

Emission Spectroscopy of Uranium(IV) Compounds: A Combined Synthetic, Spectroscopic and Computational Study

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Electronic Supplementary Information

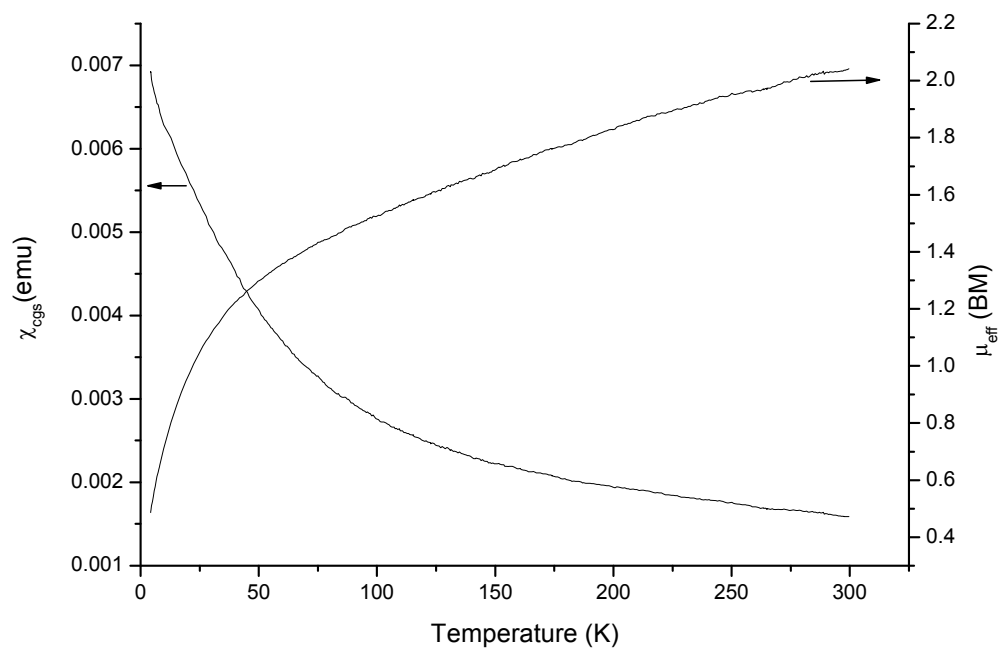


Figure S1. Variable temperature magnetic study on **1**.

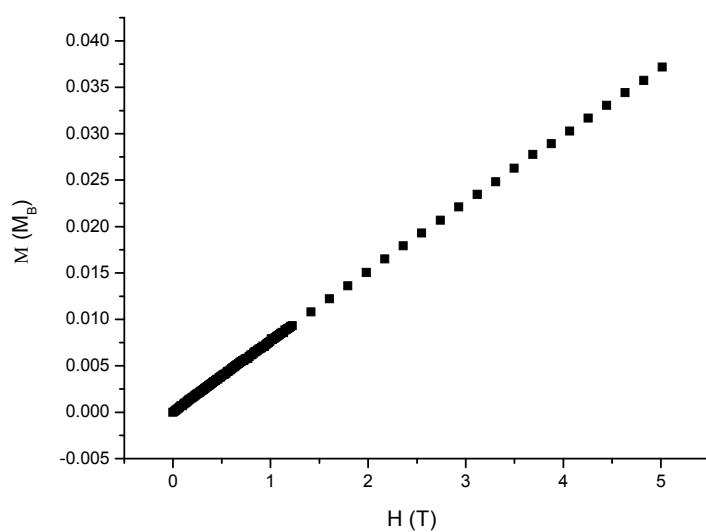


Figure S2. Variable field magnetic study of **1** at 10 K.

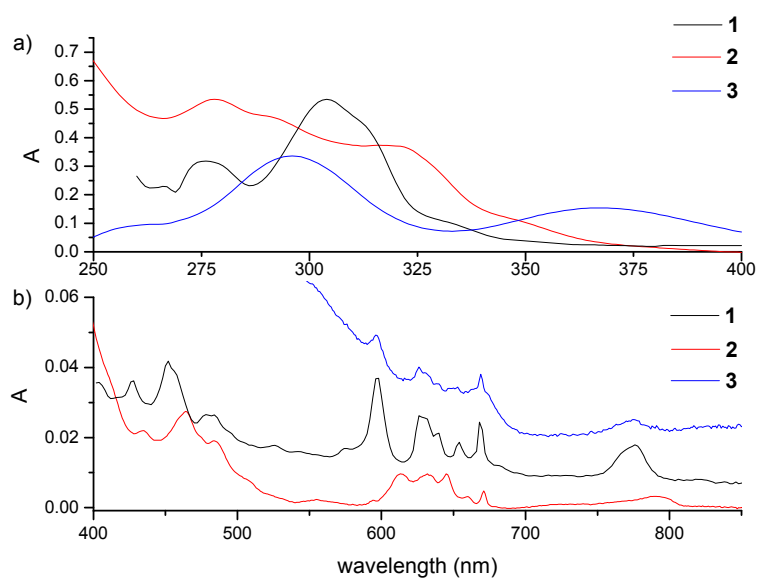


Figure S3. UV-Vis spectra of **1-3** in THF (ca. 10 mmol) showing (a) charge transfer and (b) f-f transitions.

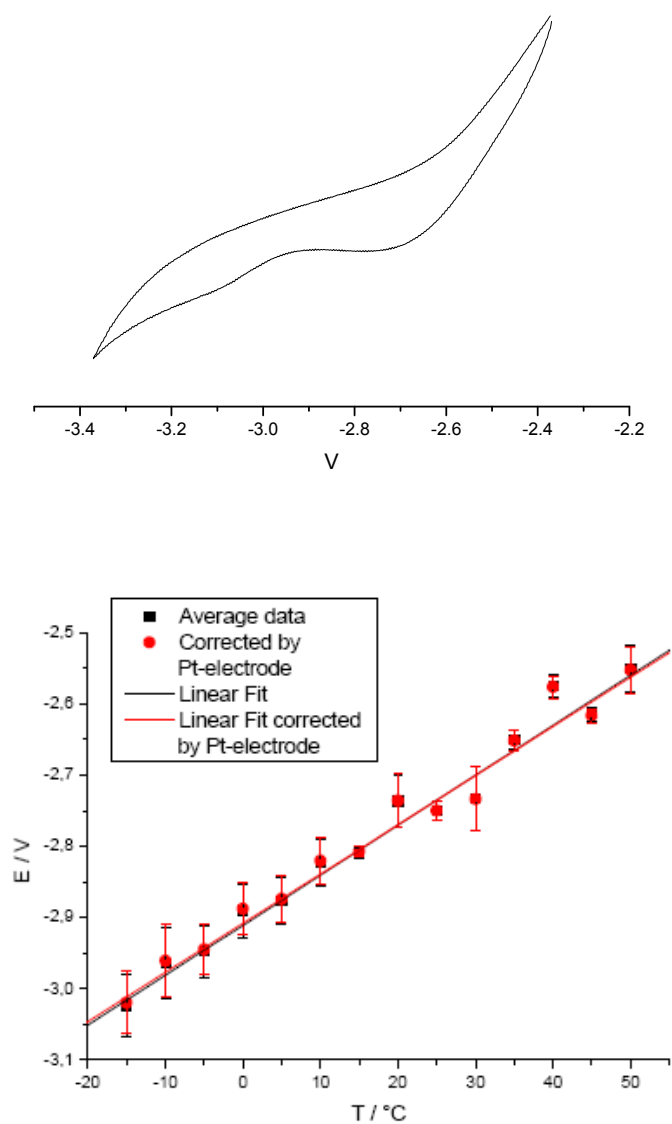


Figure S4. CV voltammogram (top) and temperature dependence of the reduction wave (bottom) of **1**.

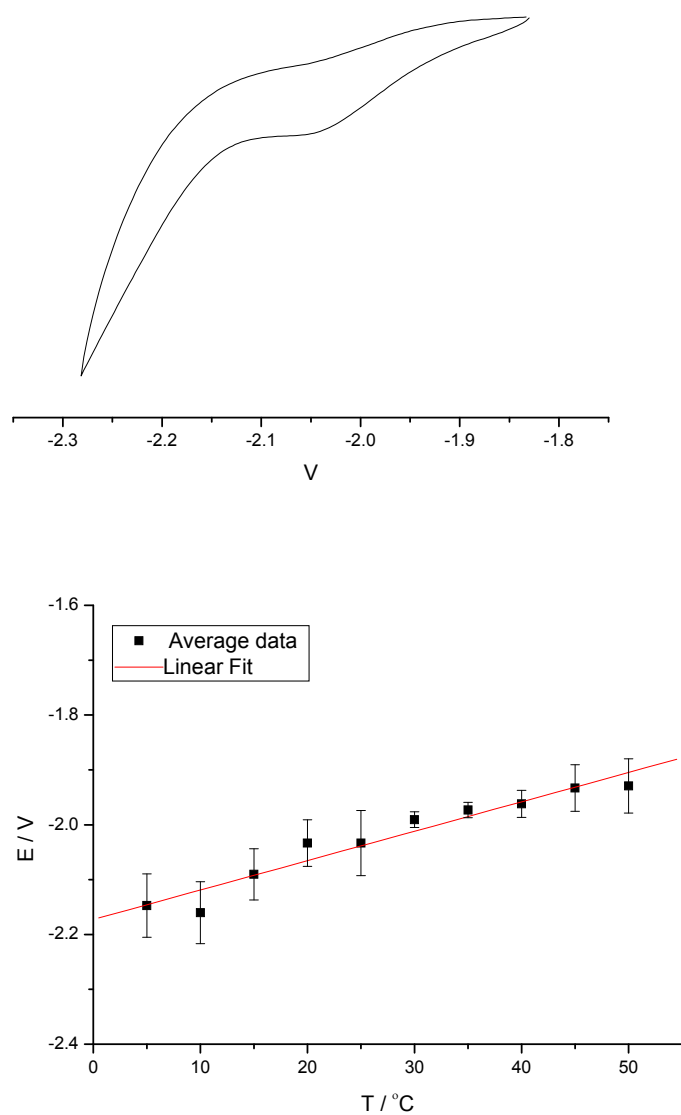


Figure S5. CV voltammogram (top) and temperature dependence of the reduction wave (bottom) of **2**.

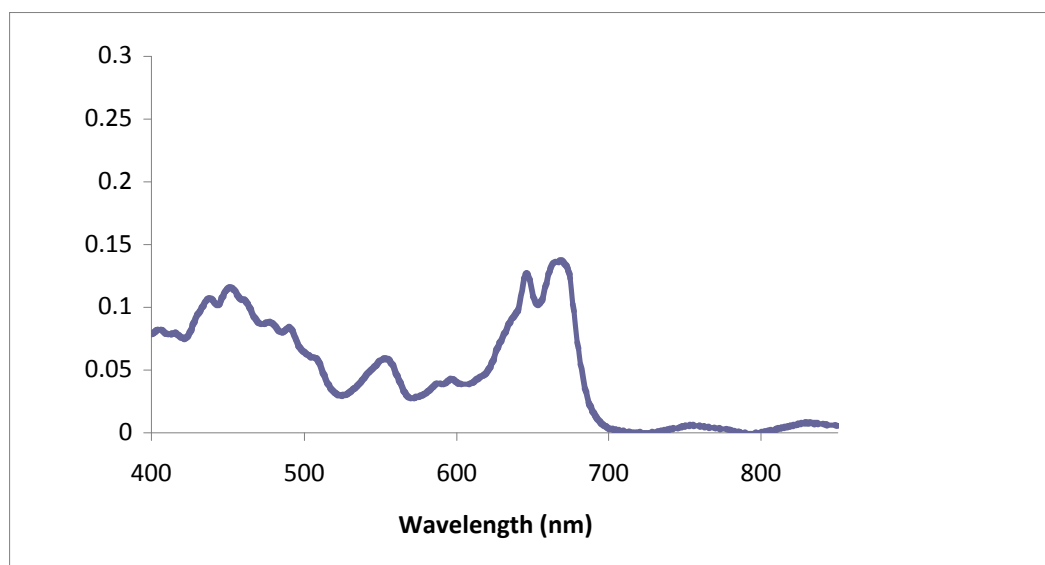


Figure S6. Vis-NIR absorption spectrum of UCl_4 in THF at 10 mM concentration.

λ / nm	260	290	334	347	442	553	646	669	757
$\epsilon / \text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$	21500	21800	12200	14200	10	6	13	14	1

Table S1. Approximate extinction coefficients of the absorptions of UCl_4 in THF.

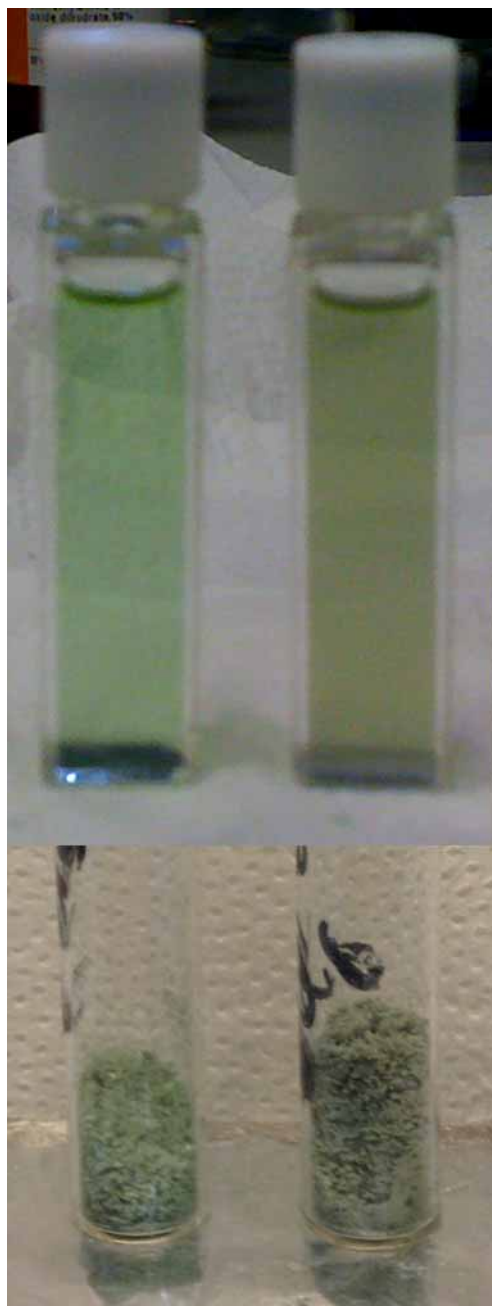


Figure S7. Picture of solid samples and equimolar solutions of $[\text{Li}(\text{THF})_4][\text{UCl}_5(\text{THF})]$ (left) and $[\text{Et}_4\text{N}]_2[\text{UCl}_6]$ (right) in THF.

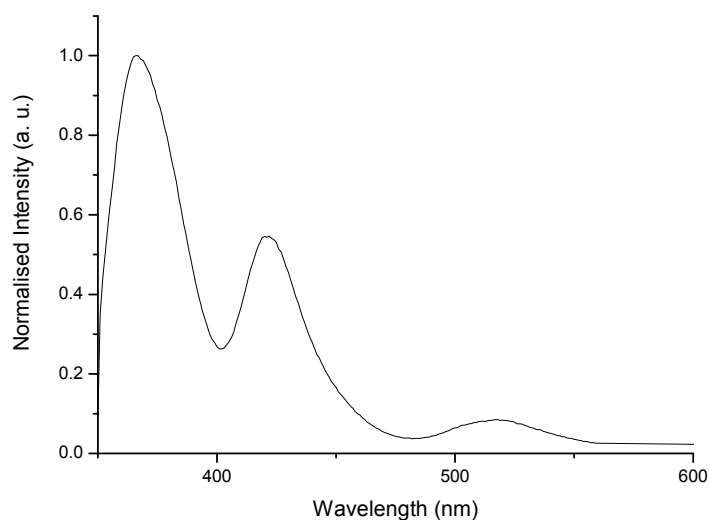


Figure S8. Emission spectrum of $[\text{UCl}_6]^{2-}$ in THF at 298 K ($\lambda_{\text{ex}} = 303$ nm).

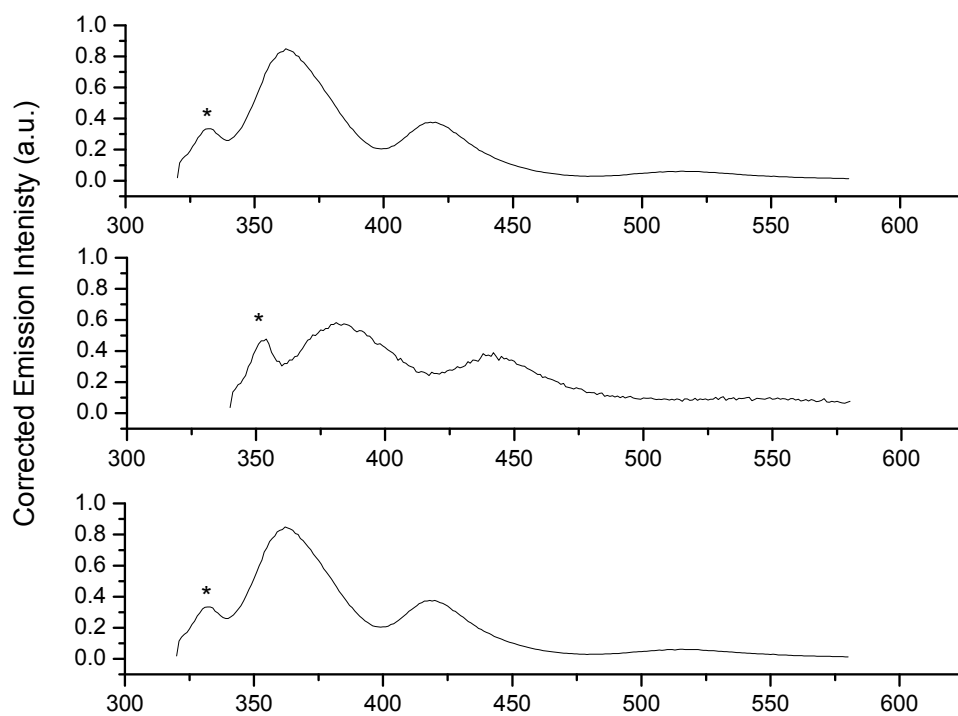


Figure S9. Emission spectra of **1** (top; $\lambda_{\text{ex}} = 303$ nm), **2** (middle; $\lambda_{\text{ex}} = 325$ nm) and $[\text{UCl}_6]^{2-}$ (bottom; $\lambda_{\text{ex}} = 303$ nm) in THF at 298 K. * indicates Raman band.

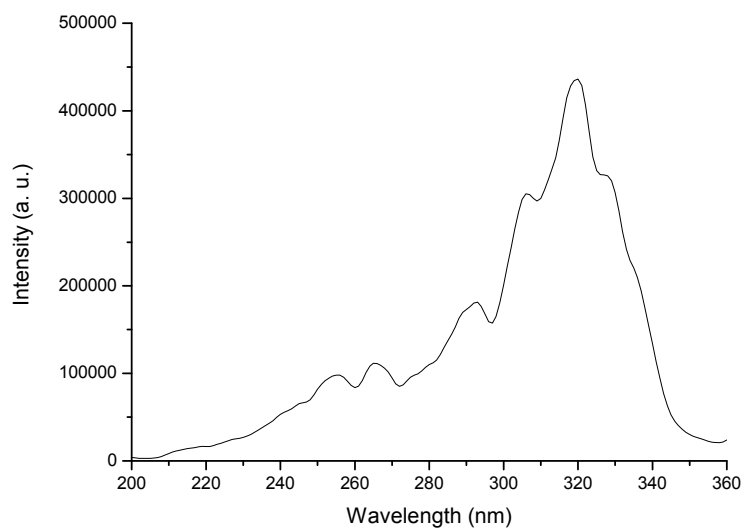


Figure S10. Excitation spectrum of [UCl₄(THF)₃] in THF at 298 K ($\lambda_{\text{em}} = 365$ nm).

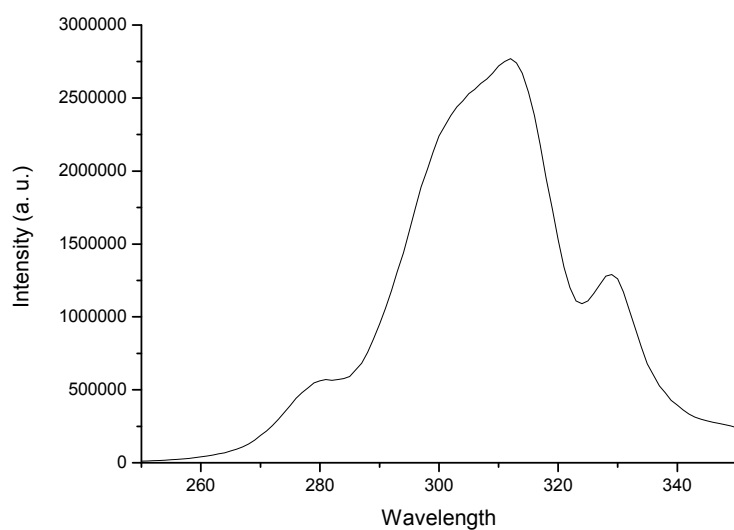


Figure S11. Excitation spectrum of **1** in THF at 298 K ($\lambda_{\text{em}} = 365$ nm).

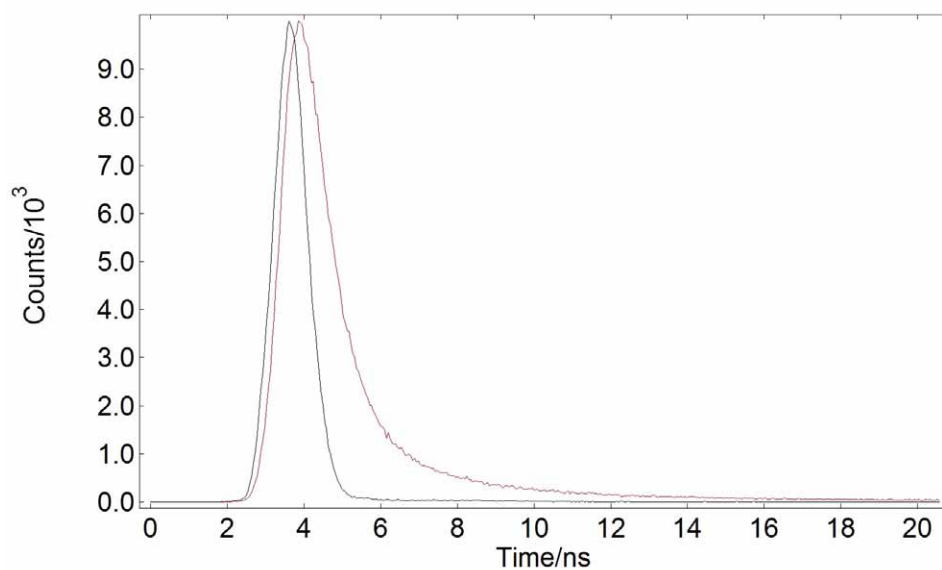


Figure S12. Typical kinetic traces obtained for $[\text{UCl}_4(\text{THF})_3]$ in THF recorded at 298 K following 375 nm excitation (red trace) and the instrument response function (using Ludox[®] as the scatterer, black trace); $\lambda_{\text{em}} = 408$ nm.

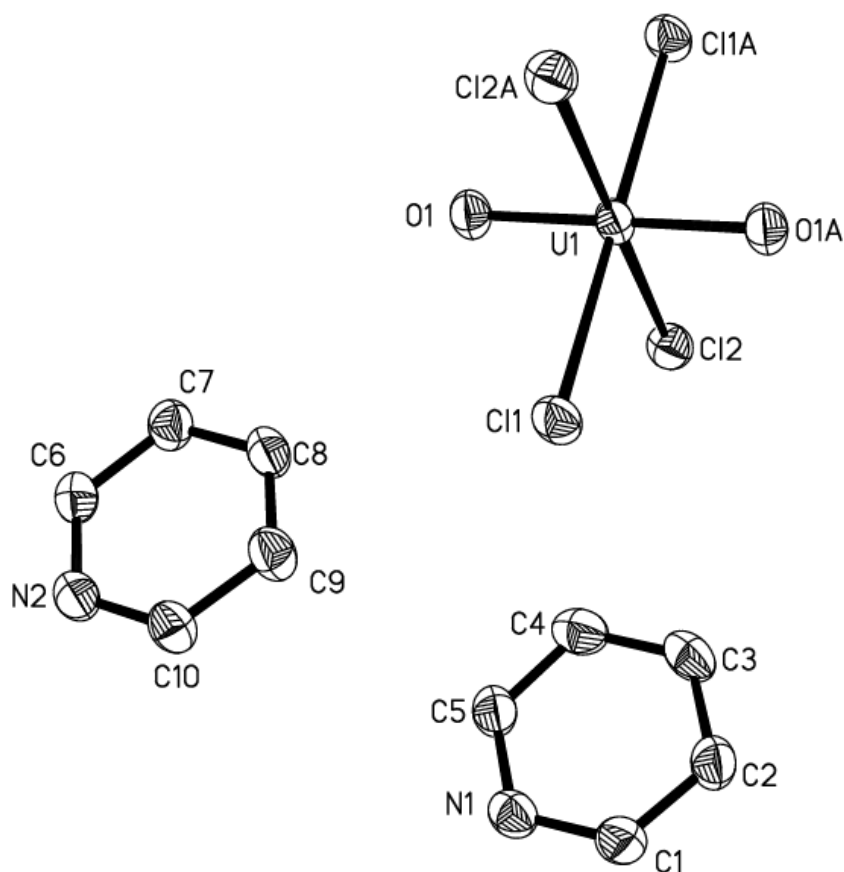


Figure S13. X-ray Structure of $[\text{PyH}]_2[\text{UO}_2\text{Cl}_4] \cdot 2\text{Py}$. Bond Lengths ($\text{\AA}$) and angles ($^\circ$): U(1)-O(1) 1.774(4); U(1)-Cl(1) 2.6523(15); U(1)-Cl(2) 2.6662(16); O(1)-U(1)-O(1A) 180.000(1); O(1)-U(1)-Cl(1) 90.21(14). Symmetry transformations used to generate equivalent atoms: $-x+1, -y+2, -z+1$.

Chemical Formula	C ₂₀ H ₂₂ Cl ₄ N ₄ O ₂ U
Formula weight	730.25
Crystal Size (mm)	0.30 x 0.20 x 0.05
Crystal Appearance	Yellow block
T (K)	108(2)
Crystal system	Triclinic
Space group	P-1
a (Å)	8.4466(17)
b (Å)	9.1058(18)
c (Å)	9.865(2)
α (°)	111.85(3)
β (°)	91.90(3)
γ (°)	115.10(3)
V (Å ³)	621.0(2)
Z	1
μ (Mo-K _α) (mm ⁻¹)	0.71073
Reflections collected	6237
(R _{int})	(0.0434)
Unique reflections	3306
R ₁ (I > 2σ(I))/all data	0.0415/0.0418
wR ₂ (I > 2σ(I))/all data	0.1060/0.1062
GOF	1.050
CCDC No	907974

Table S2. Structural and refinement data for [PyH]₂[UO₂Cl₄].2Py

	Experiment (Å and °)	BP86- TZVP	BP86- TZVPP	PBE- TZVP	B3LYP- TZVP	PBE0- TZVP
U—O	2.402(5)	2.512	2.527	2.519	2.542	2.507
U—Cl _(ax)	2.5919(19)	2.594	2.589	2.589	2.606	2.577
U—Cl _(eq)	2.612(6)	2.614	2.615	2.609	2.627	2.598
Cl-U-O	84.5-86.8	82.5 - 82.9	82.3 - 83.3	82.1 - 82.9	82.2 - 82.9	81.9 - 82.9

Table S3. Comparison of DFT calculated values of geometry optimisation of **1**.

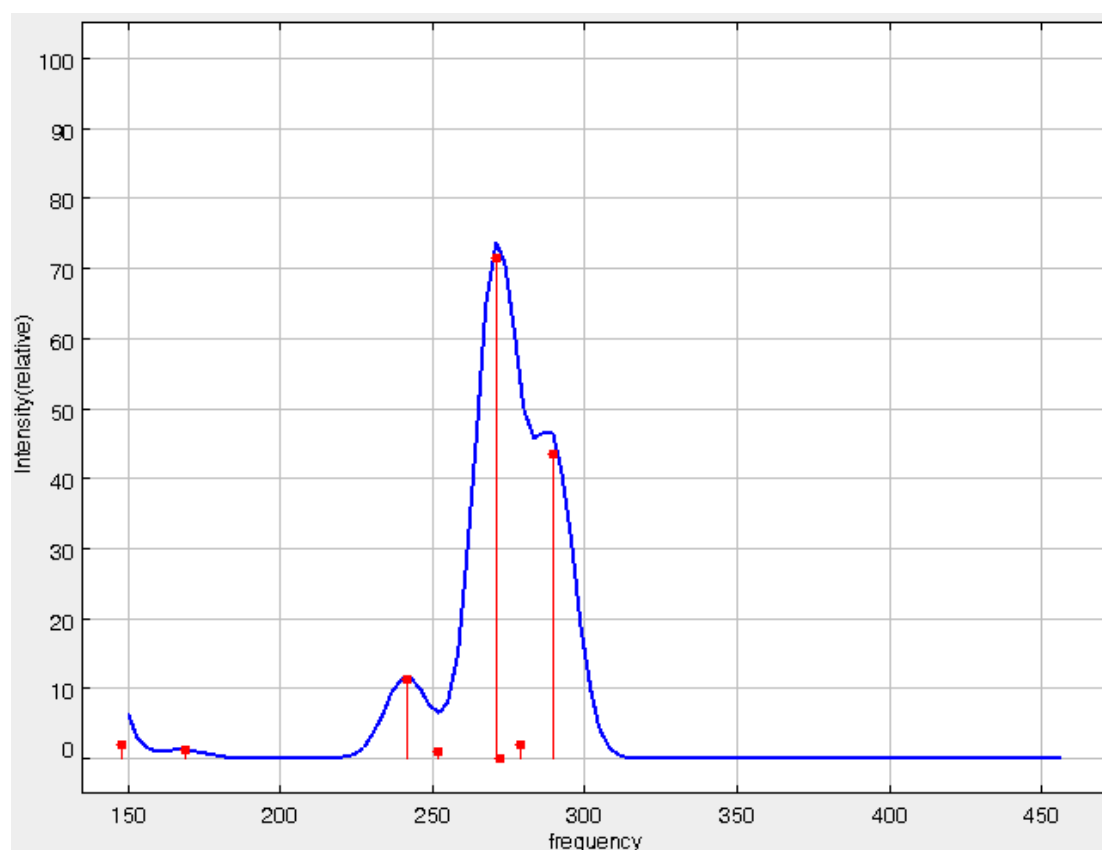


Figure S14. Calculated Raman spectrum of **1** at BP86 functional.

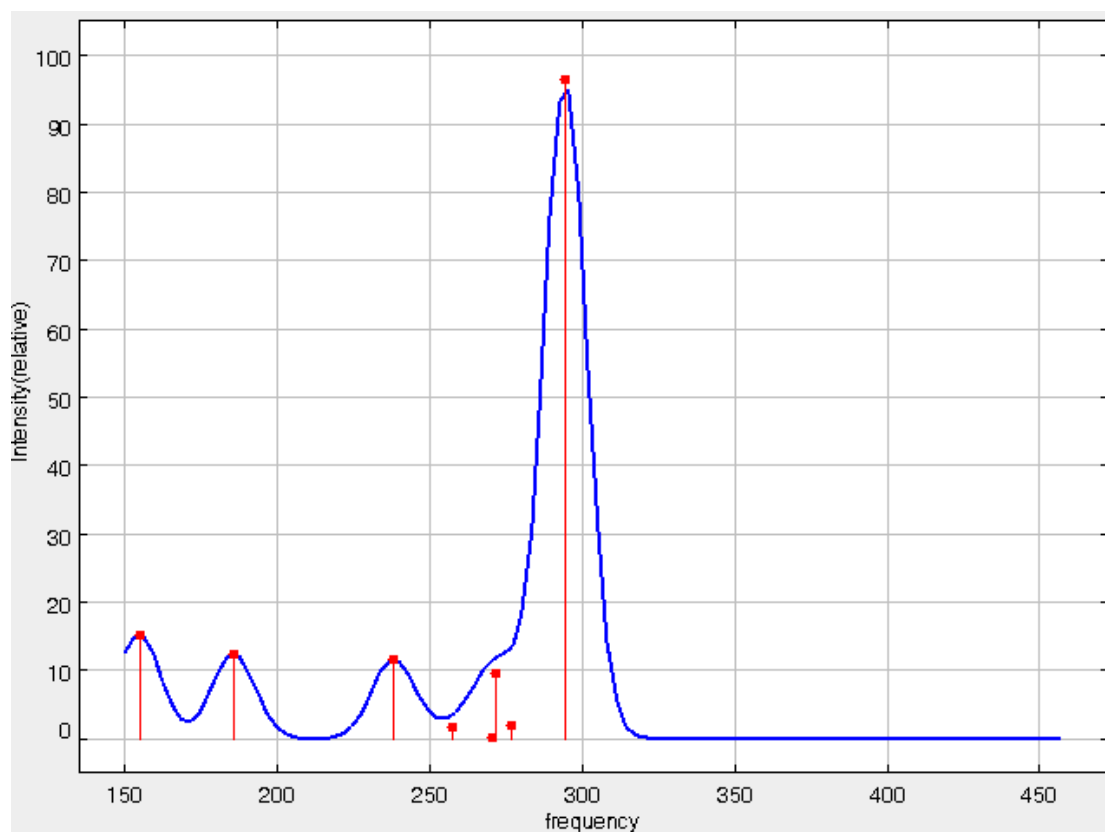


Figure S15. Calculated Raman spectrum of **1** at B3LYP functional.

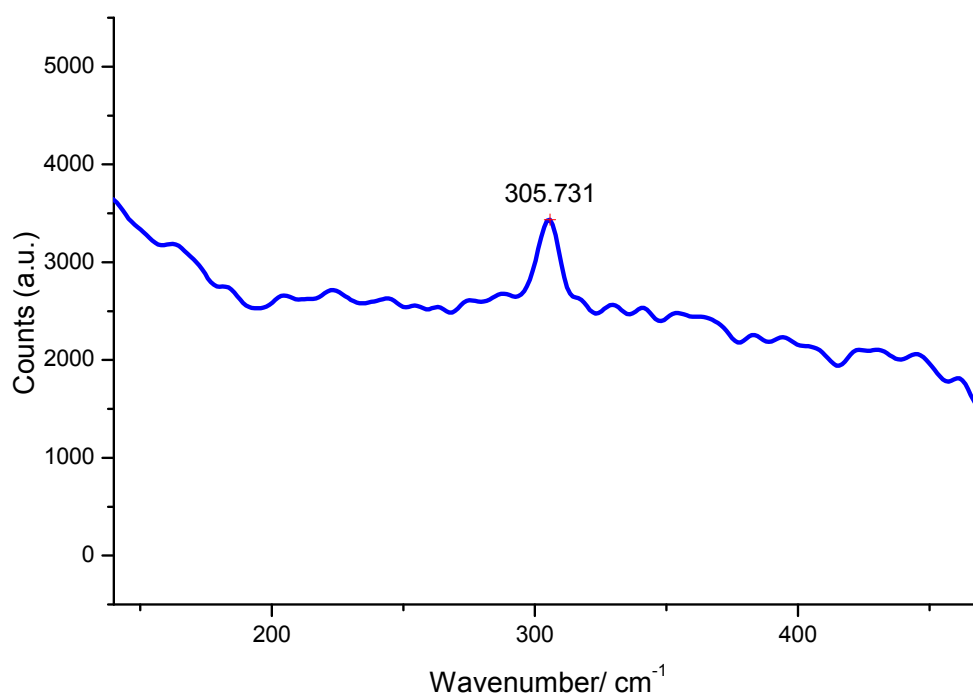


Figure S16. Experimental Raman spectrum of **1**.