# Supporting Information

1. Chemicals and synthesis

   *Caution: Experiments with uranium should be under protection although depleted uranium is weak in radioactivity.*

   All chemicals were purchased commercially and used without further purification. Purity of each chemical is higher than 98%.

   For a general synthesis procedure, 6.9 mg (0.01) tetrathafulvalene-3,4,5,6-tetrakis(4-benzoic acid) ($H_4$TTFTB) was weighted to a mixture of 1.5 mL water and 1.5 mL N,N-dimethylformamide (DMF) loaded in a 10 mL scintillation vial, then 13 mg (0.03 mmol) $UO_2(NO_3)_2{\cdot}6H_2O$ and 20 μL concentrated $HNO_3$ was added. The vial was sealed and treated with sonication for 15 min and then heated at 120℃ for 72h. Dark brown crystals was collected and wash with DMF and alcohol for each three times, the products were dried at 60℃.

2. Characterization

   Thermogravimetric analysis (TGA) was carried on NETZSCH STA 449F3 from 30℃ to 800℃under $N_2$ flow with a heating rate of 10℃/min. UV-vis spectrum was recorded from 200 nm to 800 nm on Shimazu UV3600 equipped with integrating sphere in diffuse reflectance mode, $BaSO_4$ was used as reference. Infrared spectroscopy was collected on Bruker NICOLETiS 50 spectrometer equipped with diamond as ATR reflectance accessory. All the spectral data were collected at 25℃±2℃.

   Powder x ray diffraction was collected on Bruker D8 Advance using Cu kα. = 0.15418 nm equipped with a Lynxeye one-dimensional detector in the 2θ range from 5° to 50°. Retiveld Refinement was conducted with GSAS II code with a SVD zero tolerance of 1e-6, minimum detal M/M of 1e-3 with analytical Hessian matrix.

   Single crystal x ray diffraction was performed on Bruker D8 Venture equipped with PHOTON III CMOS detector (Mo as x ray target material, kα = 0.71073). Diffraction frames were recorded with APEX4 code suite. Data integration and adsorption correction were achieved with SAINT and SADABS. Structure of SCU-125 was solved by intrinsic phase method and refined with Shelxtl 2019/1. SQEEZE routine in PLATON was engaged to remove diffraction contribution of remaining electron density corresponding to disordered molecules of starting material and solvent molecules. The total number of electrons found in the channel of metal-organic framework was 1950 for each cell (488 for each formula based on Z =4), which could be assigned to un-modelled disordered dimethylammonium (DMA) cations and solvent molecules. To meet charge balance, 104 of the electron density was assigned to 4 DMA cations. The remained 380 electron density was supposed to be 8 DMF and 6 $H_2O$ molecules. From the TGA pattern, a total weight loss of 21.0% was observed before 290 ℃. This is comparable to the weight loss in calculated amount of supposed solvent molecules and dimethylamine (20.6%). Based on the results, the full formular of SCU-125 was supposed to be $(UO_2)_4(C_{34}H_{16}O_8S_4)_3(DMF)_8(H_2O)_6(DMA)_4$. The XRD experiments were performed at 25℃±2℃.

3. Resistivity measurement

   At 25℃±2℃, the resistivity measurement was performed on four samples of TTFBTU pellets with different thickness obtained on a hydraulic machine with $d$ = 3 mm module under a pressure of 3 MPa. The *I-V* curves was collected on a four-probe system and repeated three

times for each sample. Resistivity was then calculated for each sample and an average value of all samples was offered.

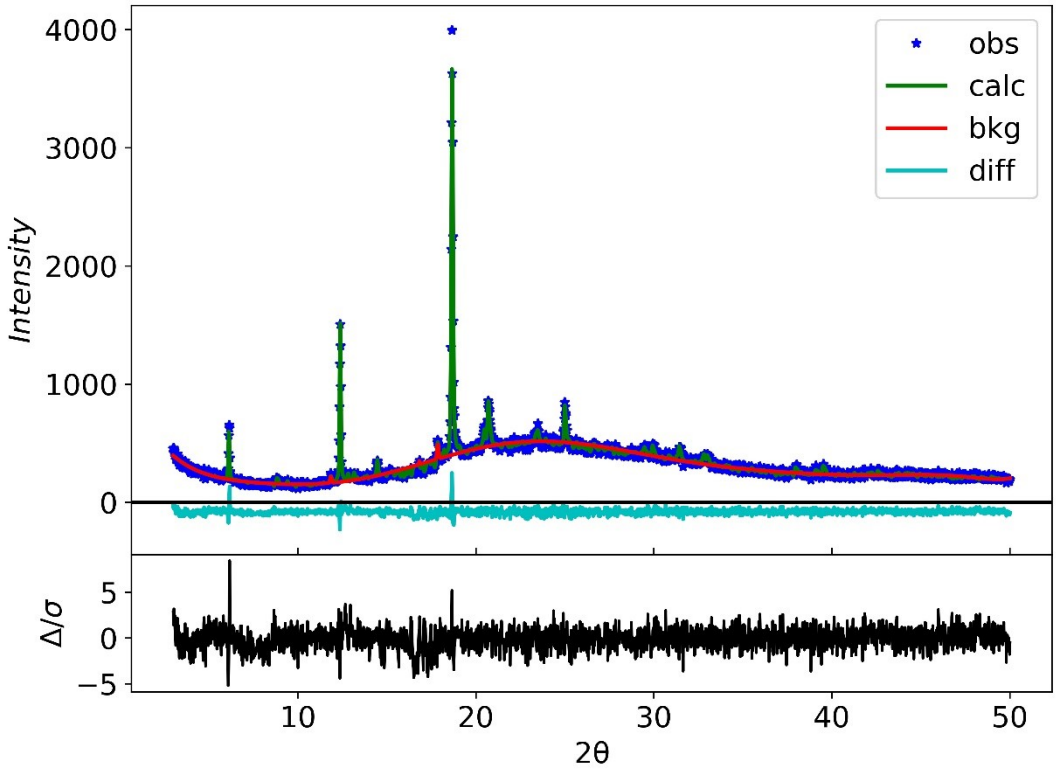


Figure S1 Retiveld refinement of SCU-125 (*wR*% = 6.65, GOF = 1.30; small peaks on the backgroud corresponds to the contamination of Cukβ and W $L_1$ radiation)

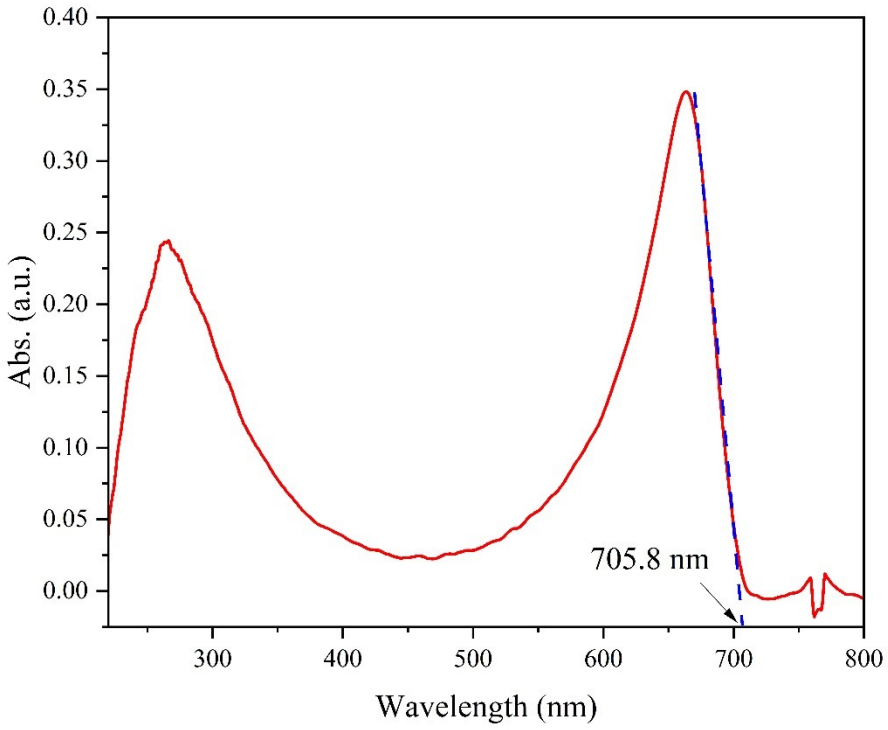


Figure S2 UV-vis spectrum of SCU-125 and the bandgap indication

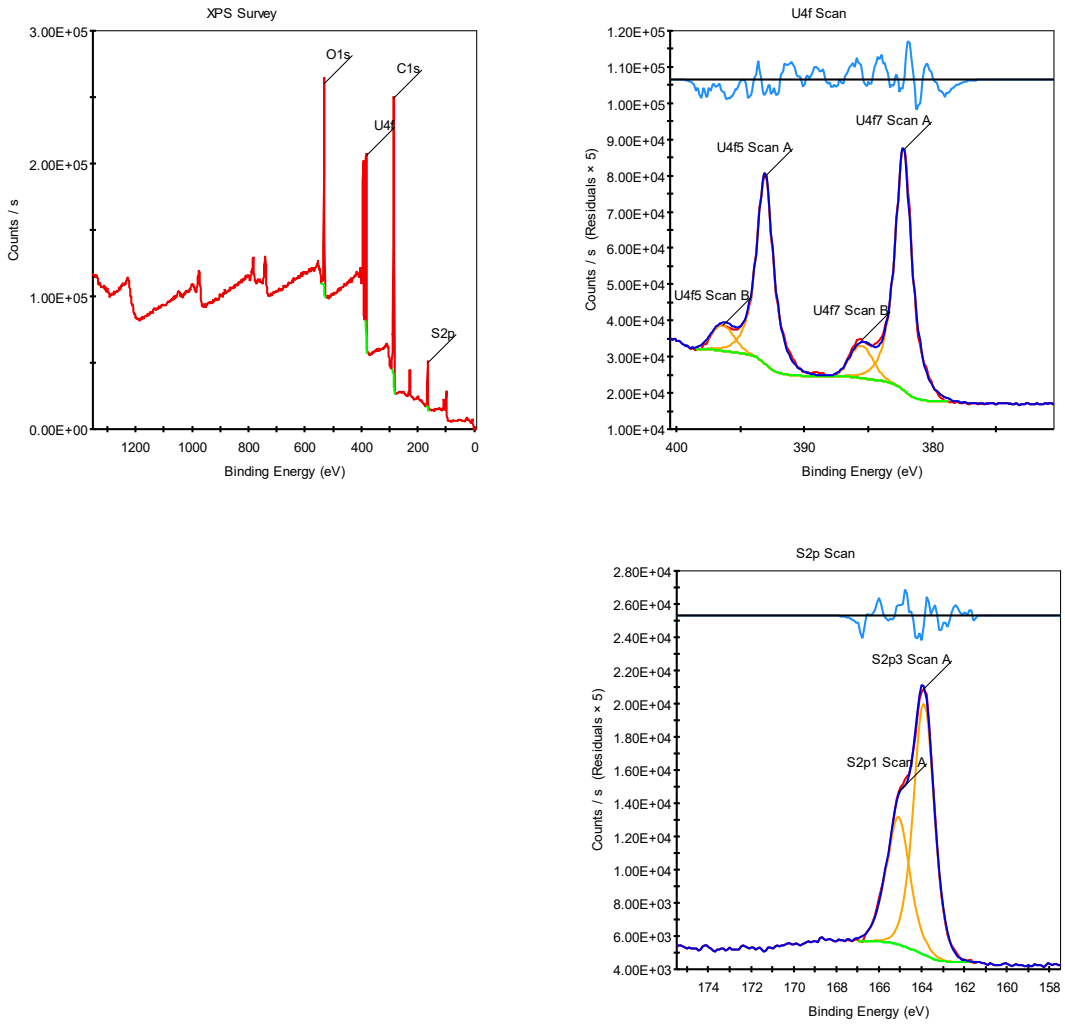


Figure S3 Valence identification of uranium and sulfur of SCU-125 by XPS

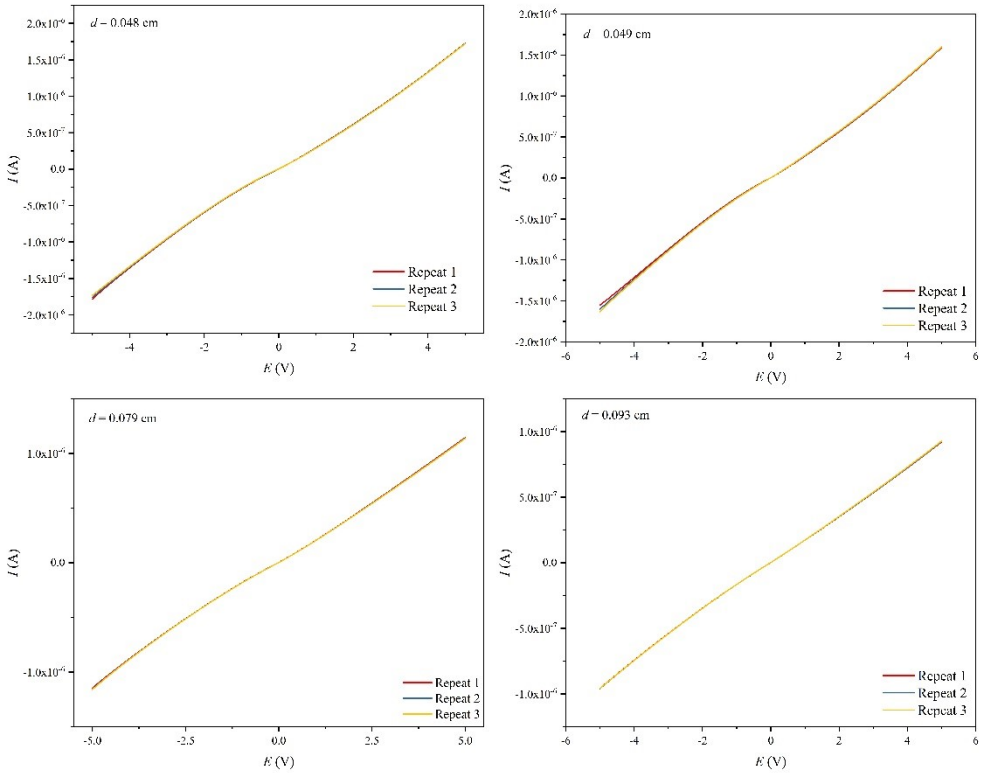


Figure S4. The *I-V* curve of each pellet sample measured on a four-probe system

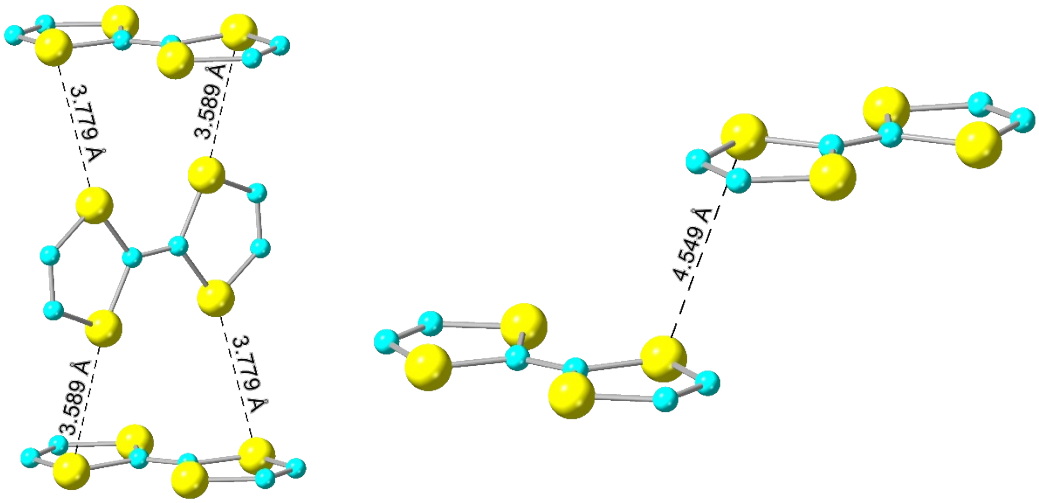


Figure S5. Inner (left) and inter (right) slab distance of neighboring S atoms. (Yellow ball for sulfur and gray ball for carbon)

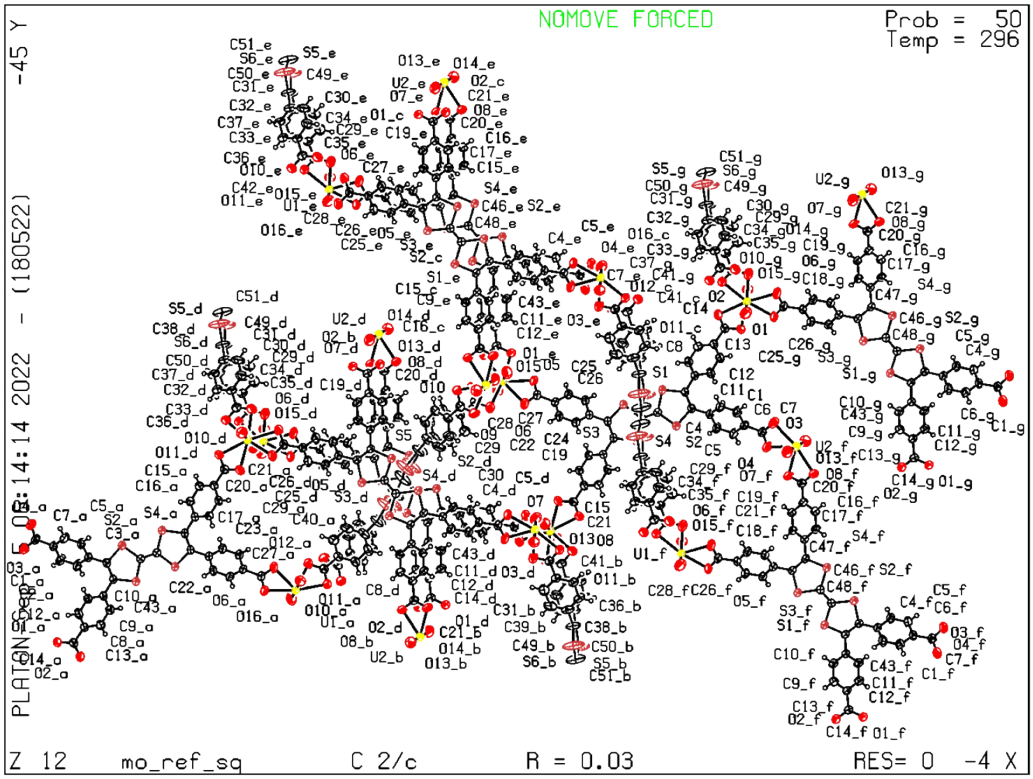


Figure S6. Ellipsoids plot of SCU-125

| Table S1 Crystallographic data of SCU-125 | |
|---|---|
| Formula | $(UO_2)_4(C_{34}H_{16}O_8S_4)_3(DMA)_4(H_2O)_6(DMF)_8$ |
| $M_r$ | 3999.53 |
| Crystal system | Monoclinic |
| Space group | *C* 2/*c* |
| a (Å) | 35.456(2) |
| b (Å) | 19.8240(9) |
| c (Å) | 30.7340(15) |
| α (°) | 90 |
| β (°) | 120.221(2) |
| γ (°) | 90 |
| *V* (Å$^3$) | 18666.2(17) |
| *Z* | 4 |
| $\rho_{calc.}$ (g/cm$^3$) | 1.423 |
| Mu (mm$^{-1}$) | 3.639 |
| F(000) | 5940 |
| T (K) | 296 |
| $R_1$[a], $wR_2$[b], *S* | 0.0301, 0.0862, 1.017 |