Electronic Supplementary Material (ESI) for Dalton Transactions

Fingerprinting the oxidation state of U(IV) by emission spectroscopy

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Supporting Information

Experimental Details

Caution! Natural uranium was used during the course of these experiments. As well as the radiological hazards, uranium is a toxic metal and care should be taken with all manipulations. Experiments using uranium materials were carried out using pre–set radiological safety precautions in accordance with the local rules of Trinity College Dublin.

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity argon. ^{1}H NMR spectra were recorded on a Bruker AV400 spectrometer operating at 400.23 MHz, and were referenced to the residual ^{1}H resonances of the solvent used. IR spectra were recorded on a Perkin Elmer Spectrum One spectrometer with attenuated total reflectance (ATR) accessory. Raman spectra were obtained using 785 nm excitation on a Renishaw 1000 micro-Raman system in sealed capillaries. Thermal and field scans of DC and AC magnetization were carried out using a 5T Quantum Design MPMS XL SQUID magnetometer from 2-300 K. Powdered samples were fixed by eicosane and mounted in gel caps, which have a temperature–independent diamagnetic susceptibility, in a glove box and the gel caps were placed in sample straws for the measurement. Diamagnetic corrections were made using Pascal's constants.[1] Multiple measurements were taken to ensure reproducibility. X-ray crystallography was measured on a Rikagu Saturn diffractometer. The structures were solved by direct methods and refined on F^2 by full matrix least squares (SHELX97)[2] using all unique data. Crystal data, details of data collections and refinement are given in Table S1. UV-vis/NIR measurements were made on a Perkin Elmer Lambda 1050 spectrometer using fused silica cells with a path length of 1 cm. Steady-state emission spectra were recorded in quartz cuvettes on a Horiba-Jobin-Yvon Fluorolog-3 spectrometer. Lifetime data were recorded following 375 nm and 405 nm excitation using time correlated single photon counting (PCS900 plug-in PC card for fast photon counting). Lifetimes were obtained by tail fit on the data obtained, and quality of fit judged by minimization of reduced chi-squared and residuals squared.

Acetonitrile was distilled over CaH_2 and degassed immediately prior to use. Spectroscopic measurements used spectroscopic grade solvents which was purchased from commercial sources and dried over molecular sieves and thoroughly degassed before use. $[Et_4N]_4[U(NCS)_8]$[3] was made *via* the literature procedure whilst bipy was obtained from commercial sources and recrystallized before use.

Synthesis of **1**. To a sample of $[Et_4N]_4[U(NCS)_8]$ (200 mg, 0.16 mmol) was added 2,2-bipyridine (51mg, 0.33mmol). Anhydrous MeCN (20 cm^3) was added and the mixture was stirred for an hour at room temperature. The solvent was reduced in vacuo and placed at -30 ^{0}C. After 48 hours pale green crystals suitable for X-ray diffraction were formed (116.5mg, 0.12mmol, 75%). IR (cm^{-1}) 2016, 1595, 1570, 1474, 1434, 1394, 1313, 1175, 1067, 1011, 764, 735, 641, 623, 553; RAMAN (cm^{-1}) 2070, 2030, 1600, 1568, 1496, 1300, 1069, 1000, 831, 768, 652, 546, 627, 416, 350.

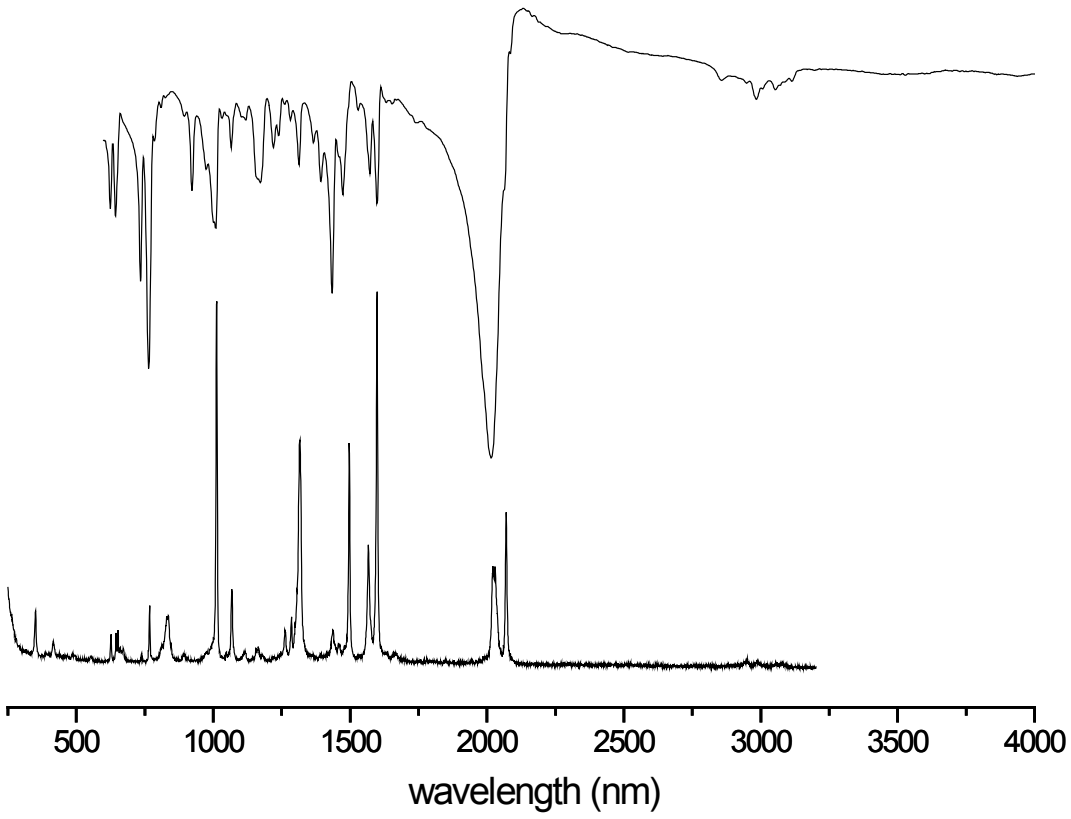

Figure S1. IR and Raman spectra of **1**.

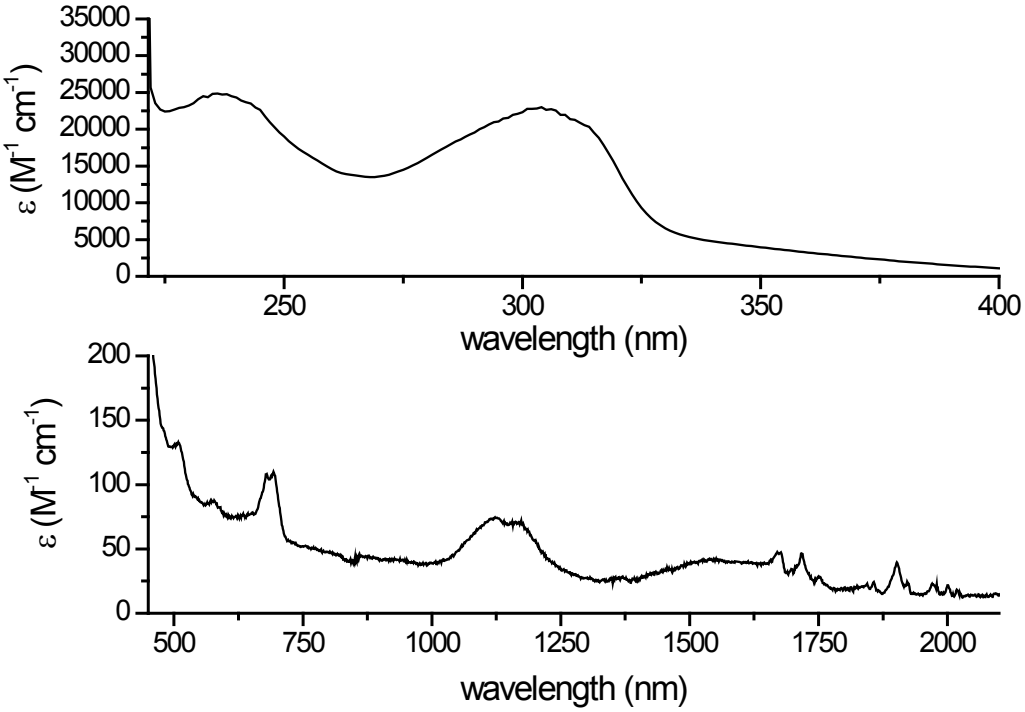

Figure S2. UV-vis/NIR spectrum of **1** in MeCN.

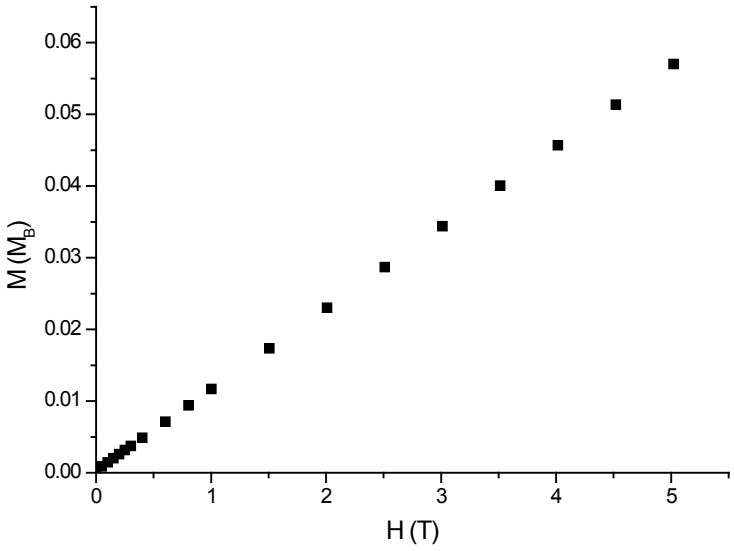

Figure S3. Variable Field Magnetization for **1** at 10 K.

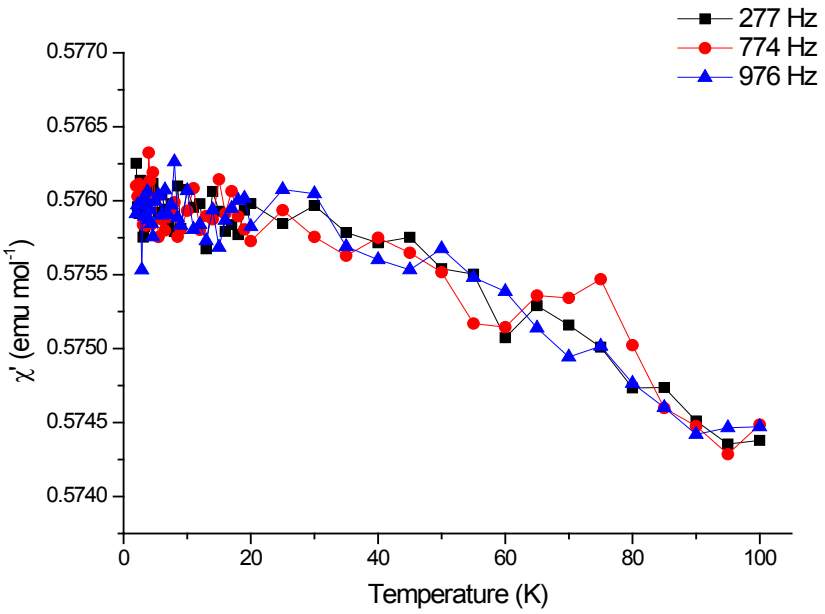

Figure S4. In-phase component of the AC-magnetic susceptibility of **1** at 0.1 T for selected AC frequencies, as labelled.

Tables S1. Refinement details for single crystals of **1**.

chemical formula	$C_{33}\ H_{36}\ N_{10}\ S_5\ U$
formula weight	971.05
space group	Monoclinic (P 21/c)
a (Å)	14.2687(6)
b (Å)	18.5947(9)
c (Å)	15.3116(7)
λ (Å)	1.54178
B	103.810(2)
T (°C)	100
μ (cm^{-1})	14.354
V ($Å^3$)	3945.1(3)
Z	4
$R(F_o^2)$	0.0420
$R_w(Fo^2)$	0.1052
CCDC No	953095

Table S2. Bond Lengths (Å) for **1**.

U4 N33 2.391(4)	U4 N38 2.430(4)
U4 N23 2.428(4)	U4 N22 2.430(4)
U4 N39 2.432(4)	U4 N21 2.625(4)
U4 N19 2.633(4)	U4 N20 2.637(4)
U4 N18 2.646(4)	S10 C68 1.624(5)
S11 C69 1.614(5)	S17 C93 1.615(5)
S21 C123 1.619(5)	S22 C124 1.618(5)
N18 C53 1.345(7)	N18 C54 1.345(6)
N19 C49 1.346(6)	N19 C50 1.357(7)
N20 C60 1.341(6)	N20 C62 1.365(6)
N21 C67 1.354(6)	N21 C63 1.356(7)
N22 C69 1.179(6)	N23 C68 1.161(7)
N33 C93 1.162(7)	N38 C123 1.161(6)
N39 C124 1.166(6)	C48 C49 1.381(8)
C48 C52 1.382(9)	C50 C51 1.405(8)
C50 C53 1.485(7)	C51 C52 1.382(8)
C53 C57 1.385(9)	C54 C55 1.397(8)
C55 C56 1.366(9)	C56 C57 1.374(9)
C58 C61 1.383(8)	C58 C59 1.400(8)
C59 C60 1.378(7)	C61 C62 1.392(7)
C62 C63 1.471(7)	C63 C64 1.391(9)
C64 C65 1.374(8)	C65 C66 1.388(8)
C66 C67 1.373(8)	N36 C112 1.513(6)
N36 C115 1.521(6)	N36 C116 1.523(6)
N36 C111 1.530(6)	C110 C111 1.504(8)

C112 C113 1.511(7)	C114 C115 1.519(7)
C116 C117 1.488(9)	

Table S3. Bond angles (°) for **1**.

N33 U4 N38 140.64(14)	N33 U4 N23 141.09(14)
N38 U4 N23 78.20(13)	N33 U4 N22 72.96(15)
N38 U4 N22 132.73(13)	N23 U4 N22 79.17(13)
N33 U4 N39 73.26(16)	N38 U4 N39 75.50(14)
N23 U4 N39 131.51(13)	N22 U4 N39 146.09(14)
N33 U4 N21 74.02(14)	N38 U4 N21 75.11(12)
N23 U4 N21 135.02(13)	N22 U4 N21 93.25(13)
N39 U4 N21 74.69(13)	N33 U4 N19 111.10(15)
N38 U4 N19 77.54(12)	N23 U4 N19 67.28(12)
N22 U4 N19 128.79(13)	N39 U4 N19 67.69(13)
N21 U4 N19 137.79(12)	N33 U4 N20 115.62(15)
N38 U4 N20 67.93(12)	N23 U4 N20 75.37(12)
N22 U4 N20 66.43(12)	N39 U4 N20 128.00(13)
N21 U4 N20 61.28(12)	N19 U4 N20 133.24(11)
N33 U4 N18 71.84(15)	N38 U4 N18 136.74(12)
N23 U4 N18 74.61(13)	N22 U4 N18 73.58(12)
N39 U4 N18 98.50(14)	N21 U4 N18 145.68(12)
N19 U4 N18 61.18(12)	N20 U4 N18 133.45(12)
C53 N18 C54 117.9(4)	C53 N18 U4 121.6(3)
C54 N18 U4 120.2(3)	C49 N19 C50 118.1(4)
C49 N19 U4 119.8(3)	C50 N19 U4 120.9(3)

C60 N20 C62 117.9(4)	C60 N20 U4 120.9(3)
C62 N20 U4 120.8(3)	C67 N21 C63 117.1(4)
C67 N21 U4 120.9(3)	C63 N21 U4 120.9(3)
C69 N22 U4 159.4(4)	C68 N23 U4 156.2(3)
C93 N33 U4 159.8(4)	C123 N38 U4 162.8(3)
C124 N39 U4 176.8(4)	C49 C48 C52 119.4(5)
N19 C49 C48 122.7(5)	N19 C50 C51 121.8(5)
N19 C50 C53 116.5(5)	C51 C50 C53 121.6(5)
C52 C51 C50 118.8(5)	C51 C52 C48 119.1(5)
N18 C53 C57 122.1(5)	N18 C53 C50 116.2(5)
C57 C53 C50 121.5(6)	N18 C54 C55 122.2(5)
C56 C55 C54 119.1(5)	C55 C56 C57 118.9(5)
C56 C57 C53 119.7(6)	C61 C58 C59 118.3(4)
C60 C59 C58 118.4(5)	N20 C60 C59 124.0(5)
C58 C61 C62 120.4(5)	N20 C62 C61 121.0(5)
N20 C62 C63 116.4(4)	C61 C62 C63 122.6(5)
N21 C63 C64 121.6(4)	N21 C63 C62 116.4(5)
C64 C63 C62 121.8(5)	C65 C64 C63 120.1(5)
C64 C65 C66 118.7(5)	C67 C66 C65 118.5(5)
N21 C67 C66 123.8(5)	N23 C68 S10 178.7(5)
N22 C69 S11 179.5(5)	N33 C93 S17 178.0(5)
N38 C123 S21 179.2(4)	N39 C124 S22 179.9(5)
C112 N36 C115 108.3(4)	C112 N36 C116 108.7(4)
C115 N36 C116 111.1(4)	C112 N36 C111 110.3(4)
C115 N36 C111 109.3(4)	C116 N36 C111 109.1(4)

C110 C111 N36 115.2(4)	C113 C112 N36 116.1(4)
C114 C115 N36 114.3(4)	C117 C116 N36 115.7(4)

[1] G.A. Bain and J.F. Berry, *J. Chem. Edu.*, 2008, **85**, 532-536.

[2] G.M. Sheldrick, SHELXL-97, University of Göttingen, Göttingen, Germany (1998).

[3] K. W. Bagnall, D. Brown and R. Colton, *J. Chem. Soc. Dalton Trans.,* 1964, 2527.