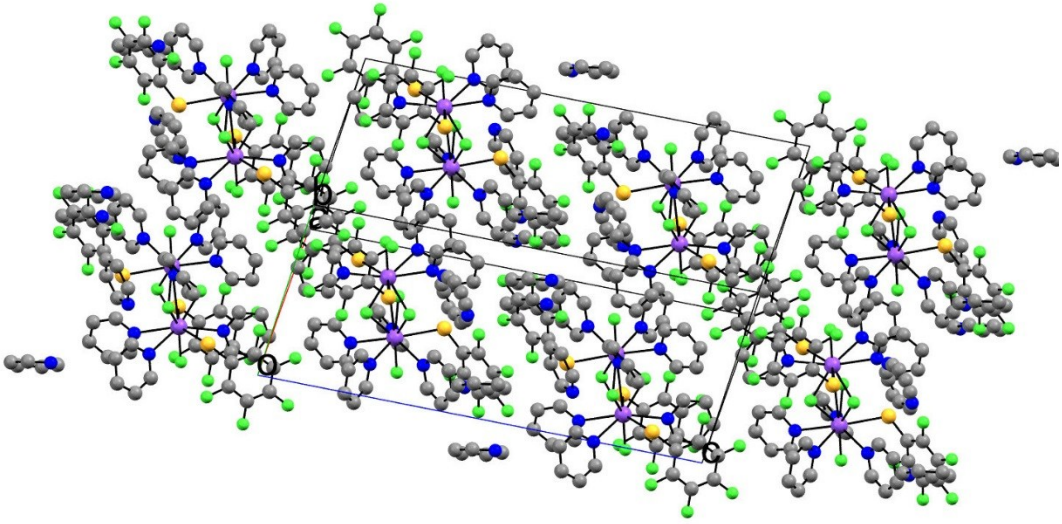

Figure *S11*. Unit cell packing for $(py)_7Th_2F_5(SC_6F_5)_3 \cdot 2py$(**2**)