

Supporting Information for:

Reversible Chalcogen Atom Transfer to a Terminal Uranium Sulfide

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Experimental

General. All reactions and subsequent manipulations were performed under anaerobic and anhydrous conditions under an atmosphere of nitrogen. Hexanes, Et₂O, and toluene were dried using a Vacuum Atmospheres DRI-SOLV Solvent Purification system and stored over 3Å sieves for 24 h prior to use. Tetrahydrofuran (THF) was distilled twice, first from calcium hydride and then from sodium benzophenone ketyl, and stored over 3Å molecular sieves for 24 h prior to use. Pyridine and pyridine-*d*₅ were dried over 3Å molecular sieves for 24 h prior to use. [K(18-crown-6)][U(S)(NR₂)₃] (**1**),¹ [U(NR₂)₃]² and [U(I)(NR₂)₃]³ were synthesized according to the previously reported procedures. All other reagents were purchased from commercial suppliers and used as received.

NMR spectra were recorded on a Varian UNITY INOVA 400, a Varian UNITY INOVA 500 spectrometer, a Varian UNITY INOVA 600 MHz spectrometer, or an Agilent Technologies 400-MR DD2 400 MHz Spectrometer. ¹H NMR spectra were referenced to external SiMe₄ using the residual protio solvent peaks as internal standards. ³¹P{¹H} NMR spectra were referenced indirectly with the ¹H resonance of SiMe₄ at 0 ppm, according to IUPAC standard,^{4,5} using the residual solvent peaks as internal standards. IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer with a NXR FT Raman Module. UV-Vis / NIR experiments were performed on a UV-3600 Shimadzu spectrophotometer. Elemental analyses were performed by the Micro-Analytical Facility at the University of California, Berkeley.

X-ray Crystallography. Data for **2**, **3**, **4**, and **5** were collected on a Bruker KAPPA APEX II diffractometer equipped with an APEX II CCD detector using a TRIUMPH

monochromator with a Mo K α X-ray source ($\alpha = 0.71073 \text{ \AA}$). The crystals were mounted on a cryoloop under Paratone-N oil, and all data were collected at 100(2) K using an Oxford nitrogen gas cryostream. Data were collected using ω scans with 0.5° frame widths. Frame exposures of 2 s (low angle), 10 s (medium angle), and 15 s (high angle) were used for **2**. Frame exposures of 2 s (low angle) and 5 s (high angle) were used for **3**. Frame exposures of 10 s (low angle) and 15 s (high angle) were used for **4** and **5**. Data collection and cell parameter determinations were conducted using the SMART program.⁶ Integration of the data frames and final cell parameter refinements were performed using SAINT software.⁷ Absorption corrections of the data were carried out using the multi-scan method SADABS.⁸ Subsequent calculations were carried out using SHELXTL.⁹ Structure determination was done using direct or Patterson methods and difference Fourier techniques. All hydrogen atom positions were idealized, and rode on the atom of attachment. Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXTL.⁹

Three of the sulfur atoms (S1, S2, and S3) in complex **4** exhibited positional disorder and were modeled over two positions in an 80:20 ratio. The anisotropic displacement parameters of these disordered atoms were constrained with the EADP command, and the bond distances between pairs of atoms, e.g. S1-S2 and S1b-S2b, were constrained with the SADI command.

Synthesis of [K(18-crown-6)][(U(η^2 -S₂)(NR₂)₃] (2**).** *Method A:* To an orange, cold (-25 °C), stirring solution of [K(18-crown-6)][U(S)(NR₂)₃] (**1**) (50.0 mg, 0.047 mmol) in a 2:1 mixture of Et₂O:tetrahydrofuran (3 mL) was added S₈ (1.6 mg 0.0062 mmol). The color of the solution became dark red-orange upon addition. The solution was allowed to

stir for 15 min, whereupon the solvent was removed in vacuo to provide a red-orange solid. The solid was then extracted with Et₂O (4 mL), and the mixture was filtered through a Celite column supported on glass wool (0.5 cm × 3 cm) to provide a dark orange-red solution. The volume of the filtrate was reduced to 1 mL in vacuo. Storage of this solution at -25 °C for 24 h resulted in the deposition of red-orange crystals, which were isolated by decanting off the supernatant (15.3 mg, 30%). The volume of the supernatant was then reduced in vacuo to 0.5 mL, and the solution was transferred to a 4 mL scintillation vial that was placed inside a 20 mL scintillation vial. Toluene (4 mL) was then added to the outer vial. Storage of this two vial system for 48 h resulted in the deposition of more red-orange crystalline solid, which was isolated by decanting off the supernatant. Total yield: 30.5 mg, 59%. Anal. Calcd for C₃₀H₇₈KN₃O₆S₂Si₆U: C, 33.16; H, 7.23; N, 3.87. Found: C, 33.48; H, 7.12; N, 3.71. ¹H NMR (400 MHz, 25 °C, pyridine-*d*₅): δ -8.18 (br s, 54H, NSiCH₃), 3.53 (br s, 24H, 18-crown-6). IR (KBr Pellet, cm⁻¹): 489 (w), 528 (w), 608 (m), 663 (m), 772 (m), 842 (s), 932 (s), 964 (m), 1110 (s), 1182 (m), 1250 (s), 1285 (w), 1352 (m), 1454 (w), 1473 (w). UV-Vis/NIR (C₄H₈O, 3.65 mM, 25 °C, L·mol⁻¹·cm⁻¹): 1024 (ε = 51), 1080 (ε = 51), 1318 (ε = 22), 1450 (ε = 10), 1594 (ε = 9), 1804 (ε = 5), 2058 (ε = 34).

Method B: To an orange, cold (-25 °C), stirring solution of [K(18-crown-6)][U(S₃)(NR₂)₃] (**3**) (91.1 mg, 0.081 mmol) in Et₂O (3 mL) was added a cold (-25 °C) solution of Et₃P (12 μL, 0.081 mmol) in Et₂O (2 mL). The color of the solution became red-orange upon addition. After 1 h, the solution was filtered through a Celite column supported on glass wool (0.5 cm × 3 cm) to provide a dark red-orange solution. Concentration of this solution in vacuo to 3 mL followed by storage at -25 °C for 24 h

resulted in the deposition of colorless crystals, subsequently identified as $\text{Et}_3\text{P}=\text{S}$ by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy (Figure S3).¹⁰ These were isolated by decanting off the supernatant. The volume of the supernatant was reduced in vacuo to 2 mL and then the solution was transferred to a 4 mL scintillation vial that was placed inside a 20 mL scintillation vial. Toluene (6 mL) was then added to the outer vial. Storage of this two vial system for 48 h resulted in the deposition of a red-orange crystalline solid, which was isolated by decanting the supernatant (52.2 mg, 59%). This material was subsequently identified as **2** by comparison of its ^1H NMR spectrum to that of independently prepared material. ^1H NMR (400 MHz, 25 °C, pyridine- d_5): δ -7.95 (br s, 54H, NSiCH_3), 3.52 (br s, 24H, 18-crown-6).

Method C: To a purple, cold (-25 °C), stirring solution of $[\text{U}(\text{NR}_2)_3]$ (129.4 mg, 0.18 mmol) in Et_2O (2 mL) was added a cold solution of $[\text{K}(18\text{-crown-6})]_2[\text{S}_4]$ (**4**) (66.9.0 mg, 0.09 mmol) in pyridine (2 mL). The color of the solution became dark red-orange upon addition. After 10 min the solvent was removed in vacuo and the resulting solids were triturated with pentane (3×3 mL) and Et_2O (3×3 mL). The red-orange powder was then extracted with Et_2O (5 mL) and filtered through a Celite column supported on glass wool ($0.5 \text{ cm} \times 3 \text{ cm}$) to provide a dark red-orange solution. The filtrate was then concentrated in vacuo to 2 mL and layered with pentane (3 mL). Storage of this solution at -25 °C for 24 h resulted in the deposition of red-orange crystals, which were isolated by decanting off the supernatant (52.2 mg, 27%). Subsequent concentration of the mother liquor and storage at -25 °C for 24 h resulted in the deposition of additional crystals. Total yield: 82.9 mg, 42%. ^1H NMR (600 MHz, 25 °C, pyridine- d_5): δ -8.20 (br s, 54H, NSiCH_3), 3.52 (br s, 24H, 18-crown-6).

Synthesis of [K(18-crown-6)][U(η^3 -S₃)(NR₂)₃] (3). *Method A:* To a red-orange, cold (-25 °C), stirring solution of [K(18-crown-6)][U(η^2 -S₂)(NR₂)₃] (2) (98.7 mg, 0.091 mmol) in tetrahydrofuran (3 mL) was added S₈ (3.6 mg, 0.014 mmol). This mixture was allowed to stir for 3 h, whereupon the solvent was removed in vacuo to provide a dark orange solid, which was triturated with Et₂O (4 mL). The resulting dark orange powder was extracted with Et₂O (4 mL) and filtered through a Celite column supported on glass wool (0.5 cm × 3 cm) to provide a dark orange solution. The volume of the filtrate was reduced in vacuo to 1 mL. The filtrate was then transferred to a 4 mL scintillation vial that was placed inside a 20 mL scintillation vial. Toluene (6 mL) was then added to the outer vial. Storage of this two vial system for 72 h resulted in the deposition of orange crystals, which were isolated by decanting off the supernatant (34.3 mg, 34%). Anal. Calcd for C₃₀H₇₈KN₃O₆S₃Si₆U: C, 32.21; H, 7.03; N, 3.76. Found: C, 32.79; H, 7.02; N, 3.79. ¹H NMR (400 MHz, 25 °C, pyridine-*d*₅): δ -7.20 (br s, 54H, NSiCH₃, FWHM = 2700 Hz), 3.65 (br s, 24H, 18-crown-6). IR (KBr Pellet, cm⁻¹): 497 (w), 608 (m), 665 (m), 773 (m), 844 (s), 891 (s), 917 (s), 964 (m), 1055 (w), 1112 (s), 1182 (w), 1249 (s), 1284 (w), 1352 (m), 1454 (w), 1473 (w). UV-Vis/NIR (C₄H₈O, 4.60 mM, 25 °C, L·mol⁻¹·cm⁻¹): 626 (ϵ = 74), 968 (ϵ = 36), 1044 (ϵ = 43), 1110 (ϵ = 40), 1262 (ϵ = 27), 1472 (ϵ = 25), 1586 (ϵ = 30), 1802 (ϵ = 29), 1938 (ϵ = 45).

Method B: To a cold (-25 °C), stirring mixture of [U(I)(NR₂)₃] (124.9 mg, 0.15 mmol) in tetrahydrofuran (3 mL) was added a cold solution of [K(18-crown-6)]₂[S₄] (4) (94.0 mg, 0.13 mmol) in pyridine (4 mL). The color of the solution became dark orange upon addition. The solution was allowed to stir for 30 min, whereupon the solvent was then removed in vacuo to provide a dark orange solid, which was then triturated with

hexanes (5 mL), Et₂O (5 mL), hexanes (3 mL), and Et₂O (3 mL). The resulting dark orange powder was then extracted with Et₂O (10 mL), and the mixture was filtered through a Celite column supported on glass wool (0.5 cm × 3 cm) to provide a dark orange solution. The volume of the filtrate was reduced to 3 mL in vacuo. Storage of this solution at -25 °C for 24 h resulted in the deposition of orange crystals, which were isolated by decanting the supernatant (105.7 mg, 64%). The supernatant was further concentrated to 1 mL in vacuo and storage of this solution at -25 °C for 24 h resulted in the deposition of more orange crystals. Total yield: 111.2 mg, 67%. ¹H NMR (400 MHz, 25 °C, pyridine-*d*₅): δ -7.05 (br s, 54H, NSiCH₃, FWHM = 2150 Hz), 3.56 (br s, 24H, 18-crown-6).

Synthesis of [K(18-crown-6)][U(η²-SSe)(NR₂)₃] (5). To an orange, cold (-25 °C), stirring solution of [K(18-crown-6)][U(S)(NR₂)₃] (1) (124.5 mg, 0.12 mmol), in a 2:1 mixture of Et₂O:tetrahydrofuran (4 mL), was added Se powder (12.9 mg, 0.16 mmol). This mixture was allowed to stir for 2 h, whereupon the color darkened to orange-red. The solvent was removed in vacuo and triturated with pentane (4 mL), which afforded a dark orange-red powder. This powder was then extracted with Et₂O (4 mL) and filtered through a Celite column supported on glass wool (0.5 cm × 3 cm) to provide a dark orange-red solution. The volume of the filtrate was reduced to 2 mL in vacuo. The filtrate was then transferred to a 4 mL scintillation vial that was placed inside a 20 mL scintillation vial. Toluene (6 mL) was then added to the outer vial. Storage of this two vial system for 72 h resulted in the deposition of dark orange-red crystals, which were isolated by decanting the supernatant (70.0 mg, 52%). Anal. Calcd for C₃₀H₇₈KN₃O₆SSeSi₆U: C, 31.79; H, 6.94; N, 3.71. Found: C, 32.20; H, 7.01; N, 3.62.

^1H NMR (400 MHz, 25 °C, pyridine- d_5): δ -7.73 (br s, 54H, NSiCH₃), 3.46 (br s, 24H, 18-crown-6). IR (KBr Pellet, cm⁻¹): 608 (w), 662 (w), 685 (w), 772 (w), 843 (s), 885 (w), 931 (m), 963(w), 1109 (s), 1182 (w), 1250 (m), 1285 (w), 1352 (m), 1454 (w), 1473 (w). UV-Vis/NIR (C₄H₈O, 4.14 mM, 25 °C, L·mol⁻¹·cm⁻¹): 1026 (ϵ = 32), 1082 (ϵ = 34), 1328 (ϵ = 18), 1456 (ϵ = 12), 1506 (ϵ = 13), 1618 (ϵ = 11), 1808 (ϵ = 13).

Reaction of [K(18-crown-6)][U(S)(NR₂)₃] (1) with Te. In a 20 mL scintillation vial, an orange solution of **1** (9.4 mg, 0.0089 mmol), in benzene- d_6 (0.75 mL), was added to Te powder (20.0 mg 0.16 mmol). This mixture was then transferred to an NMR tube fitted with a J-Young valve and the reaction was monitored by ^1H NMR spectroscopy over the course of 60 h. No reaction was observed (Figure S8). ^1H NMR (400 MHz, 25 °C, benzene- d_6): δ -2.03 (br s, 54H, NSiCH₃, **1**), -1.06 (br s, 24H, 18-crown-6, **1**).

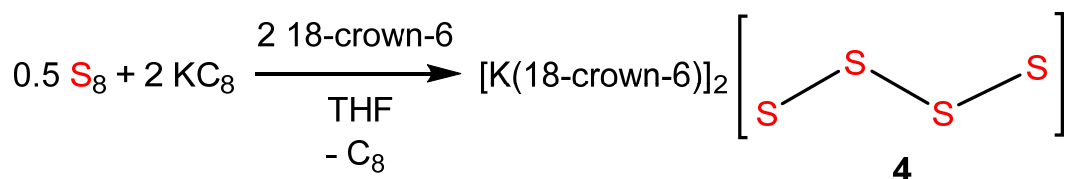
NMR scale reaction of [K(18-crown-6)][U(η^2 -S₂)(NR₂)₃] (2) with PPh₃. To a solution of **2** (9.7 mg, 0.0089 mmol) in pyridine- d_5 (0.5 mL), in an NMR tube fitted with a J-Young valve, was added a solution of Ph₃P (3.3 mg, 0.013 mmol) in pyridine- d_5 (0.5 mL). The color of the solution immediately lightened upon addition. The reaction was monitored by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopies over the course of 72 h, which revealed the formation of [K(18-crown-6)][U(S)(NR₂)₃] (**1**) and Ph₃P=S (Figures S9 and S10).¹⁰ The identity of **1** was confirmed by comparison of the ^1H spectrum with that of authentic material.¹ ^1H NMR (400 MHz, 25 °C, pyridine- d_5): δ -2.21 (br s, **1** 54H, NSiCH₃), 3.30 (br s, 24H, **1** 18-crown-6), 7.35-7.38 (m, 9H, Ph₃P overlapping resonances from *m*-CH and *p*-CH), 7.40-7.50 (m, 15H, overlapping resonances from *o*-CH of Ph₃P and *m*-CH and *p*-CH of Ph₃P=S), 7.92-7.99 (m, 6H, Ph₃P=S, *o*-CH). $^{31}\text{P}\{^1\text{H}\}$ NMR (161.92 MHz, 25 °C, pyridine- d_5): δ -5.40 (s, Ph₃P), 42.85 (s, Ph₃P=S).

Reaction of [K(18-crown-6)][U(η^2 -SSe)(NR₂)₃] (5**) with PEt₃.** To a solution of **5** (21.9 mg, 0.019 mmol) in pyridine-*d*₅ (0.75 mL), in an NMR tube fitted with a J-Young valve, was added Et₃P (3 μ L, 0.020 mmol). The color of the solution immediately lightened upon addition. After 5 min, ¹H and ³¹P{¹H} spectra were recorded. These revealed the formation of [K(18-crown-6)][U(S)(NR₂)₃] (**1**) and Et₃P=Se (Figures S11 and S12).¹¹ The identity of **1** was confirmed by comparison of the ¹H NMR spectrum with of authentic material. ¹H NMR (400 MHz, 25 °C, pyridine-*d*₅): δ -2.23 (br s, **1** 54H, NSiCH₃), 1.11 (dt, 9H, CH₃, $J_{\text{P-H}} = 18.8$ Hz, $J_{\text{H-H}} = 8$ Hz), 1.84 (dq, 6H, CH₂, $J_{\text{P-H}} = 11.6$ Hz, $J_{\text{H-H}} = 7.6$ Hz), 3.11 (s br, **1** 24H, 18-crown-6). ³¹P NMR (161.92 MHz, 25 °C, pyridine-*d*₅): δ 46.77 (s with Se satellites, Et₃P=Se, $J_{\text{P-Se}} = 348$ Hz).

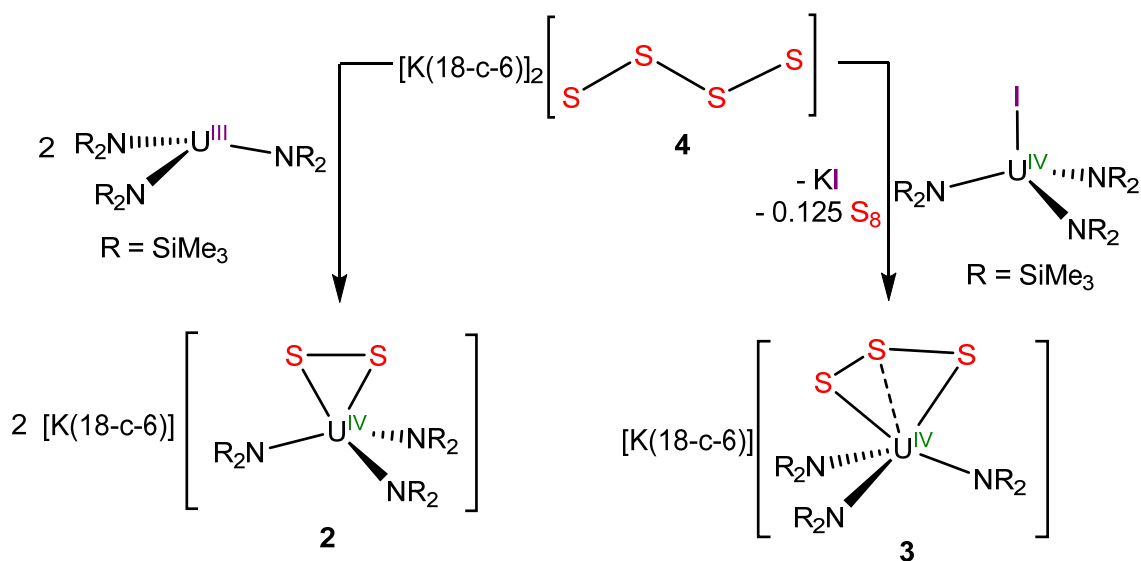
Synthesis of [K(18-crown-6)₂][S₄] (4**).** To a stirring mixture of S₈ (17.7 mg, 0.069 mmol) and 18-crown-6 (151.7 mg, 0.574 mmol), in tetrahydrofuran (4 mL), was added KC₈ (75.3 mg, 0.557 mmol). There was an immediate color change to red upon addition. After stirring for 5 min, the color of the mixture became a deep blue, concomitant with the deposition of a dark black precipitate. This mixture was allowed to stir overnight, whereupon it was filtered through a Celite column supported on glass wool (0.5 cm \times 2 cm). This provided a black plug and a faint yellow filtrate. The filtrate was then discarded, while the black solid that remained on the Celite was rinsed with acetonitrile (5 mL) to provide a solution that appeared red to transmitted light and green to reflected light. The filtrate was then reduced in vacuo to 2 mL and layered with Et₂O (6 mL). Storage of this solution at -25 °C for 24 h resulted in the deposition of orange crystals (76.1 mg, 75%). Anal. Calcd for C₂₄H₄₈K₂O₁₂S₄: C, 39.22; H, 6.58. Found: C, 38.60; H, 6.60. ¹H NMR (600 MHz, 25 °C, CD₃CN): δ 3.60 (s, 18-crown-6). IR (KBr Pellet, cm⁻¹

¹): 482 (m), 495 (w), 529 (w), 840 (m), 965 (s), 1108 (s), 1251 (m), 1285 (m), 1351 (s), 1435 (w), 1452 (w), 1472 (m). UV-Vis/NIR (CH₃CN, 0.353 mM, 25 °C, L·mol⁻¹·cm⁻¹): 270 (ε = 5809), 336 (sh) (ε = 1540), 438 (ε = 374), 612 (ε = 4192).

Scheme S1. Synthesis of [K(18-crown-6)]₂[S₄] (**4**)



Scheme S2. Alternate Syntheses of Complexes **2** and **3**



Discussion of the chemistry in Scheme S2: Complexes **2** and **3** can also be prepared by reaction of [U(NR₂)₃] and [U(I)(NR₂)₃] with the potassium polysulfide, [K(18-crown-6)]₂[S₄] (**4**). Thus, addition of 0.5 equiv of **4**, in pyridine, to a cold (-25 °C) solution of [U(NR₂)₃], in Et₂O, results in an immediate color change from dark purple to red-orange. Crystallization of the resulting material from Et₂O/pentane affords complex **2**, as red-orange crystals in 42% yield (Scheme S2). Formally, the [S₄]²⁻ anion is acting as a 2e⁻ oxidant in this transformation; two U(III) metal centers reduce the [S₄]²⁻ anion, which

breaks the central S-S bond and results in the formation of two $[\eta^2\text{-S}_2]^{2-}$ ligands. Furthermore, the addition of 1 equiv of **4** to a cold mixture of $[\text{U}(\text{I})(\text{NR}_2)_3]$ in tetrahydrofuran results in a color change to dark orange and, over the course of 30 min, the deposition of a white powder. From this mixture, complex **3** can be isolated in 64% yield (Scheme S2). The formation of the $[\eta^3\text{-S}_3]^{2-}$ ligand in **3** only accounts for three of the four sulfur atoms in **4**. We suggest that coordination of the $[\text{S}_4]^{2-}$ moiety to the uranium center, upon salt metathesis, results in the ejection of a single S atom from the polysulfide chain due to the steric demands of the tris(amide) platform, thereby generating the observed $[\eta^3\text{-S}_3]^{2-}$ ligand.

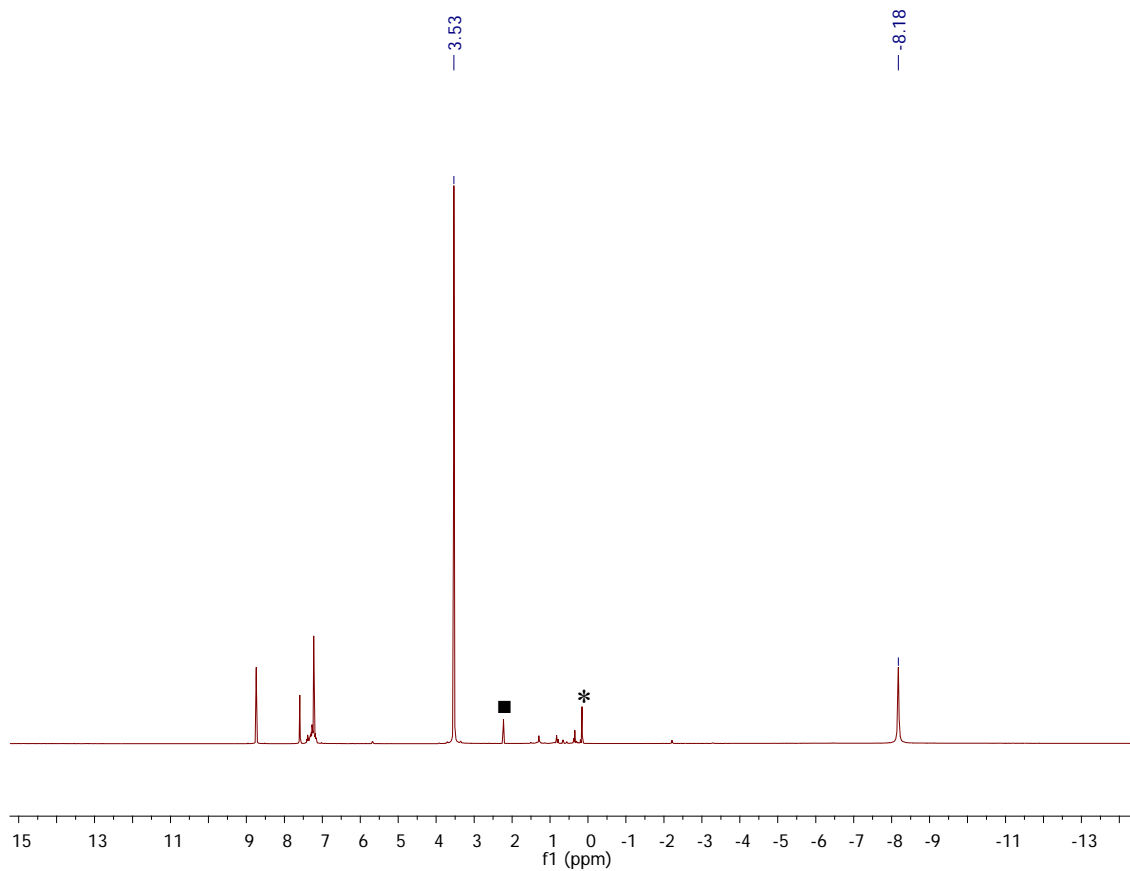


Figure S1. ^1H NMR spectrum of $[\text{K}(18\text{-crown-6})][\text{U}(\eta^2\text{-S}_2)(\text{NR}_2)_3]$ (**2**), in pyridine- d_5 , isolated from the reaction of $[\text{K}(18\text{-crown-6})][\text{U}(\text{S})(\text{NR}_2)_3]$ (**1**) with S_8 . (*) indicates the presence of $\text{HN}(\text{SiMe}_3)_2$ and (■) indicates the presence of toluene.

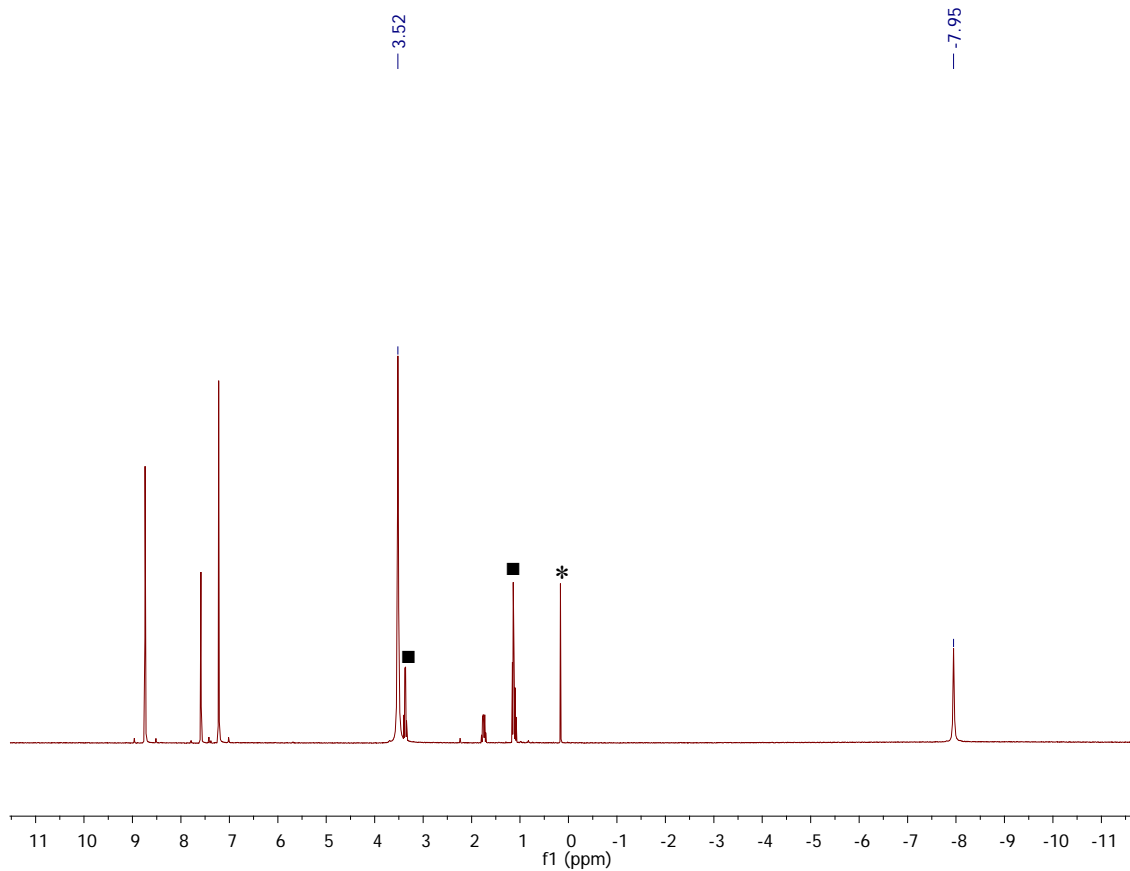


Figure S2. ^1H NMR spectrum of $[\text{K}(\text{18-crown-6})][\text{U}(\eta^2\text{-S}_2)(\text{NR}_2)_3]$ (**2**), in pyridine- d_5 , isolated from the reaction of $[\text{K}(\text{18-crown-6})][\text{U}(\eta^3\text{-S}_3)(\text{NR}_2)_3]$ (**3**) with Et_3P . (*) indicates the presence of $\text{HN}(\text{SiMe}_3)_2$, (■) indicates the presence of $\text{Et}_3\text{P}=\text{S}$.

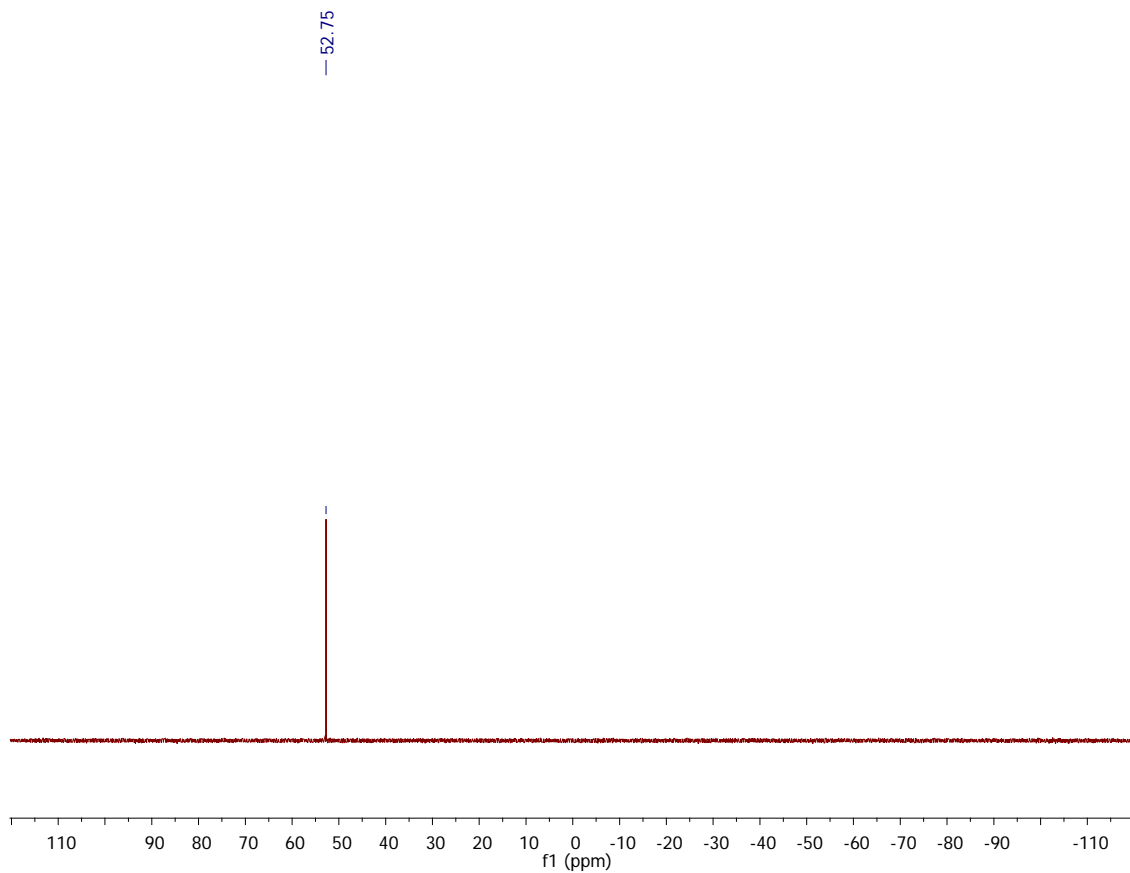


Figure S3. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $\text{Et}_3\text{P}=\text{S}$, in pyridine- d_5 , isolated from the reaction of $[\text{K}(18\text{-crown-6})][\text{U}(\eta^3\text{-S}_3)(\text{NR}_2)_3]$ (**3**) with Et_3P .

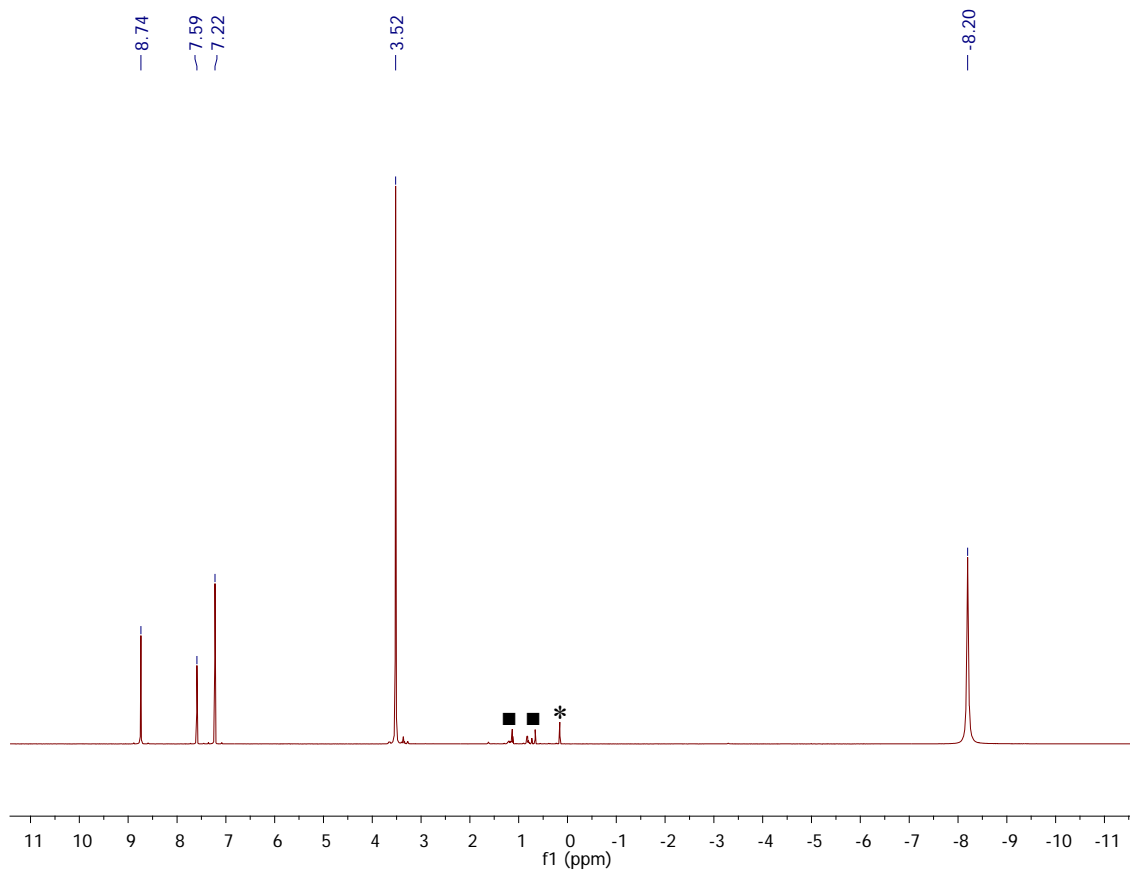


Figure S4. ^1H NMR spectrum of $[\text{K}(18\text{-crown-}6)][\text{U}(\eta^2\text{-S}_2)(\text{NR}_2)_3]$ (**2**), in pyridine- d_5 , isolated from the reaction of $[\text{U}(\text{NR}_2)_3]$ with $[\text{K}(18\text{-crown-}6)]_2[\text{S}_4]$ (**4**). (*) indicates the presence of $\text{HN}(\text{SiMe}_3)_2$, and (■) indicates the presence of pentane.

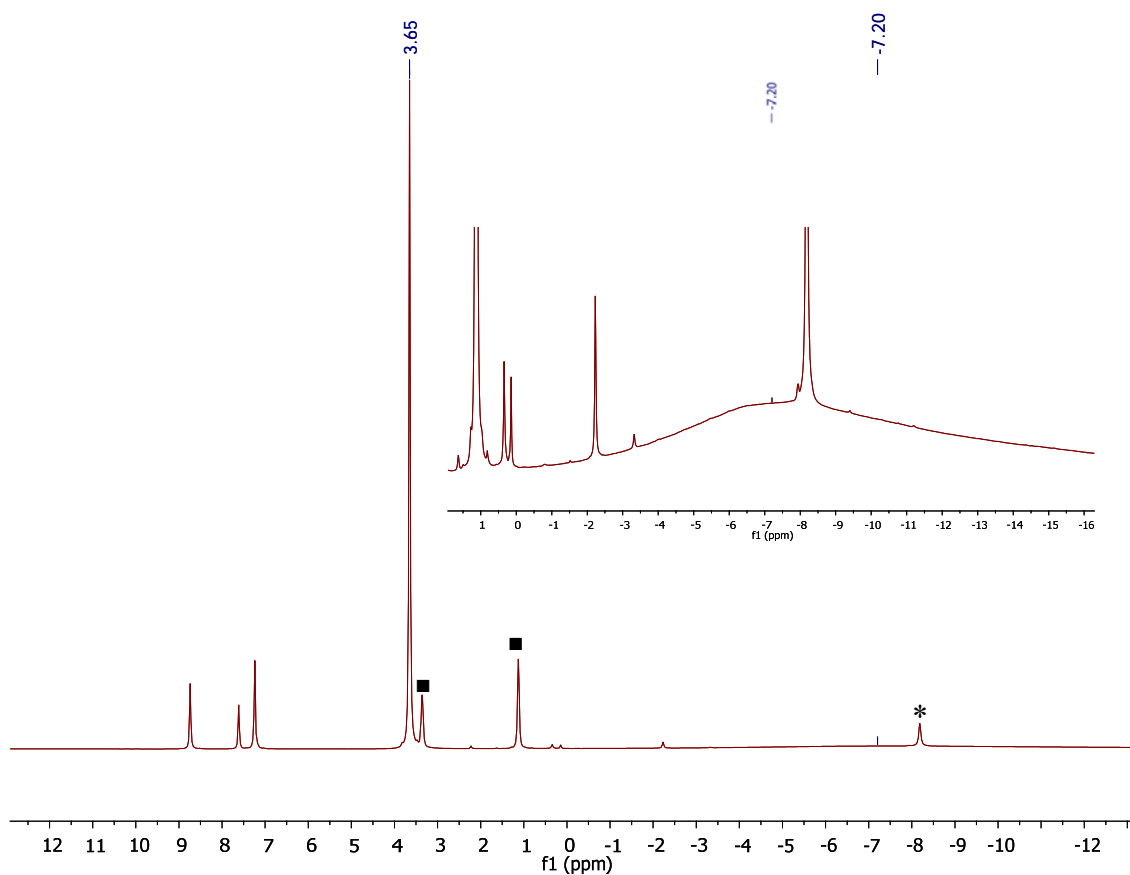


Figure S5. ^1H NMR spectrum of $[\text{K}(\text{18-crown-6})][\text{U}(\eta^3\text{-S}_3)(\text{NR}_2)_3]$ (**3**), in pyridine- d_5 , isolated from the reaction of $[\text{K}(\text{18-crown-6})][\text{U}(\eta^2\text{-S}_2)(\text{NR}_2)_3]$ (**2**) and S_8 . (*) indicates the presence of unreacted $[\text{K}(\text{18-crown-6})][\text{U}(\eta^2\text{-S}_2)(\text{NR}_2)_3]$ (**2**), (■) indicates the presence of diethyl ether. Inset: portion of the spectrum showing the broad resonance at -7.20 ppm, assignable to the methyl resonances of **3**.

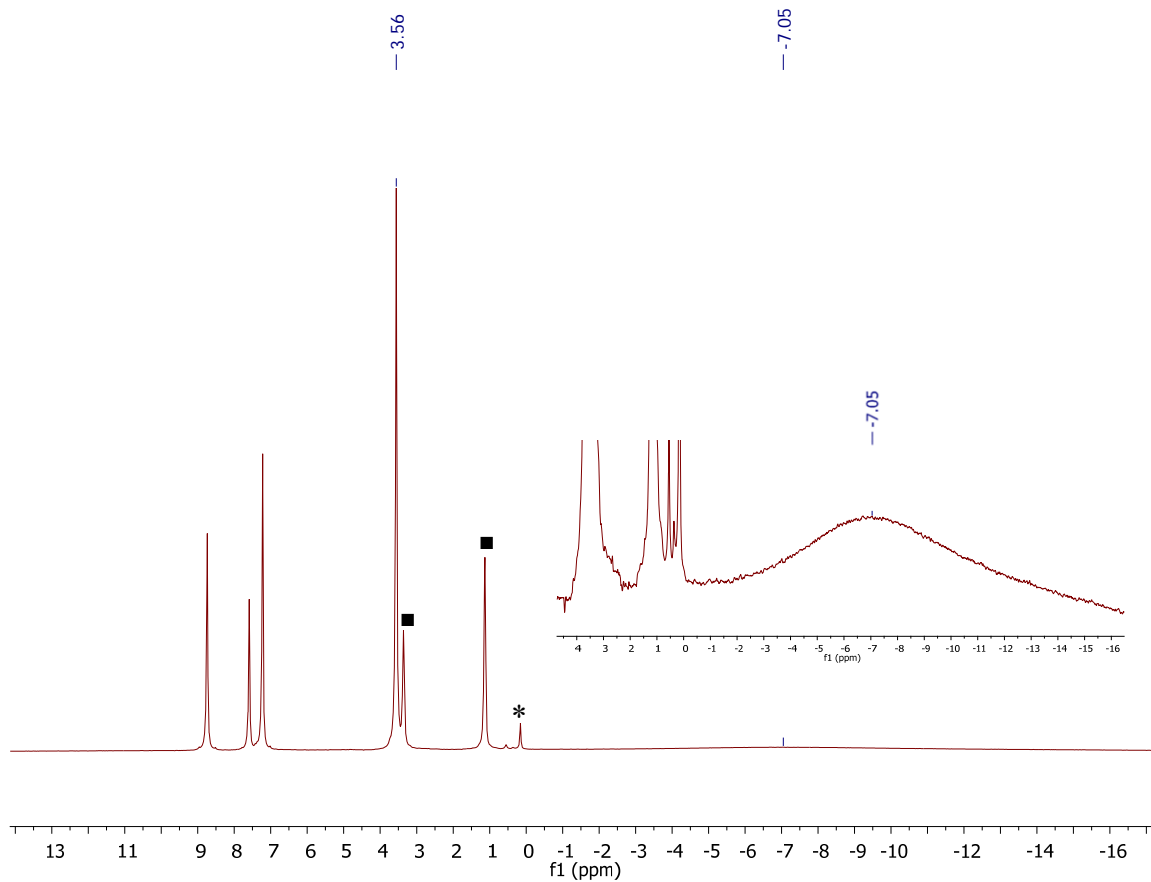


Figure S6. ^1H NMR spectrum of $[\text{K}(18\text{-crown-6})][\text{U}(\text{S}_3)(\text{NR}_2)_3]$ (**3**), in pyridine- d_5 , isolated from the reaction of $[\text{U}(\text{I})(\text{NR}_2)_3]$ with $[\text{K}(18\text{-crown-6})]_2[\text{S}_4]$ (**4**). (*) indicates the presence of $\text{HN}(\text{SiMe}_3)_2$, and (■) indicates the presence of Et_2O . Inset: portion of the spectrum showing the broad resonance at -7.05 ppm, assignable to the methyl resonances of **3**.

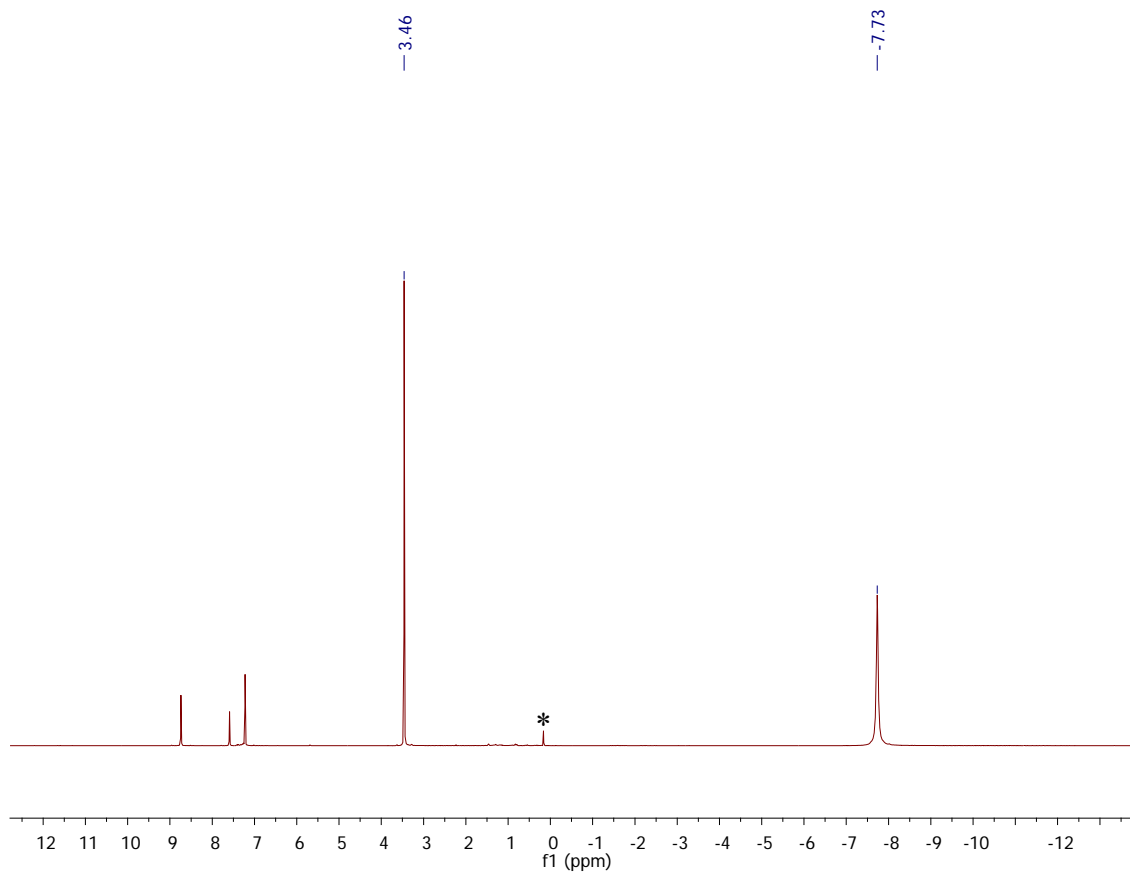


Figure S7. ^1H NMR spectrum of $[\text{K}(18\text{-crown-}6)][\text{U}(\eta^2\text{-SSe})(\text{NR}_2)_3]$ (**5**) in pyridine- d_5 . (*) indicates the presence of $\text{HN}(\text{SiMe}_3)_2$.

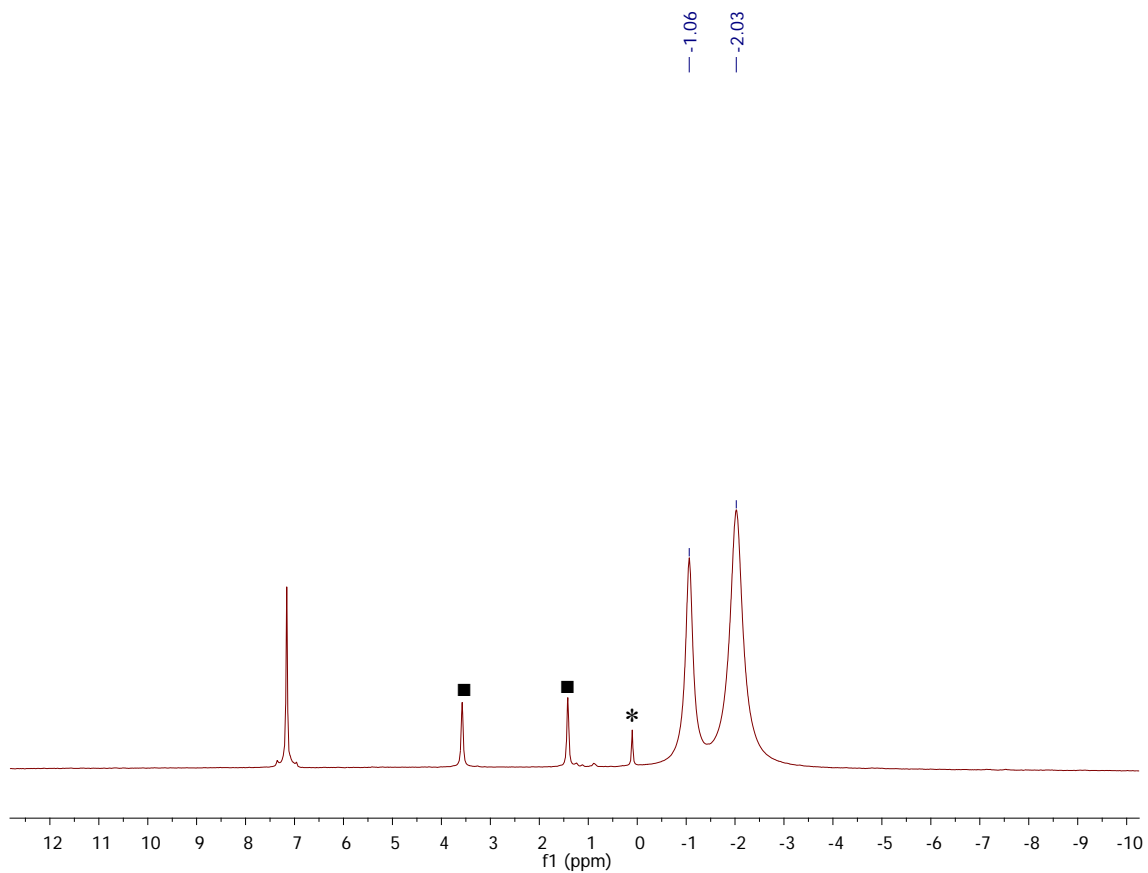


Figure S8. In situ ^1H NMR spectrum of the reaction of $[\text{K}(18\text{-crown-}6)][\text{U}(\text{S})(\text{NR}_2)_3]$ (**1**) and Te in benzene- d_6 , after 60 h. (*) indicates the presence of $\text{HN}(\text{SiMe}_3)_2$, and (■) indicates the presence of tetrahydrofuran.

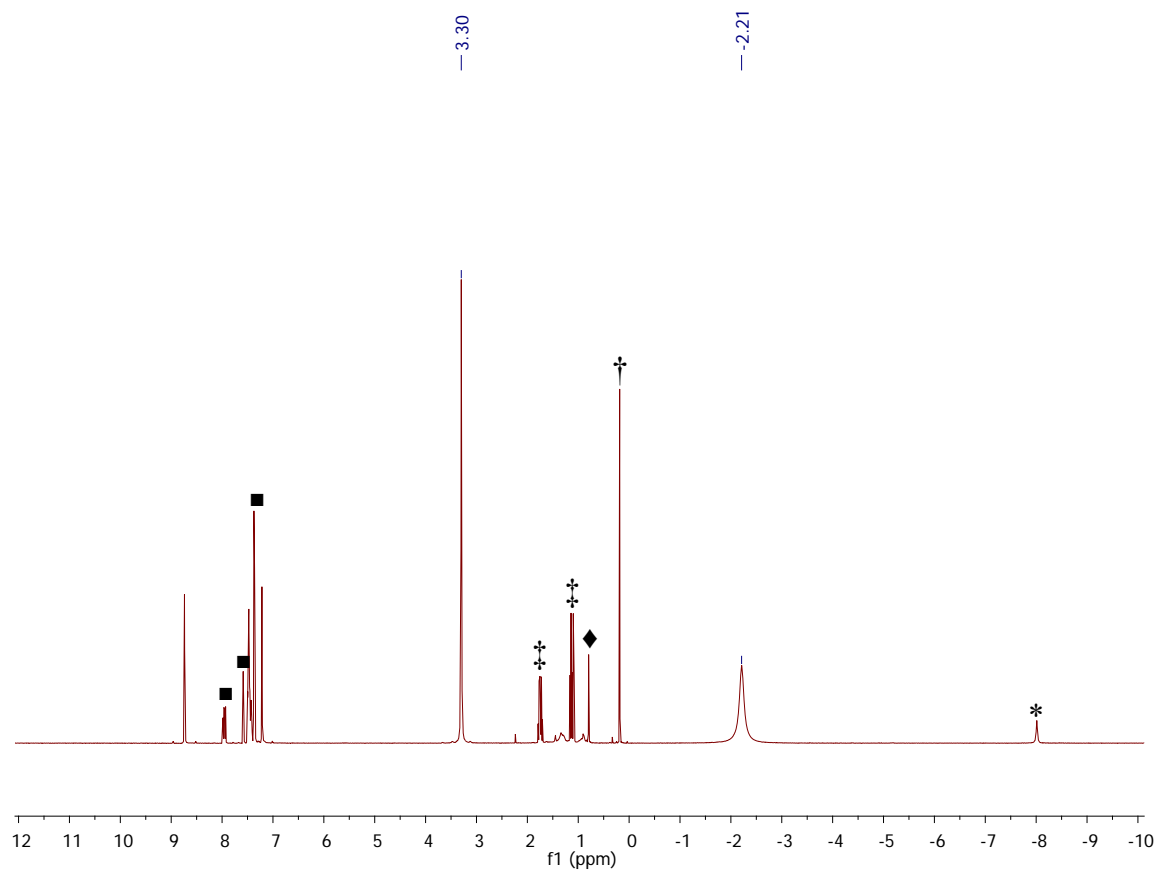


Figure S9. In situ ^1H NMR spectrum of the reaction of $[\text{K}(18\text{-crown-}6)][\text{U}(\eta^2\text{-S}_2)(\text{NR}_2)_3]$ (**2**) with Ph_3P in pyridine- d_5 . (*) indicates the presence of unreacted **2**, (■) indicates the presence of Ph_3P and $\text{Ph}_3\text{P}=\text{S}$, (†) indicates the presence of $\text{HN}(\text{SiMe}_3)_2$, (‡) indicates the presence of Et_2O , and (◆) indicates the presence of hexanes.

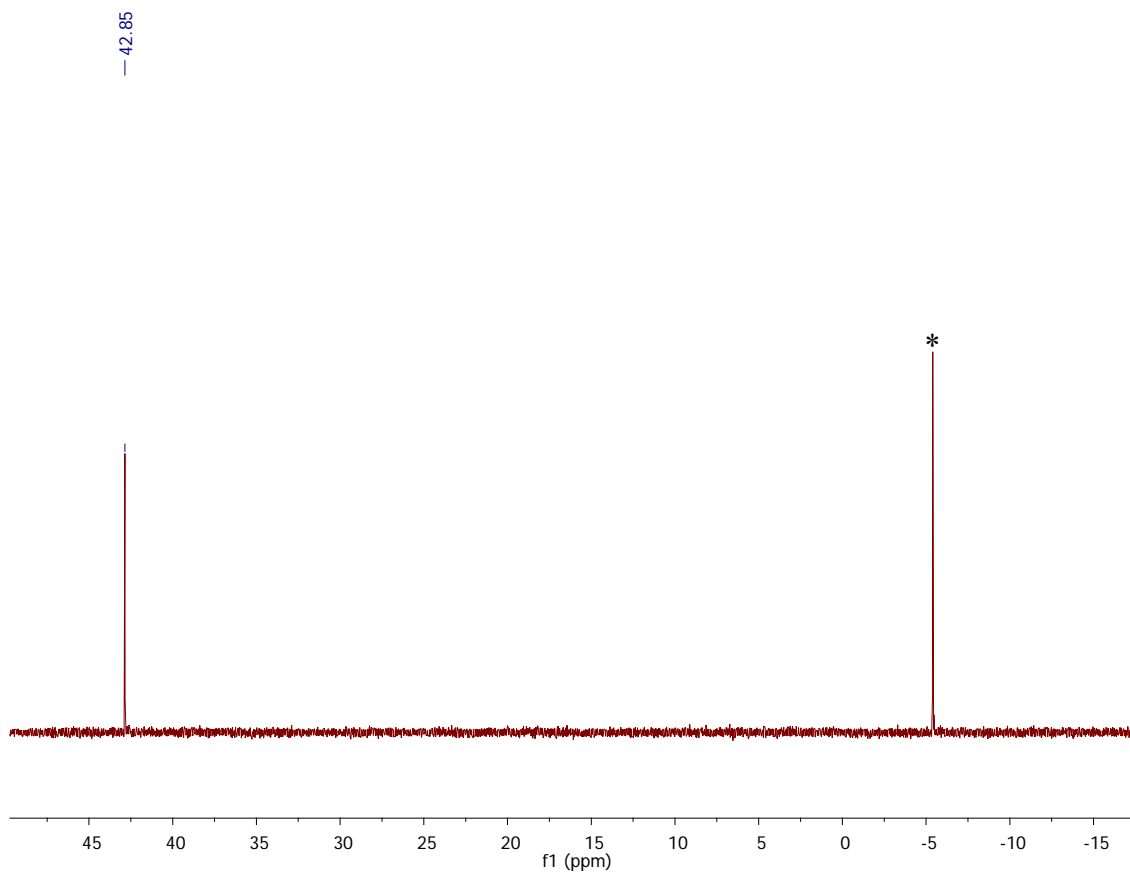


Figure S10. In situ $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction of $[\text{K}(\text{18-crown-6})][\text{U}(\eta^2\text{-S}_2)(\text{NR}_2)_3]$ (**2**) with Ph_3P in pyridine- d_5 . (*) indicates the presence of unreacted Ph_3P .

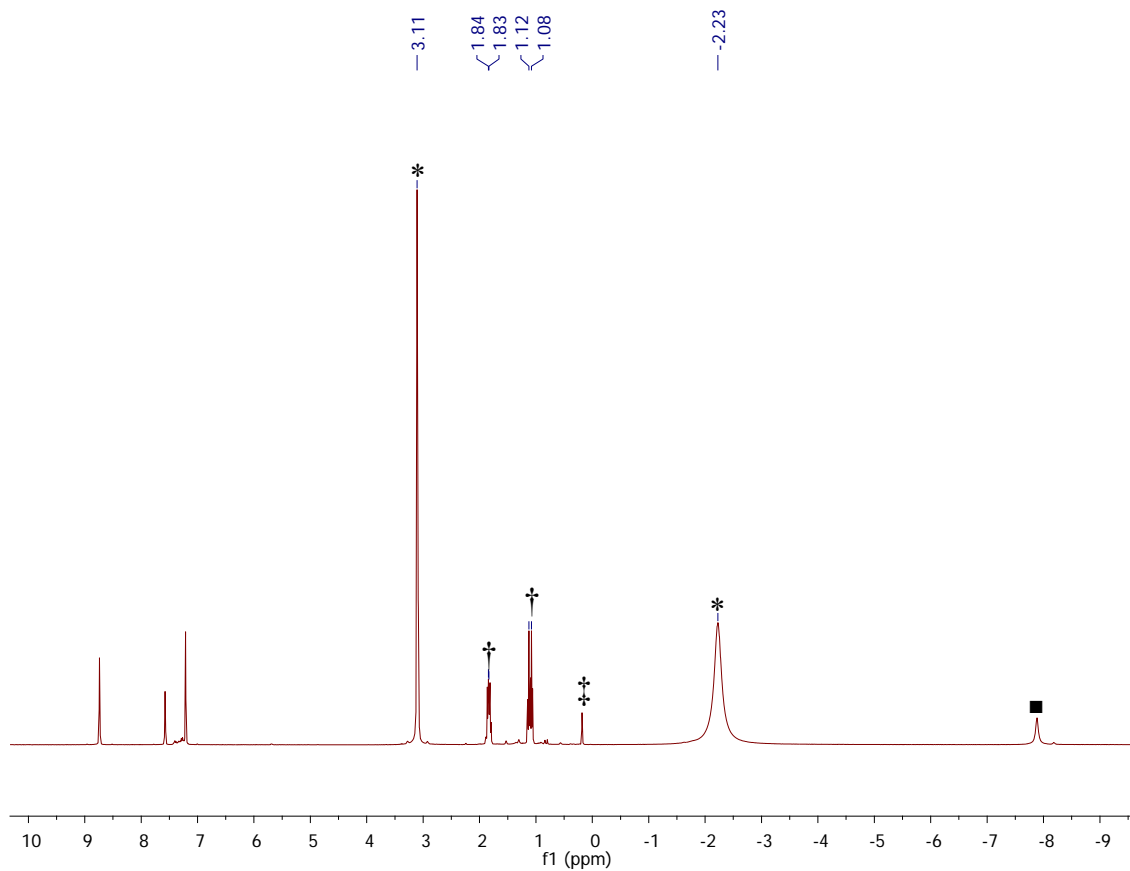


Figure S11. In situ ^1H NMR spectrum of the reaction of $[\text{K}(18\text{-crown-6})][\text{U}(\eta^2\text{-SSe})(\text{NR}_2)_3]$ (**5**) with Et_3P in $\text{pyridine-}d_5$. (*) indicates the presence of $[\text{K}(18\text{-crown-6})][\text{U}(\text{S})(\text{NR}_2)_3]$ (**1**), (■) indicates the presence of unreacted $[\text{K}(18\text{-crown-6})][\text{U}(\eta^2\text{-SSe})(\text{NR}_2)_3]$ (**5**), (†) indicates the presence of $\text{Et}_3\text{P}=\text{Se}$, and (‡) indicates the presence of $\text{HN}(\text{SiMe}_3)_2$.

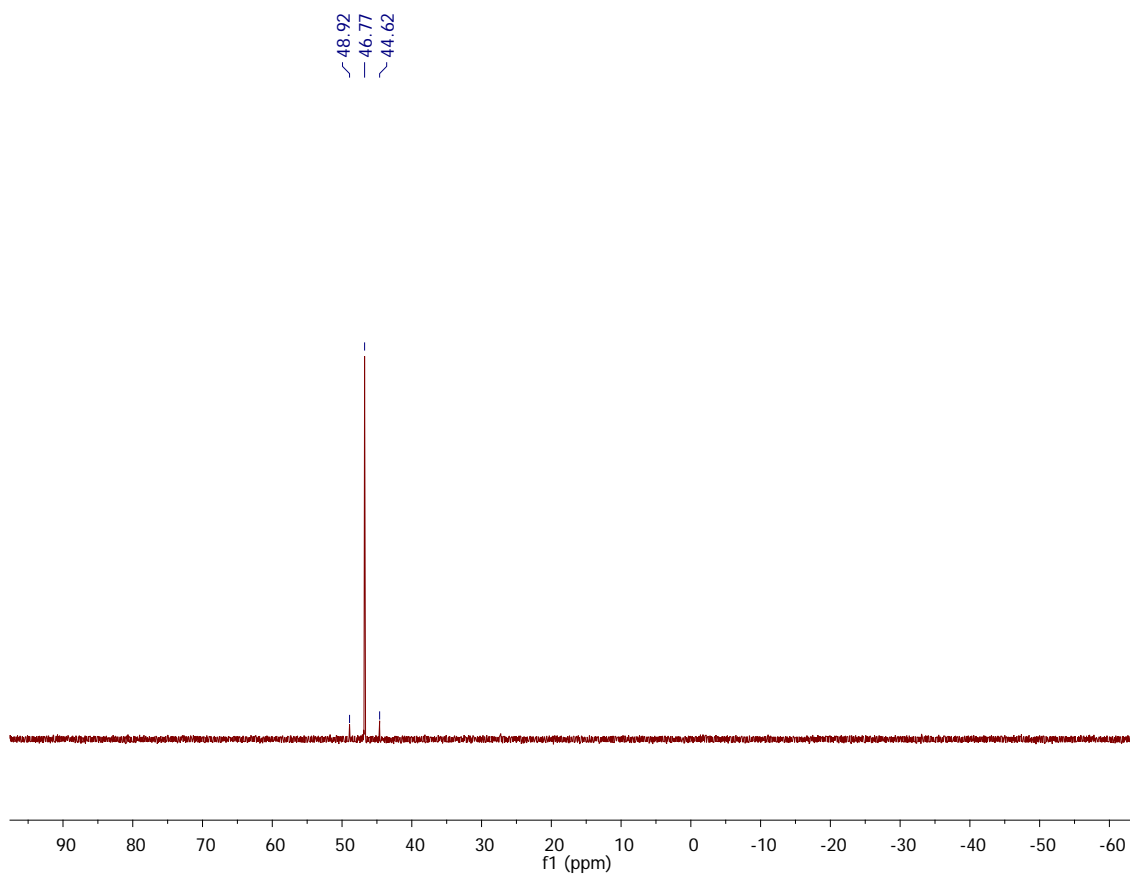


Figure S12. In situ $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction of $[\text{K}(18\text{-crown-6})][\text{U}(\eta^2\text{-SSe})(\text{NR}_2)_3]$ (**5**) with Et_3P in pyridine- d_5 .

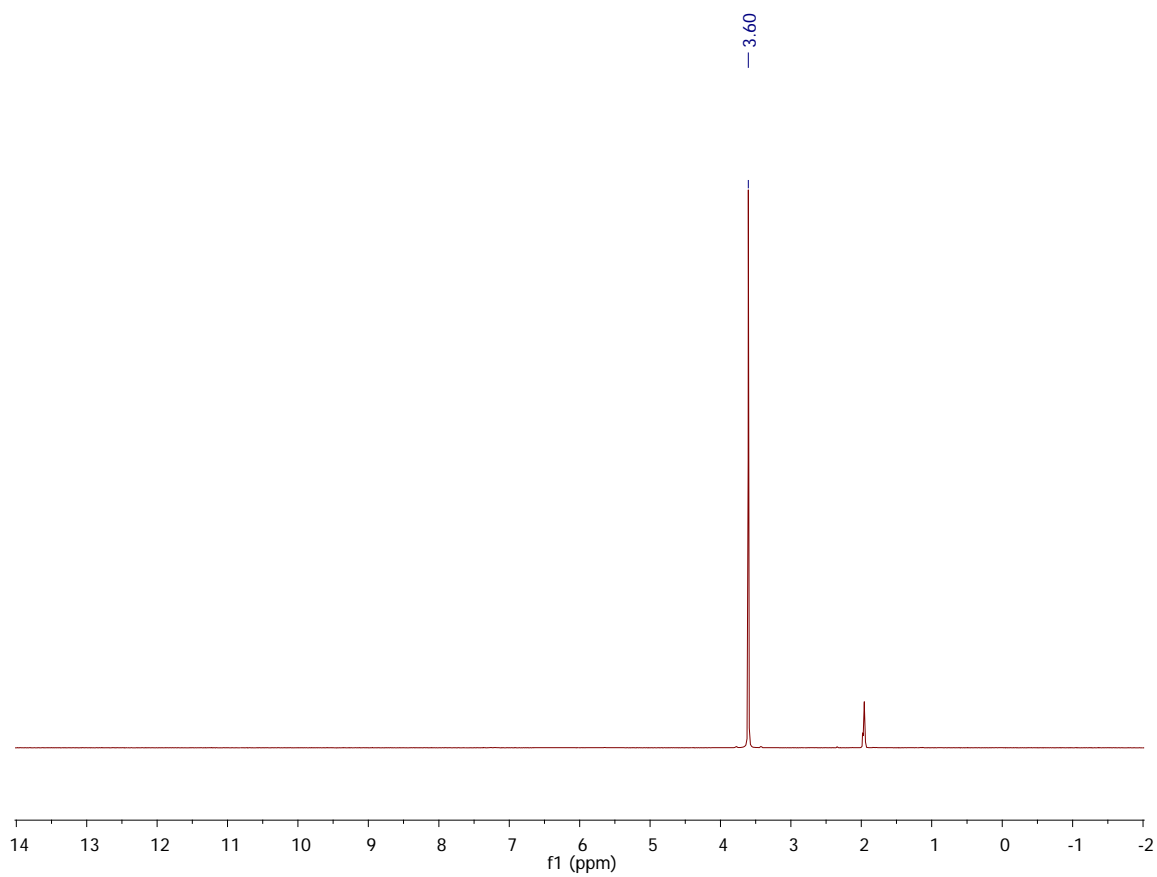


Figure S13. ^1H NMR spectrum of $[\text{K}(\text{18-crown-6})]_2[\text{S}_4]$ (**5**) in CD_3CN .

Table S1. X-ray Crystallographic Data for **2**, **3**, **4**, and **5**.

	2	3 ·C ₄ H ₁₀ O	4	5
empirical formula	C ₃₀ H ₇₈ KN ₃ O ₆ S ₂ Si ₆ U	C ₃₄ H ₈₈ KN ₃ O ₇ S ₃ Si ₆ U	C ₂₄ H ₄₈ K ₂ O ₁₂ S ₄	C ₃₄ H ₇₈ KN ₃ O ₆ SSeSi ₆ U
crystal habit, color	block, red-orange	block, orange	block, orange-yellow	block, orange-red
crystal size (mm)	0.1 × 0.1 × 0.1	0.2 × 0.1 × 0.1	0.1 × 0.1 × 0.1	0.2 × 0.1 × 0.1
space group	<i>P</i> 2 ₁ /n	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ /n	<i>P</i> 2 ₁
volume (Å ³)	5031.6(3)	2777.9(6)	3478.9(2)	5073.7(6)
<i>a</i> (Å)	12.9305(4)	11.255(1)	11.9285(5)	13.1630(9)
<i>b</i> (Å)	17.8735(5)	12.934(2)	18.5061(6)	17.804(1)
<i>c</i> (Å)	22.5628(7)	20.934(3)	16.5489(6)	22.488(1)
α (deg)	90	98.456(2)	90	90
β (deg)	105.223(2)	96.945(2)	107.769(2)	105.691(4)
γ (deg)	90	110.308(2)	90	90
<i>Z</i>	4	2	4	2
formula weight (g/mol)	1086.74	1192.92	735.06	1133.65
density (calculated) (Mg/m ³)	1.435	1.426	1.403	1.484
absorption coefficient (mm ⁻¹)	3.571	3.279	0.566	4.218
<i>F</i> ₀₀₀	2216	1224	1560	2288
total no. reflections	32568	31228	19483	31505
unique reflections	11110	12268	7107	22136
<i>R</i> _{int}	0.0418	0.0726	0.0514	0.0514
final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0814 w <i>R</i> ₂ = 0.2165	<i>R</i> ₁ = 0.0345 w <i>R</i> ₂ = 0.0853	<i>R</i> ₁ = 0.0792 w <i>R</i> ₂ = 0.2091	<i>R</i> ₁ = 0.0537 w <i>R</i> ₂ = 0.1450
largest diff. peak and hole (e ⁻ Å ⁻³)	8.120 and -3.889	3.638 and -2.427	3.392 and -3.781	6.095 and -2.458
GOF	1.053	1.040	1.124	0.851

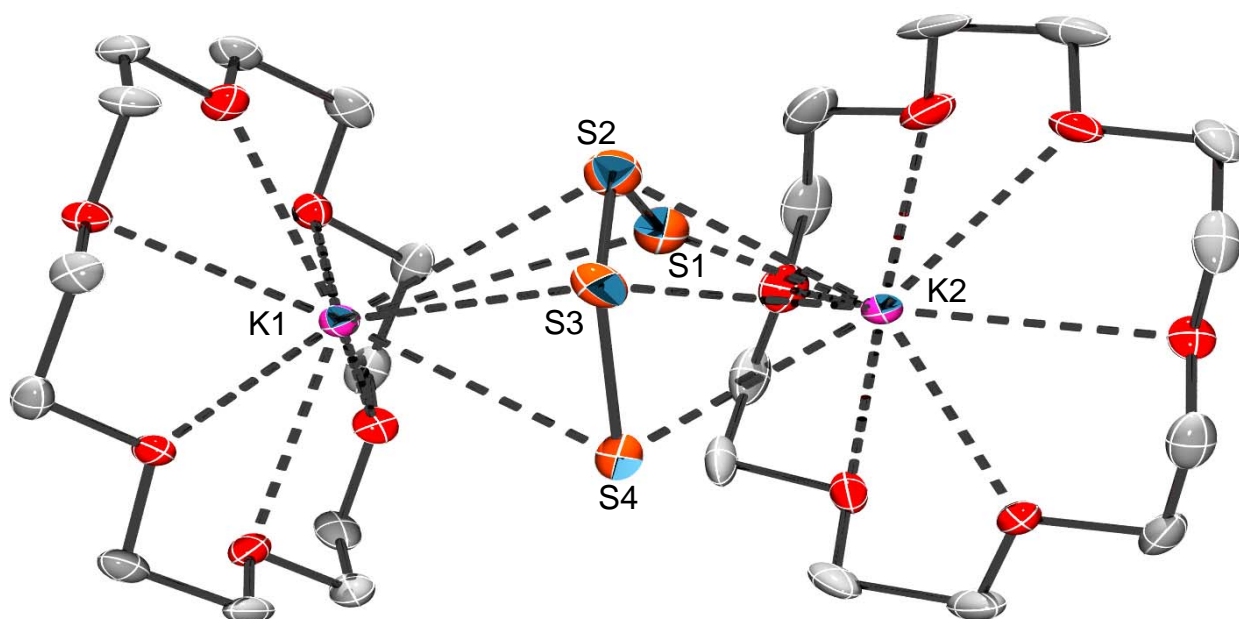


Figure S14. Solid state molecular structure of $[\text{K}(\text{18-crown-6})]_2[\text{S}_4]$ (**4**) with 50% probability ellipsoids. Hydrogen atoms and disordered sulfur atoms omitted for clarity. Selected bond lengths (\AA): $\text{S1-S2} = 1.98(1)$, $\text{S2-S3} = 1.84(1)$, $\text{S3-S4} = 2.230$, $\text{K1-S1} = 3.334(9)$, $\text{K1-S2} = 3.192(9)$, $\text{K1-S3} = 3.191(8)$, $\text{K1-S4} = 3.262(2)$. For comparison, the S-S bond lengths in **4** (av. 2.011 \AA) are similar to those in other structurally characterized alkali/alkaline earth metal complexes of the $[\text{S}_4]^{2-}$ anion (av. 2.062 \AA).^{12,13}

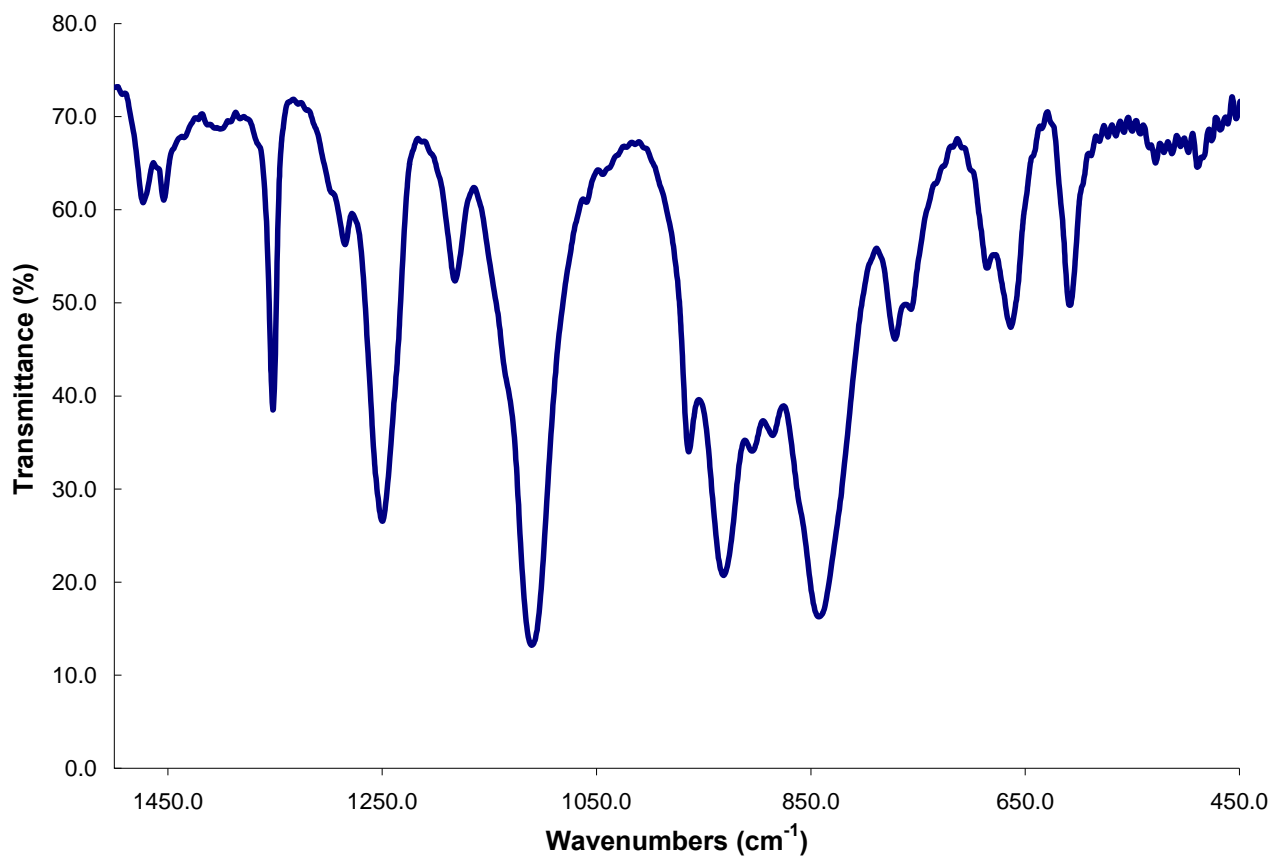


Figure S15. Partial IR spectrum of [K(18-crown-6)][U(η^2 -S₂)(NR₂)₃] (**2**) (KBr pellet).

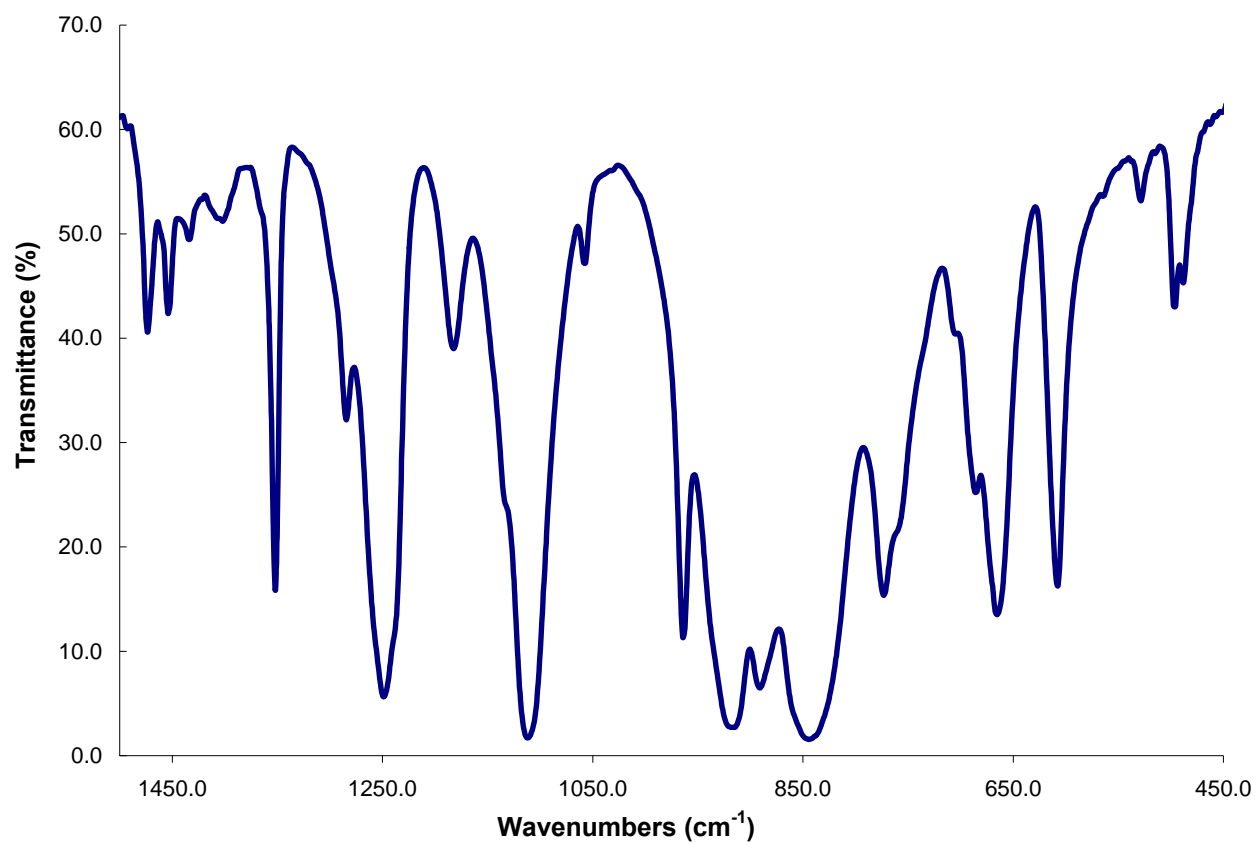


Figure S16. Partial IR spectrum of $[\text{K}(\text{18-crown-6})][\text{U}(\eta^3\text{-S}_3)(\text{NR}_2)_3]$ (**3**) (KBr pellet).

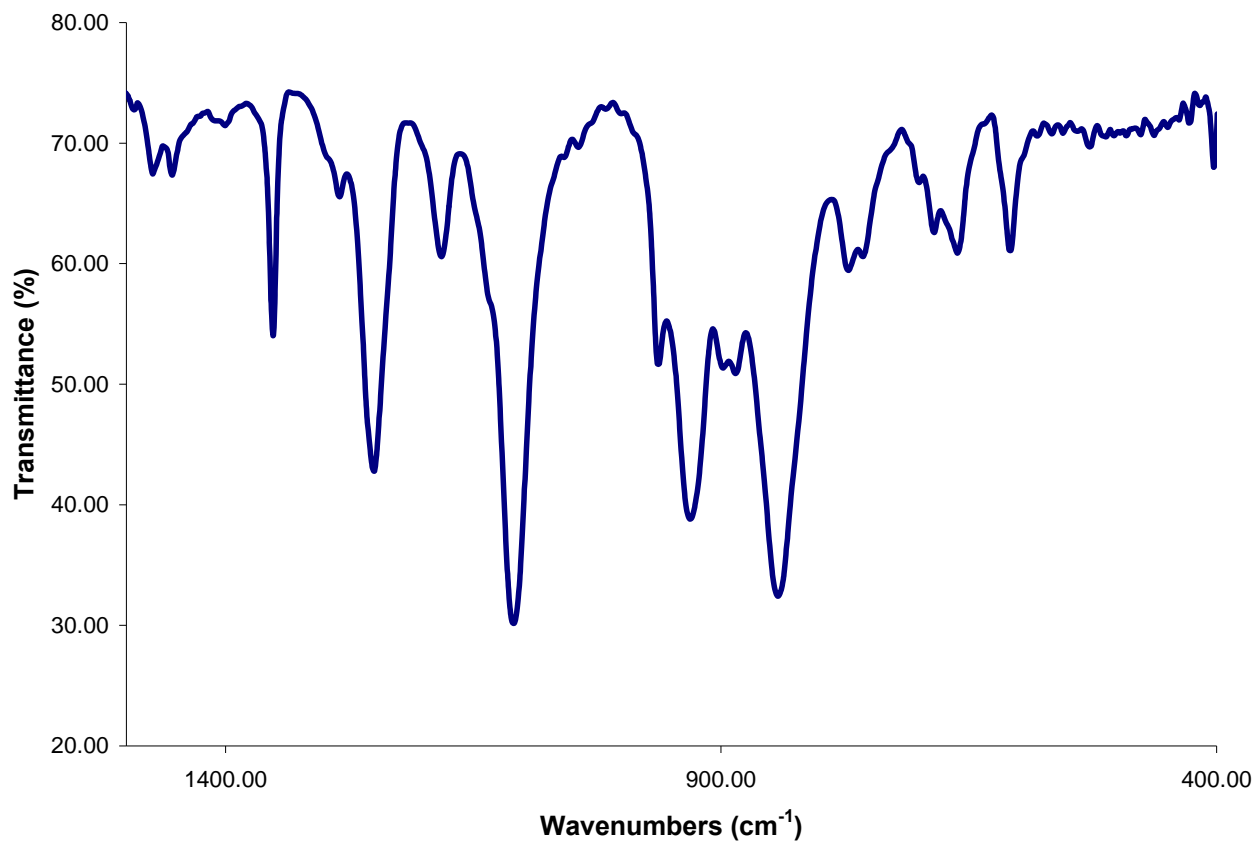


Figure S17. Partial IR spectrum of $[\text{K}(\text{18-crown-6})][\text{U}(\eta^2\text{-SSe})(\text{NR}_2)_3]$ (**5**) (KBr pellet).

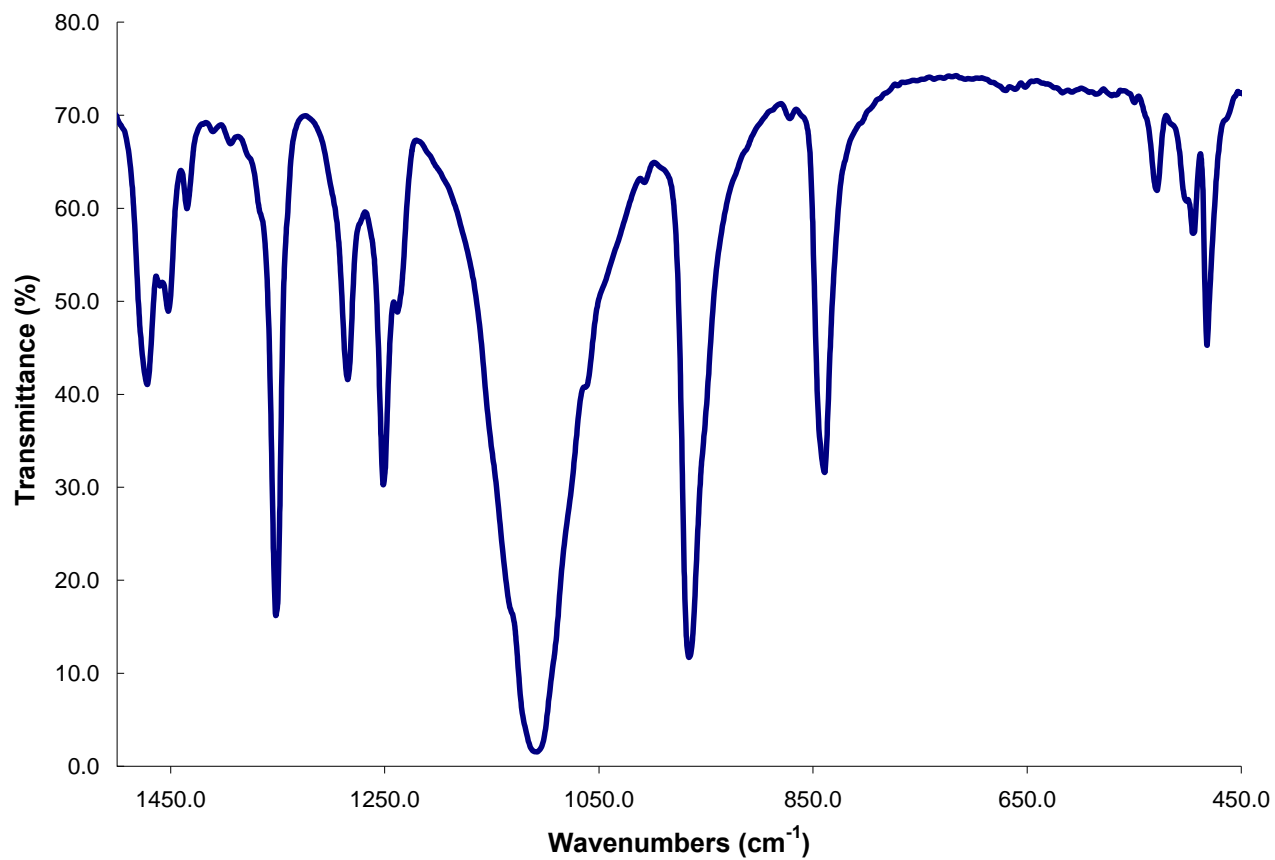


Figure S18. Partial IR spectrum of $[K(18\text{-crown-}6)][S_4]$ (**4**) (KBr pellet).

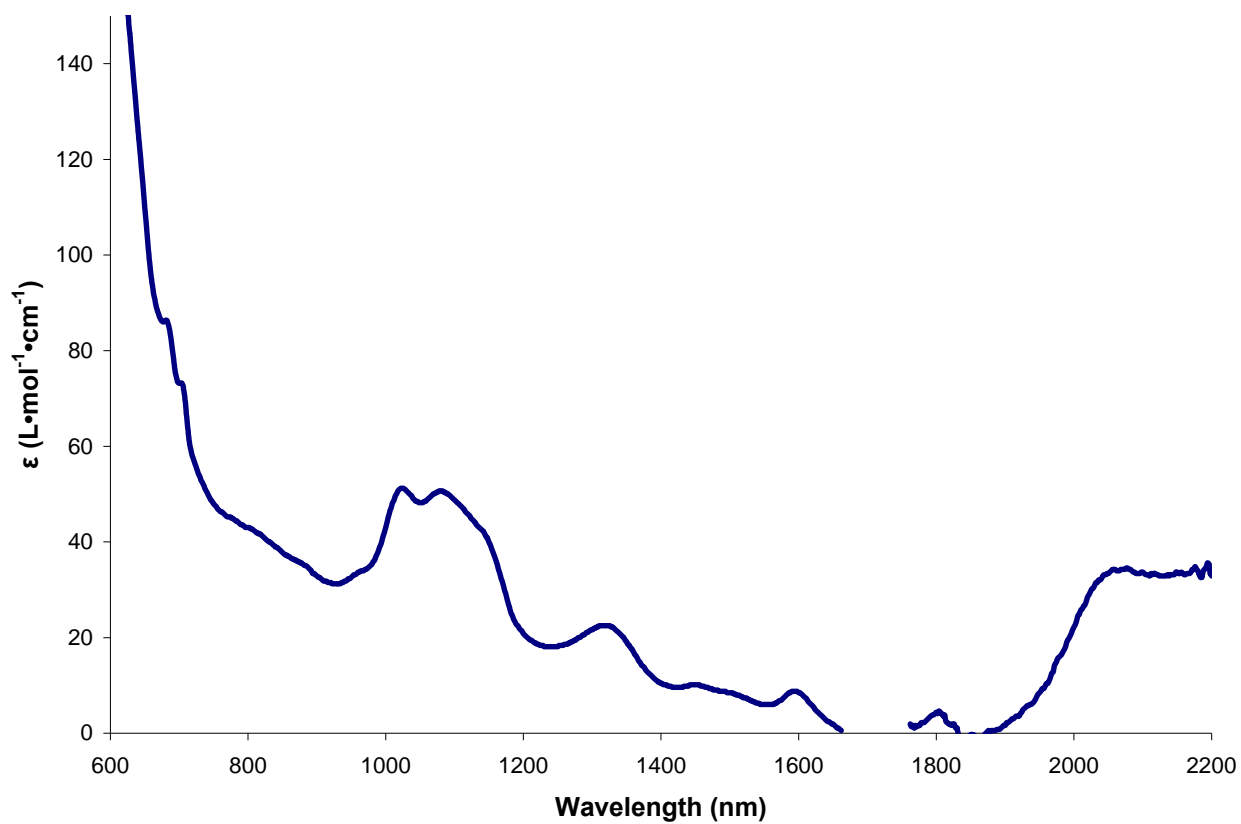


Figure S19. UV-Vis / NIR spectrum of [K(18-crown-6)][U(η^2 -S₂)(NR₂)₃] (**2**) (3.65 mM, C₄H₈O).

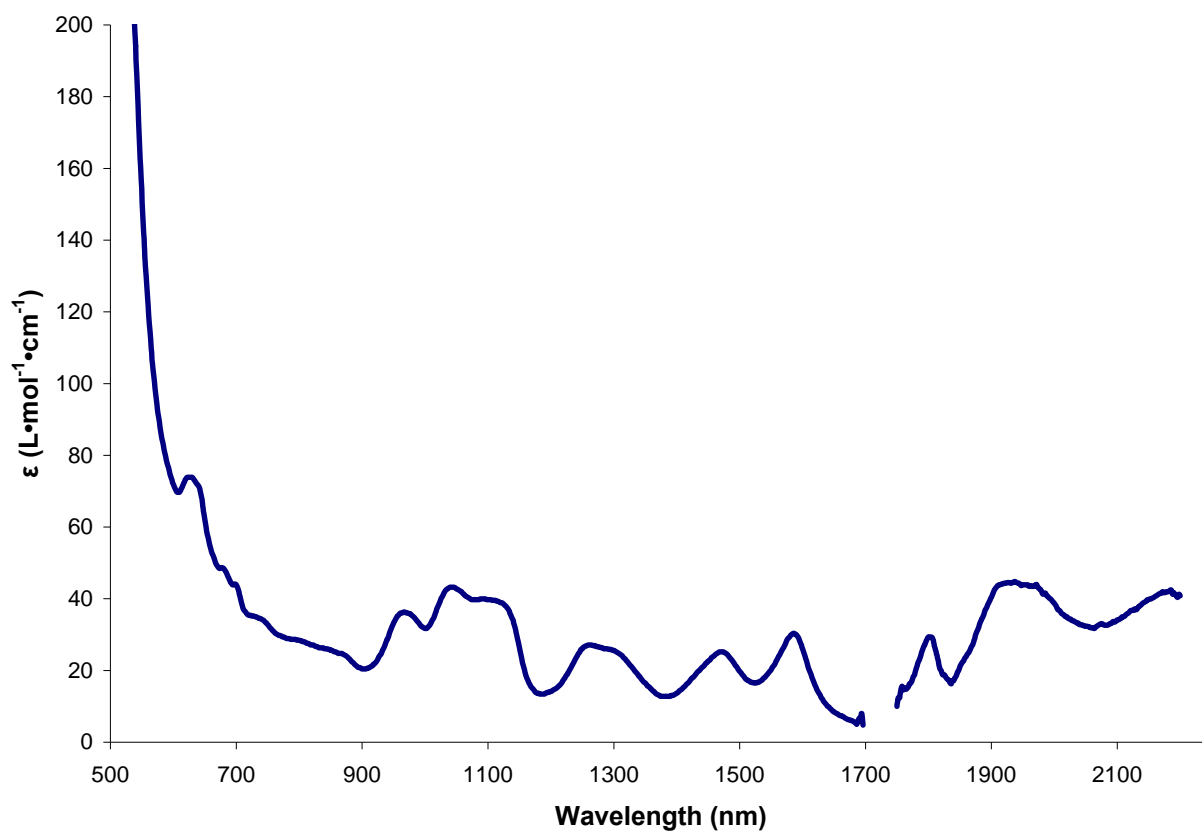


Figure S20. UV-Vis / NIR spectrum of [K(18-crown-6)][U(η^3 -S₃)(NR₂)₃] (**3**) (4.60 mM, C₄H₈O).

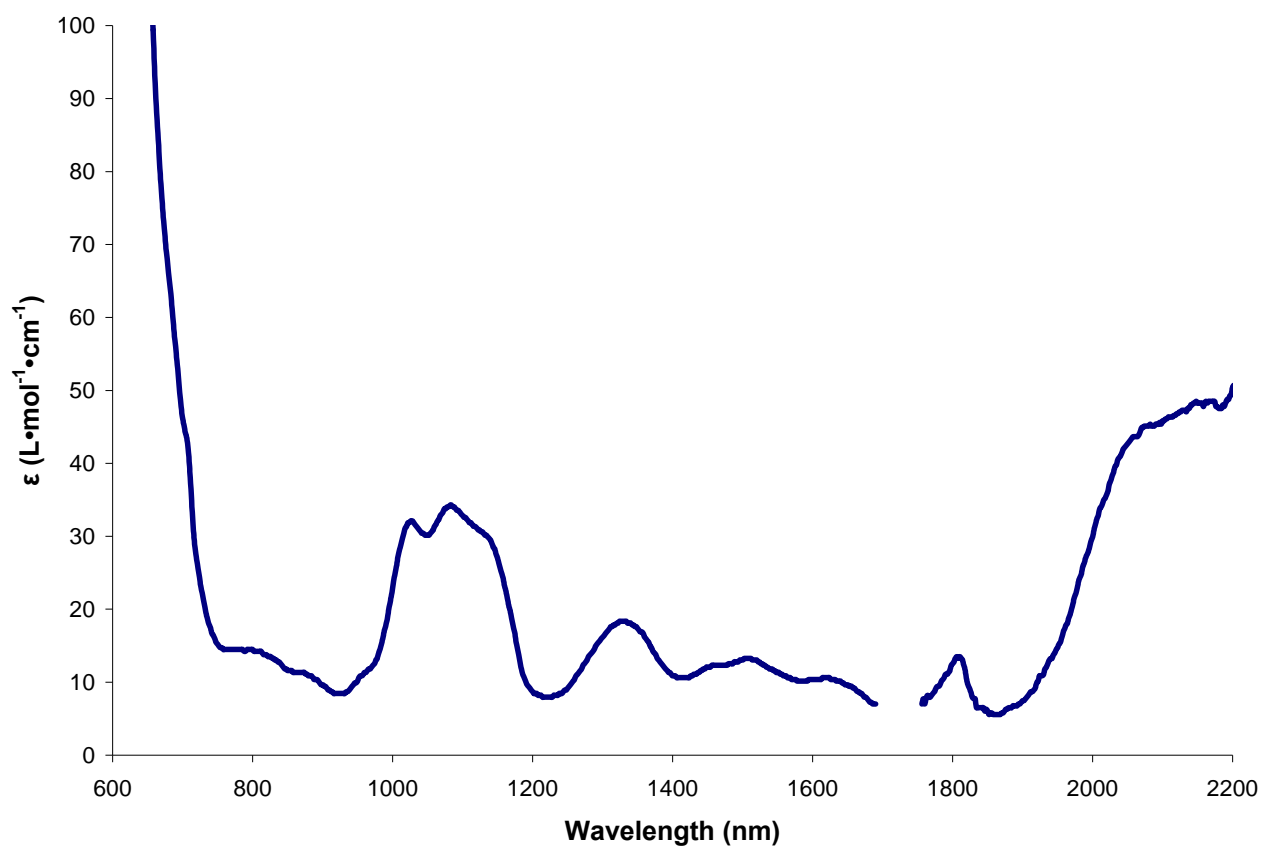


Figure S21. UV-Vis / NIR spectrum of $[K(18\text{-crown-6})][U(\eta^2\text{-SSe})(NR_2)_3]$ (**5**) (4.14 mM, C_4H_8O).

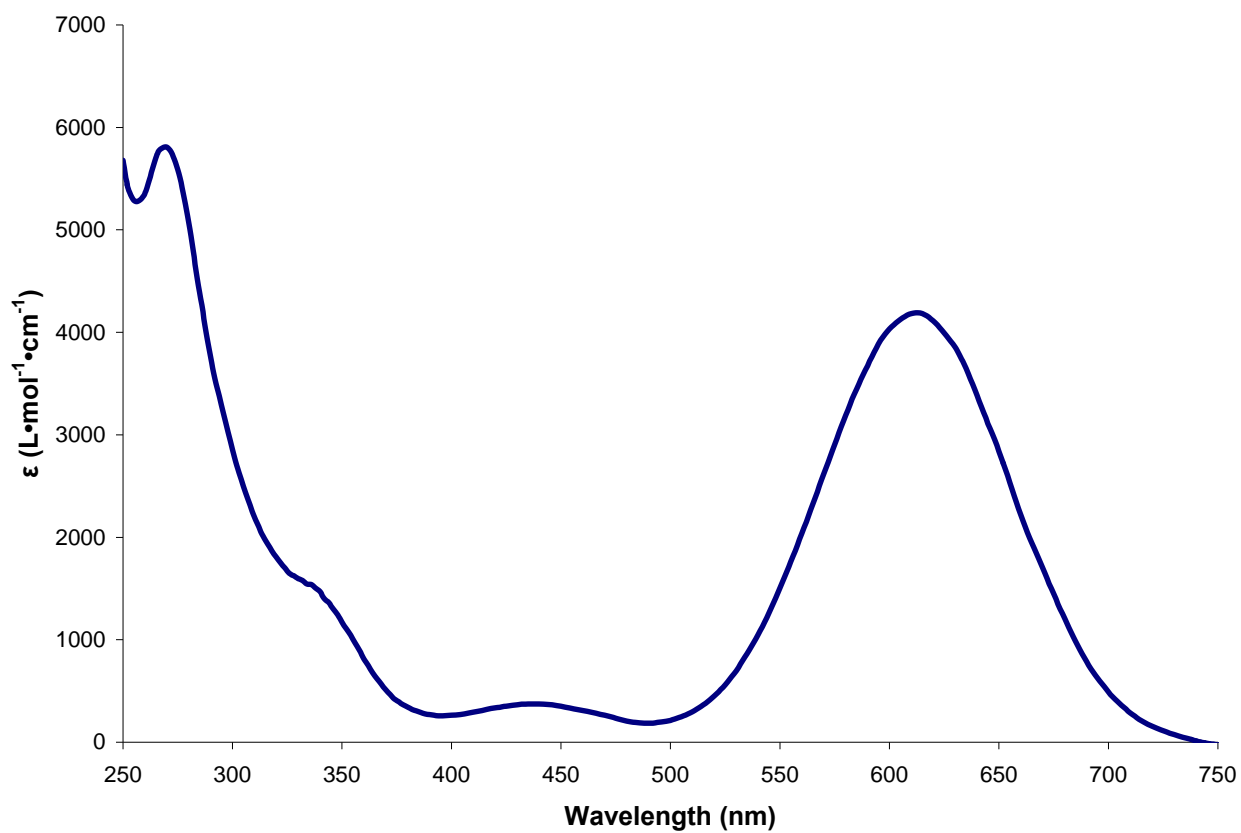


Figure S22. UV-Vis Spectrum of [K(18-crown-6)]₂[S₄] (**4**) (0.353 mM, CH₃CN).

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