# ELECTRONIC SUPPORTING INFORMATION

# A TRINUCLEAR METALLASILSESQUIOXANE OF URANIUM(III).

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#### **Experimental Procedures**

**General Considerations** Unless otherwise noted, all manipulations were carried out at ambient temperature under an inert argon atmosphere using Schlenk techniques and an MBraun glovebox equipped with a purifier unit. The water and oxygen levels were always kept at less than 0.1 ppm. Glassware was dried overnight at 140 °C before use.

**NMR experiments** were carried out using NMR tubes adapted with J. Young valves. <sup>1</sup>H spectra were recorded on a Bruker 400 MHz. NMR chemical shifts are reported in ppm with solvent as internal reference.

**Elemental analyses** were performed using a Thermo Scientific Flash 2000 Organic Elemental Analyzer at the Institute of Chemistry and Chemical Engineering at EPFL.

**Magnetic Measurements.** Magnetic measurements in solid state were performed using a QuantumDesign MPMS-5T superconducting quantum interference device (SQUID) magnetometer. The DC susceptibility was only measured up to 250 K due to the thermal sensitivity of the compounds. The crushed crystalline sample was enclosed in an evacuated and flame-sealed quartz capsule and placed inside a plastic straw. The measurements were reproduced from at least two different synthetic batches. Diamagnetic corrections were applied to the data using Pascal's constants.<sup>1</sup>

The magnetic moment per uranium of complex 1 and 2 was calculated at all temperatures using the formula:

$$\mu_{eff} = \sqrt{\frac{8\chi_{corr}T}{3}}$$

where  $\chi_{corr} = \chi_{meas} - \chi_{dia}$ ,  $\chi_{dia}$  was calculated using Pascal's constants.

**Starting materials** Unless otherwise noted, reagents were purchased from commercial suppliers and used without further purification. The solvents were purchased from Aldrich or Cortecnet (deuterated solvents) in their anhydrous form, conditioned under argon and vacuum distilled from K/benzophenone (toluene, hexane, THF, THF-*d*<sub>8</sub>, toluene-*d*<sub>8</sub>). DMSO-*d*<sub>6</sub> and cyclohexane-*d*<sub>12</sub> were freeze-degassed and dried over 3 Å molecular sieves for several days before use. <sup>15</sup>N<sub>2</sub> (98% <sup>15</sup>N) was purchased from Cortecnet and transferred to a flask equipped with a J-Young valve containing activated 3 Å molecular sieves prior to use. Precise amounts of labelled gases are added to reaction flasks or NMR tubes equipped with a J-Young valve using a short connector of known volume adapted on a Schlenk line equipped with a pressure sensor. Depleted uranium was purchased from Ibilabs, Florida, USA. [U<sup>III</sup>{N(SiMe<sub>3</sub>)<sub>3</sub>]<sup>2</sup>, and KC<sub>8</sub><sup>3</sup> were prepared according to the published procedures.

UV/Vis and NIR data were recorded using 1.0 mm cuvettes equipped with a J-Young valve and a Perkin Elmer 950 spectrometer.

IR spectra were recorded with a Perkin Elmer 1600 Series FTIR spectrophotometer flushed with nitrogen.

Caution: Depleted uranium (primary isotope <sup>238</sup>U) is a weak  $\alpha$ -emitter (4.197 MeV) with a half-life of 4.47×10<sup>9</sup> years. Manipulations and reactions should be carried out in monitored fume hoods or in an inert atmosphere glovebox in a radiation laboratory equipped with  $\alpha$ - and  $\beta$ -counting equipment.

### **Syntheses**

#### Synthesis of $[U_3(^{iBu}POSS)_3]$ , 1.

A cold (-40 °C) colorless solution of 1,3,5,7,9,11,14-Heptaisobutyltricyclo[7.3.3.1<sup>5,11</sup>]heptasiloxane-endo-3,7,14-triol, (<sup>i</sup>Bu)<sub>7</sub>Si<sub>7</sub>O<sub>9</sub>(OH)<sub>3</sub>, POSS<sup>*i*Bu</sup>H<sub>3</sub>, (<sup>i</sup>Bu = iso-butyl) (1.39 g, 1.76 mmol, 1 equiv.) in hexane (16.5 mL) was added to a stirring cold (-40 °C) dark purple suspension of [U<sup>III</sup>{N(SiMe<sub>3</sub>)<sub>3</sub>] (1.26 g, 1.76 mmol, 1 equiv.) in hexane (21 mL). The reaction mixture turned immediately dark brown and was stirred at -40 °C for 16 h yielding a dark brown solution. All volatiles were removed under vacuum for 16 h by alternating between -20 °C and short periods at 25°C (max 15 mins). The resulting sticky solid was then triturated in 5.0 mL of cold (-40 °C) hexane and dried for 3h. This step was repeated three times to remove all HN(SiMe<sub>3</sub>)<sub>3</sub>. The resulting dark powder was then dissolved in 10 mL of cold (-40 °C) hexane and storage at -40 °C for 12 h afforded XRD suitable black crystals of [**U**<sub>3</sub>(<sup>*i*Bu</sup>**POSS**)<sub>3</sub>], **1** (340.2 mg, 18.8% yield). <sup>1</sup>H NMR (400 MHz, cyclohexane-*d*<sub>12</sub>, 298 K):  $\delta$  18.56 ppm (s, 6H),  $\delta$  12.48 ppm (s, 6H),  $\delta$  9.83 ppm (s, 3H),  $\delta$  6.28 ppm (s, 18H),  $\delta$  4.05 ppm (s, 3H),  $\delta$  0.14 ppm (s, 18H),  $\delta$  0.13 ppm (s, 3H),  $\delta$  1.07 ppm (s, 3H),  $\delta$  0.51 ppm (s, 6H),  $\delta$  -3.46 ppm (s, 18H),  $\delta$  -3.74 ppm (s, 3H),  $\delta$  -4.20 ppm (s, 6H),  $\delta$  -6.58 ppm (s, 6H),  $\delta$  -7.46 ppm (s, 6H),  $\delta$  -10.45 ppm (s, 6H) (**Figure S1**). Anal. Calcd. for C<sub>84</sub>H<sub>189</sub>O<sub>36</sub>U<sub>3</sub>Si<sub>21</sub>: C: 32.77%; H: 6.19%; N: 0.00%. Found: C: 32.75%; H: 6.26%; N: 0.00%.

Attempts to recover additional amounts of the highly soluble trinuclear complex **1** by concentrating the hexane solution resulted in a product contaminated by another species that could be identified by X-ray diffraction as a tetranuclear complex  $[U_4({}^{iBu}POSS)_4]$  complex. Complex **1** was found to be unstable in toluene- $d_8$  and thf-  $d_8$  when warmed up to 25 °C (Figure S9 and Figure S10).

The protonolysis reaction performed in toluene in the same conditions resulted in a complicated reaction mixture with multiple resonances in the <sup>1</sup>H NMR spectrum (**Figure S7**), in which **1** could not be identified. The protonolysis performed in THF at 25°C resulted also in a complicated mixture with multiple resonances in the <sup>1</sup>H NMR spectrum, in which **1** could not be identified.

#### Synthesis of $[U_3(^{iBu}POSS)_3(crypt-\kappa^2-O,O')]$ , 2.

A cold (-40 °C) midnight blue-purple solution of **1** (61.2 mg, 0.0199 mmol, 1 equiv.) in hexane (2 mL) was added to prechilled (-40 °C) solid 2.2.2-cryptand (7.5 mg, 0.0199 mmol, 1 equiv.) The reaction mixture slowly turned to dark green-brown and was stirred at -40 °C for 72 h. The resultant solution was concentrated to 0.2 mL and storage at -40 °C for 12 h afforded dark red crystals of  $[U_3(^{iBu}POSS)_3(crypt-\kappa^2-O,O')]$ , **2** (36.1 mg, 52% yield). <sup>1</sup>H NMR (400 MHz) was recorded at 298 K in both cyclohexane- $d_{12}$  (Figure S13). Anal. Calcd. for  $C_{102}H_{225}N_2O_{42}U_3Si_{21}$ : C: 35.45%; H: 6.56%; N: 0.81%. Found: C: 35.87%; H: 6.65%; N: 0.52%.

Upon dissolution of **2** in THF- $d_8$ , cryptand is displaced giving the <sup>1</sup>H NMR spectrum of complex **1** (Figure S14).

Complexes **1** and **2** did not show any reaction with N<sub>2</sub> in cyclohexane (**Figure S12**) or THF (**Figure S11**) that could be detected by <sup>1</sup>H NMR spectroscopy.

#### Reaction of 1 with HCl under Argon.

Under an argon atmosphere, 1 mL of a cold (-80 °C) 2M solution of HCl in Et<sub>2</sub>O (2 mmol, 778 equiv.) was added to prechilled (-80 °C) complex **1** (7.9 mg, 0.00257 mmol, 1 equiv.) and the reaction mixture was left to react for 1 h at -80 °C before being vacuum-dried for 2 h to afford a mixture of dark and white solid. <sup>1</sup>H NMR in DMSO-d<sub>6</sub> with 2.1 mg of dimethylsulfone as internal standard allowed to observe the formation of 0.1 equiv. of NH<sub>4</sub>Cl although the batch of complex **1** used was certified free of nitrogen content by elemental analysis (**Figure S16**). This value was further used as blank value that was subtracted from the quantitative experiments that were conducted under an N<sub>2</sub> atmosphere with the same batch of complex **1**.

#### Reaction of 1 with N<sub>2</sub> in presence of excess KC<sub>8</sub> in THF.

Under an N<sub>2</sub> atmosphere, a cold (-40 °C) dark brown solution of **1** (4.2 mg, 0.00136 mmol, 1 equiv.) in THF (0.4 mL) was added to prechilled (-40 °C) solid KC<sub>8</sub> (1.8 mg, 0.0136 mmol, 10 equiv.) and was stirred at -40 °C for 5 days. After filtration of the reaction mixture on a cold (-40 °C) glass frit, a slightly lighter brown solution was obtained and was vacuum-dried for 1 h in a J. Young valve NMR tube (**Figure S17**). Then 1 mL of a cold (-80 °C) 2M solution of HCl in Et<sub>2</sub>O (2 mmol, 1470 equiv.) was added and the reaction mixture was left to react for 1 h at -80 °C before being vacuum-dried

for 2 h to afford a white solid. <sup>1</sup>H NMR in DMSO-d<sub>6</sub> with 5.1 mg of dimethylsulfone as internal standard allowed to observe the formation of 2.0 equiv. of  $NH_4Cl$  after blank correction (**Figure S18**).

# Reaction of 1 with $^{15}\text{N}_2$ in presence of excess KC\_8 in THF.

In a J. Young valve NMR tube, a cold (-40 °C) dark brown solution of **1** (6.2 mg, 0.0020 mmol, 1 equiv.) in THF (0.5 mL) was added to prechilled (-40 °C) solid KC<sub>8</sub> (2.7 mg, 0.0201 mmol, 10 equiv.). The J. Young valve NMR tube was then exposed to  ${}^{15}N_2$  (98%  ${}^{15}N$ , 800 mbar) and stored at -40 °C for 7 days. After filtration of the reaction mixture on a cold (-40 °C) glass frit, a slightly lighter brown solution was obtained and was vacuum-dried for 1 h in another J. Young valve NMR tube. Then 1 mL of a cold (-80 °C) 2M solution of HCl in Et<sub>2</sub>O (2 mmol, 1000 equiv.) was added and the reaction mixture was left to react for 30 minutes at -80 °C before being vacuum-dried for 30 minutes to afford a white solid. <sup>1</sup>H NMR in DMSO-d<sub>6</sub> with 2.3 mg of dimethylsulfone as internal standard allowed to observe the formation of 1.2 equiv. of NH<sub>4</sub>Cl after blank correction (**Figure S19**).

# Reaction of 1 with $N_2$ in presence of excess $KC_8$ in hexane.

Under an N<sub>2</sub> atmosphere, a cold (-40 °C) midnight blue-purple solution of **1** (8.0 mg, 0.0026 mmol, 1 equiv.) in hexane (0.8 mL) was added to prechilled (-40 °C) solid KC<sub>8</sub> (3.5 mg, 0.026 mmol, 10 equiv.) and was stirred at -40 °C for 7 days. After filtration of the reaction mixture on a cold (-40 °C) glass frit, a midnight blue-purple solution was obtained and was vacuum-dried for 1 h in a J. Young valve NMR tube, showing the presence of **1** (Figure S20). Then 1 mL of a cold (-80 °C) 2M solution of HCl in Et<sub>2</sub>O (2 mmol, 770 equiv.) was added and the reaction mixture was left to react for 1 h at -80 °C before being vacuum-dried for 2 h to afford a mixture of dark and white solid. <sup>1</sup>H NMR in DMSO-d<sub>6</sub> with 2.1 mg of dimethylsulfone as internal standard allowed to observe the formation of 0.3 equiv. of NH<sub>4</sub>Cl after blank correction (Figure S21).

#### **NMR Spectra**





Figure S4. <sup>1</sup>H NMR spectrum (400 MHz, 298 K) evolution of complex 1 upon solvent change.: top complex 1 in cyclohexane- $d_{12}$ , middle: complex 1 in thf- $d_8$ , bottom, complex 1 after dissolution in THF, thorough drying and dissolution in cyclohexane- $d_{12}$ .



**Figure S5.** <sup>1</sup>H NMR spectrum (400 MHz, cyclohexane-*d*<sub>12</sub>, 298 K) of the *in-situ* mixture resulting from the addition of 1.0 equiv. of <sup>*iBu*</sup>POSSH<sub>3</sub> to 1.0 equiv. of U(N(SiMe<sub>3</sub>)<sub>2</sub>)<sub>3</sub> after 3 and 5 days at -40 °C in hexane.



**Figure S6:** <sup>1</sup>H NMR spectra (400 MHz, cyclohexane- $d_{12}$ , 298 K) comparison of complex **1** isolated from the reaction mixture after addition of 1.0 equiv. of <sup>*iBu*</sup>POSSH<sub>3</sub> to 1.0 equiv. of U(N(SiMe<sub>3</sub>)<sub>2</sub>) (top) and a mixture of crystals of **1** and **[U<sub>4</sub>(iBuPOSS)<sub>4</sub>]** isolated as a second crop of crystals from the same reaction mixture.







Figure S8. <sup>1</sup>H NMR spectrum (400 MHz, cyclohexane-d<sub>12</sub>, 298 K) evolution of complex 1 at 25 °C in cyclohexane-d<sub>12</sub>.



Figure S10. <sup>1</sup>H NMR spectrum (400 MHz, toluene-*d*<sub>8</sub>, 233 K) evolution of a solution of complex **1** in toluene-*d*<sub>8</sub> at 298 K.



Chemical Shift (ppm)

**Figure S12:** <sup>1</sup>H NMR spectrum (400 MHz, cyclohexane- $d_{12}$ , 298 K) of the reaction mixture obtained 1 week after addition of N<sub>2</sub> (1 atm.) to complex **1** at 25°C in cyclohexane- $d_{12}$ .









Figure S17. <sup>1</sup>H NMR (400 MHz, THF- $d_8$ , 233 K). *in-situ* mixture after exposing complex 1 to N<sub>2</sub> (1 atm.) in presence of excess KC<sub>8</sub> (10 equiv.) after 5 days in THF.



8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0 Chemical shift (ppm)

Figure S18. <sup>1</sup>H NMR spectrum (400 MHz, DMSO- $d_6$ , 298 K) of the reaction mixture after exposing complex 1 to N<sub>2</sub> (1 atm) in presence of excess KC<sub>8</sub> (10 equiv.) for 5 days in THF at -40°C, followed by the addition of HCl (2M in Et<sub>2</sub>O).





**Figure S20:** <sup>1</sup>H NMR (400 MHz, cyclohexane-*d*<sub>12</sub>, 298 K). *in-situ* mixture after exposing complex **1** to N<sub>2</sub> (1 atm.) in presence of excess KC<sub>8</sub> (10 equiv.) after 7 days in hexane at -40°C.



**Figure S21:** <sup>1</sup>H NMR spectrum (400 MHz, DMSO-*d*<sub>6</sub>, 298 K) of the reaction mixture after exposing complex **1** to N<sub>2</sub> (1 atm) in presence of excess KC<sub>8</sub> (10 equiv.) for 7 days in hexane at -40°C, followed by the addition of HCl (2M in Et<sub>2</sub>O).

## Estimation of the hydrodynamic radius of complex 1

DOSY NMR experiments were performed at 298K for complex **1** dissolved cyclohexane- $d_{12}$  and thf- $d_8$  to obtain its diffusion coefficient in both solvents.

The spherical hydrodynamic radius (Stokes radius) of complex **1** was calculated from the Stokes-Einstein equation and compared to the value obtained from the solid-state structure and with a similar reference compound in the same solvent:

$$r_{sph} = \frac{k_B T}{6\pi\eta D}$$

where  $\eta$  (Pa.s<sup>-1</sup>) = viscosity of the medium,  $k_B$  (m<sup>2</sup>.kg.s<sup>-2</sup>.K<sup>-1</sup>) = Boltzmann constant, T = absolute temperature (K), D = diffusion coefficient (m<sup>2</sup>.s<sup>-1</sup>).

**Table S1.** Diffusion coefficient values for complex **1** dissolved in cyclohexane- $d_{12}$  and thf- $d_8$  ( $\eta$  (THF, 298K) = 0.46 mPa.s<sup>-1</sup> and  $\eta$  (cyclohexane, 298K) = 0.90 mPa.s<sup>-1</sup>).

	D (m <sup>2</sup> .s <sup>-1</sup> )	Stokes radii (Å)	Radius evaluated from crystal structure (Å)
Cyclohexane-d <sub>12</sub>	2.00 10 <sup>-10</sup>	12.1	10.3
THF-d <sub>8</sub>	4.16 10 <sup>-10</sup>	11.4	/

### X-ray crystallography

Suitable crystals were selected and mounted on various Rigaku diffractometers (XtaLAB Synergy R, DW system, HyPix-Arc 150 detector or SuperNova, Dual, Cu at home/near, AtlasS type detectors). The crystals were kept at a steady T = 140.00(10) K during data collection. Data were measured using scans with Cu or Mo K<sub> $\alpha$ </sub> radiations. The diffraction patterns were indexed and the total number of runs and images were based on the strategy calculation from the program CrysAlisPro 1.171.42.57a (Rigaku OD, 2022).<sup>4</sup> The unit cells were refined using CrysAlisPro 1.171.42.57a (Rigaku OD, 2022).<sup>2</sup> The unit cells were performed using CrysAlisPro 1.171.42.57a (Rigaku OD, 2022).<sup>4</sup> The unit cells were performed using CrysAlisPro 1.171.42.57a (Rigaku OD, 2022).<sup>4</sup> The unit cells were performed using CrysAlisPro 1.171.42.57a (Rigaku OD, 2022).<sup>4</sup> The unit cells were performed using CrysAlisPro 1.171.42.57a (Rigaku OD, 2022).<sup>4</sup> The unit cells were performed using CrysAlisPro 1.171.42.57a (Rigaku OD, 2022).<sup>4</sup> The unit cells were performed using CrysAlisPro 1.171.42.57a (Rigaku OD, 2022).<sup>4</sup> (Rigaku OD, 2022).

The structures were solved with the ShelXT<sup>5</sup> (Sheldrick, 2015) solution program using dual methods and by using Olex2  $1.5^6$  as the graphical interface. The models were refined with ShelXL<sup>7</sup> 2019/3 using full matrix least squares minimization on  $F^2$ . All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

Comments on structure problems and structure description:

The structural characterization of **1** was found to be disordered.

The disorder affects the entire structure and it is evidenced by two different orientations of the  $U_3$  core, being the occupancy of the main part equal to 0.770(2). Concerning the ligand, it was nonetheless impossible to establish the orientation of the minor component and, as expected, several restraints were needed to get acceptable displacement or geometric parameters. In particular for the anisotropic refinement, rigid bond restraints were applied to all atoms (RIGU card of the SHELXL refinement program) and same Uij restrictions were used for the carbon atoms (SIMU card). The isobutyl chains underwent some geometric restraints to adjust the atomic distances and angles. In particular some C-C, C...C were restrained by fixing their values in angstrom (DFIX 1.54, 2.5, respectively) or restrained to be equal (SADI card). In some cases, Si-C and Si...C distances were also fixed (DFIX 1.9, DFIX 3.5, DFIX 4.2).

The crystal structure of **U**<sub>4</sub>(*i<sup>Bu</sup>***POSS**)<sub>4</sub> displays disorder problems as well and similar restraints/constraints were applied to the alkyl chains in order to get reasonable displacement parameters (RIGU, SIMU, EADP and ISOR cards) and atomic distances (SADI, DFIX cards). The crystal shows twinning issues (BASF parameter = 0.451(2)) and the solvent (5.5 hexane) was finally removed from the model in the last stages of the refinement by the SQUEEZE/BYPASS procedure.

The three uranium centres in **2** show different coordination environments, U1 is bound to three anionic siloxide oxygens and one silyl ether oxygen atom of the coordinated <sup>*iBu*</sup>POSS ligand and three bridging siloxide oxygens from the two adjacent U(<sup>*iBu*</sup>POSS) moieties. U2 is coordinated by five siloxide oxygens and two oxygen atoms from the cryptand and U3 is bound by five siloxide oxygens and two silyl ether oxygen atoms of the <sup>*iBu*</sup>POSS ligand backbone.

The four uranium centers in  $[U_4(^{iBu}POSS)_4]$  are each coordinated by seven oxygen atoms, six of them being anionic siloxide oxygens one. In the core of the structure, eight bridging oxygens can be found. Four of them are bridging three uranium centres while the other four are only bridging two uranium ions. Selected bond lengths (Å): U1-U2 3.597(1), U1-U3 4.256(1), U1-U4 3.598(1), U2-U3 3.588(1), U2-U4 4.257(2), U3-U4 3.597(1).

Complex	1	2	U₄( <sup>iBu</sup> POSS)₄
Formula	$C_{93}H_{21}O_{36}Si_{21}U_{3}$	$C_{102}H_{225}N_2O_{42}Si_{21}U_3$	$C_{112}O_{48}Si_{28}U_4$
<i>D<sub>calc.</sub></i> / g cm <sup>-3</sup>	1.427	1.407	1.305
<i>μ</i> /mm⁻¹	11.897	10.314	3.523
Formula Weight	3018.08	3455.81	3851.76
Colour	Brown-red	clear dark red	lustrous dark brown
Shape	irregular	prism-shaped	irregular-shaped
Size/mm <sup>3</sup>	0.34×0.25×0.21	0.17×0.09×0.07	0.42×0.32×0.22
Т/К	140.00(10)	139.98(11)	140.00(10)
Crystal System	triclinic	triclinic	monoclinic
Space Group	<i>P</i> -1	<i>P</i> -1	C2/c
a/Å	14.7163(7)	18.0726(4)	33.7165(7)
b/Å	22.3387(9)	19.3200(4)	33.7274(5)
<i>c</i> /Å	24.0090(11)	25.3604(5)	35.2400(9)
$\alpha / $	65.307(4)	98.4318(18)	90
βſ°	87.504(4)	90.6353(18)	101.864(2)
γ/°	78.555(4)	110.969(2)	90
V/Å <sup>3</sup>	7021.6(6)	8159.7(3)	39218.0(15)
Ζ	2	2	8
Ζ'	1	1	1
Wavelength/Å	1.54184	1.54184	0.71073
Radiation type	Cu K $_{\alpha}$	<b>Cu K</b> <sub>α</sub>	Μο Κα
$\Theta_{min}/^{\circ}$	3.411	2.804	2.685
$\Theta_{max}/^{\circ}$	66.600	72.657	26.372
Measured Refl's.	56710	67579	77282
Indep't Refl's	24790	31473	77282
Refl's I≥2 <i>o</i> (I)	13031	22680	55856
R <sub>int</sub>	0.0967	0.0475	/
Parameters	1325	1573	1718
Restraints	2254	2719	2761
Largest Peak	3.331	5.045	3.264
Deepest Hole	-1.187	-2.632	-6.528
GooF	1.202	1.038	1.087
$wR_2$ (all data)	0.3936	0.1848	0.3366
wR <sub>2</sub>	0.3490	0.165	0.3271
$R_1$ (all data)	0.1968	0.0891	0.1456
<i>R</i> <sub>1</sub>	0.1307	0.0634	0.1234
CCDC #	2304632	2240989	2304633

Table S2. X-ray data for complexes 1 and 2 and [U<sub>4</sub>(<sup>iBu</sup>POSS)<sub>4</sub>].

# **SQUID** magnetometry



Figure S22. Solid-state temperature-dependent magnetic susceptibility of  $U_3$ <sup>(*iBu*</sup>POSS)<sub>3</sub>, **1**, recorded at 1 T, plotted as (a)  $\mu_{eff}$ /complex vs T (b)  $\chi$ T vs T, (c)  $\chi$  vs T and (d) 1/ $\chi$  vs T.



Figure S23. Solid-state temperature-dependent magnetic susceptibility of  $U_3(^{iBu}POSS)_3(crypt-\kappa^2-O,O')$ , 2, recorded at 1 T, plotted as (a)  $\mu_{eff}/U$  center vs T (b)  $\chi$ T vs T, (c)  $\chi$  vs T and (d)  $1/\chi$  vs T.



Figure S25: UV/Vis spectrum of a 2.5 mM hexane solution of complex 2 at 25°C.



Figure S26: UV/Vis spectrum of a 2.5 mM THF solution of complex 1 at 25°C.



Figure S27: NIR spectrum of a 2.5 mM hexane solution of complex 1 at 25°C.



Figure S28: NIR spectrum of a 2.5 mM hexane solution of complex 2 at 25°C.

IR data



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