Supporting Information

Neptunyl(VI) Centred Visible LMCT Emission Directly Observable in the Presence of Uranyl(VI)

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Experimental Details

Caution! *^{238}U, ^{237}Np, are all high specific activity nuclides and represent a serious internal and/ or external hazard. All experiments were performed following the pre-set radiological safety precautions in accordance with the local rules of The University of Manchester and the KIT-INE, Karlsruhe.*

General

All chemicals were purchased from the Aldrich Chemical Company. The ligand NaTPIP and the complex [Gd(TPIP)$_3$] were prepared as previously described.[1]

Stock solutions of NpO$_2$(V) in HCl were provided by KIT-INE radioisotope stocks. [NpO$_2$(O$_4$Cl)$_2$] solutions were prepared by heating the NpO$_2$(V) stock solution (typically 0.006 or 0.007 mM aliquots) to dryness in a glass vial placed in an aluminium heating block inside a designated negative pressure glove box and adding 60% perchloric acid. This solution was heated to ca. 200 °C or until fuming for several hours and then evaporated to dryness. The residue was then dissolved in H$_2$O (1 mL) to yield the Np(VI) aqua ion (pink colour).[2] Subsequent removal of the water by heating and addition of the required solvent for complexation studies led to yellow solutions of NpO$_2$(VI). Samples of **1** were shipped to The University of Manchester for X-ray crystallographic, optical and further NMR studies and all subsequent manipulations were performed in a designated fumecupboard in the CRR.

Mass spectra were obtained using positive electrospray on a Micromass Platform II spectrometer or by MALDI with an ALPHA matrix on a Shimadzu Axima

Confidence spectrometer. Accurate mass spectra were recorded on a Waters QTOF. Solutions were made up using DCM, acetonitrile or methanol. Elemental Analyses were performed by the microanalytical services at the University of Manchester using a Carlo ERBA Instruments CHNS-O EA1108 elemental analyzer (C, H and N analysis) and a Fisons Horizon elemental analysis ICP-OED spectrometer for U, P, and halides.

All NMR spectra of were recorded on a Bruker Avance 400 spectrometer (Manchester) and on a Bruker Avance III 400 spectrometer with a gradient inverse detection probe used for proton measurements and a broadband observe probe with direct *x*-magnetisation detection for non-proton measurements (INE, Karlsruhe). Operating frequencies 400 MHz (^{1}H), 101 MHz (^{13}C), 162 MHz (^{31}P), variable temperature unit set at 300 K unless otherwise stated. The NMR machines were controlled remotely using Bruker Topspin 2.1 or 3.1 software. Chemical shifts are reported in parts per million relative to TMS and referenced to the residual proton resonances in *d*-chloroform or d_2-dichloromethane. Neptunium samples for analysis were transferred to a Teflon insert tube, which were subsequently placed into 5mm walled, 8" NMR tubes manufactured by Wilmad-LabGlass.

Absorption spectra were recorded in DCM, methanol or a mixture on a T60U spectrometer (PG Instruments Ltd.) (**2**) using fused quartz cells with a path length of 1 cm or on a on a Shimadzu UV-2600 (**1**).

Single crystal X-Ray diffraction was performed on an Oxford Diffraction Crysalis CCD diffractometer at 100 K (**2**) or an Agilent Technologies SuperNova 4-circle diffractometer at 150 K (**1**), both with Mo/ K microfocus source. Data were solved using direct methods with OLEX-2 software.[3] The non-H atoms were refined anisotropically. Hydrogen atoms were positioned in idealised sites and were allowed to ride on their parent C or N atoms. Neptunium crystals suitable for single crystal X-ray diffraction were isolated in fomblin oil in the designated neptunium fumehood in the Centre for Radiochemistry Research (CRR). The crystals were then transported in double containment to the CRR microscope and inserted into a capillary, which was subsequently mounted onto a goniometer (which had been designated specifically for use with neptunium crystals) and fixed in place with Araldite.

Steady state emission and excitation spectra were recorded on an Edinburgh Instrument FP920 Phosphorescence Lifetime Spectrometer equipped with a 5 watt microsecond pulsed xenon flashlamp (with single 300 mm focal length excitation and emission monochromators in Czerny Turner configuration) and a red sensitive photomultiplier in peltier (air cooled) housing, (Hamamatsu R928P) and a liquid nitrogen cooled nIR photomultiplier (Hamamatsu). Lifetime data were recorded following excitation with either the microsecond flashlamp, an EPL 375 and EPL 405 picosecond pulsed diode laser (Edinburgh Instruments), or a picosecond pulsed Supercontinuum laser at 420 nm (Fianium) 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 or by a reconvolution fit using a solution of Ludox® in the scatterer, and quality of fit judged by minimization of reduced chi-squared and residuals squared.

Preparation of Complexes 1 and 2

Synthesis of $[NpO_2(TPIP)_2(Ph_3PO)]$ (1).

From $[NpO_2(V)Cl]$

In a designated negative pressure glove box (KIT-INE, Karlsruhe), $[NpO_2Cl]$ in hydrochloric acid (200 μL; 0.006 mmol ^{237}Np stock solution) was heated until dry and dissolved in MeOD 1:8 $CDCl_3$ (1 mL). NaTPIP (5 mg, 0.011 mmol) and Ph_3PO (1 mg, 0.004 mmol) were added and the green solution transferred to an NMR tube. Standing for three months led to the precipitation of yellow crystals of **1**. The sample was shipped by courier to The University of Manchester, CRR, where the crystals were isolated after washing and air drying. UV/vis (DCM): λ_{max}/ nm = 243, 266, 273, 290 (sh), 585, 1232. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz) δ (ppm): -28.5 (br, Np-TPIP), 20.6 (br, Np-Ph_3PO), 29.2 (Ph_3PO); ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 6.80-8.10 (overlapping resonances, Np-TPIP + Np-Ph_3PO + Ph_3PO), 7.39 (t, $^3J_{HH}$ = 7.0 Hz, Np-TPIP), 7.48 (t, 7.0 Hz, Np-TPIP), 7.58 (br, Np-TPIP).

From $[NpO_2(VI)(O_4Cl)_2]$

In a designated negative pressure glove box (KIT-INE, Karlsruhe) or in a designated fumehood (Manchester) $[NpO_2(O_4Cl)_2]$ in perchloric acid (330 μL; 0.007 mmol

^{237}Np) was heated until dry and dissolved in deionised water (1 mL). The solution was again heated to dryness and dissolved in CH_2Cl_2 or CD_2Cl_2. NaTPIP (6 mg, 0.014 mmol) and Ph_3PO (2 mg, 0.007 mmol) were added and the yellow-green solution transferred to an NMR tube Teflon insert, vial or screw cap quartz cuvette for spectroscopic analysis.

Synthesis of [$UO_2(TPIP)_2(Ph_3PO)$] (2)

NaTPIP (51 mg, 0.12 mmol) was suspended in absolute ethanol (10 mL) and added to a stirred solution of uranyl nitrate hexahydrate (30 mg, 0.06 mmol) in deionised water (10 mL) to produce a cloudy green solution. After stirring for 1 h. the solution was filtered, rinsed with absolute ethanol and the solid left to air dry. The solid was collected in a sample vial and dissolved in THF (10 mL). Ph_3PO (12 mg, 0.043 mmol) was added to the solution and the sample left to stir over the weekend. Evaporation of the solvent resulted in a precipitate which was dissolved in DCM and layered with hexane. After a couple of days standing pale green needles were deposited in the vial (82 mg, 67 %). UV/vis (DCM): λ_{max}/ nm (ε/ cm^{3}mol^{-1}cm^{-1}) = 404 (33), 417 (35), 429 (37), 442 (34), 454 (27). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 162 MHz) δ (ppm): 24.3 (s, $(OP(Ph)_2)_2N$), 40.2 (s, Ph_3PO); ^1H NMR (CD_2Cl_2, 400 MHz) δ (ppm): 7.1 – 7.5 (br m, 33H, $_{ph}$CH), 7.6 – 8.3 (br m, 22H, $_{ph}$CH); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 101 MHz) δ (ppm): 128.2 (d, $^2J_{PC}$ = 13.0 Hz, $_{ph}$C), 128.9 (d, $^3J_{PC}$ = 12.5 Hz, $_{ph}$C), 130.7 (s, $_{ph}$C), 131.7 (d, $^2J_{PC}$ = 10.4 Hz, $_{ph}$C), 132.7 (s, $_{ph}$C), 133.2 (d, $^3J_{PC}$ = 9.0 Hz, $_{ph}$C). IR (3500–400 cm^{-1}, solid sample on ATR cell): 3074 (w), 3058 (w), 3043 (w), 2966 (w), 1969 (w), 1909 (w), 1591 (w), 1521 (w), 1485 (w), 1437 (m), 1286 (w), 1263 (w), 1205 (m), 1180 (m), 1142 (sh), 1121 (s), 1089 (s), 1067 (s), 1048 (m), 1027 (s), 998 (m), 932 (m), 916 (s), 825 (m), 750 (m), 722 (s), 691 (s), 587 (m), 555 (s), 536 (s), 512 (s), 508 (s), 502 (s), 498 (s), 496 (m), 486 (s), 478 (m), 470 (s), 463 (s), 453 (vs), 450 (m), 437 (m), 431 (s), 424 (s), 417 (s), 406 (s); Raman (solid on glass slide, 3500 – 100 cm^{-1}): 3066 (w), 1592 (m), 1574 (w), 1188 (w), 1164 (w), 1114 (w), 1029 (m), 999 (s), 839 (m), 825 (m), 694 (m), 617 (m), 250 (w), 206 (w), 112 (s). Anal. Calculated for $C_{66}H_{55}N_2O_7P_5U_1.CH_2Cl_2$: C, 54.89; H, 3.92; N, 1.91; P, 10.56; U, 16.24. Found: C, 54.18; H, 3.68; N, 1.86; P, 9.94; U, 15.31.

Titration of $[UO_2(TPIP)_2(Ph_3PO)]$ into $[Np(VI)O_2(TPIP)_2(Ph_3PO)]$

A solution of **1** (1.5 mL, ~2 mM) was transferred to a screw-cap cuvette. Aliquots of **2** in CH_2Cl_2 (150 µL, 0.2 mM) were added to the cuvette and the UV-vis and emission spectrum recorded at each point. Aliquots were added until there was 1950 µL of **2** (2.6 mM) in the sample. $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 162 MHz) δ (ppm): 15.6 (br), 16.2 (br), 19.5 (br), 21.2-25.9 (overlapping resonances, U-TPIP), 27.4 (s, Ph_3PO), 34.2 (br), 40.6 (br, U-Ph_3PO); ^{1}H NMR (CD_2Cl_2, 400 MHz) δ (ppm): 6.51-8.40 (overlapping resonances). The sample was divided into two portions and diluted further for a repeat spectroscopic analysis at lower concentration.

Computational details

All DFT calculations were performed using the version 6.4 of the TURBOMOLE code,[4] employed the hybrid-GGA PBE0 exchange correlation functional and Ahlrichs-style basis sets of polarised triple-ξ quality. Actinide ions incorporated effective core potentials, replacing 60 core electrons. All geometry optimisations were performed in C1 symmetry with default convergence criteria in the presence of a COSMO continuum solvent model with the relative permittivity, ε_r, set to 8.9 to represent the DCM solvent. Numerical frequency analyses were also performed in the presence of the continuum solvent and the absence of any imaginary frequencies indicated that the converged structures were energetic minima.

Optimised structures

Figure S1 shows the structures of the simplified complexes resulting from the geometry optimisations. Cartesian coordinates are given below.

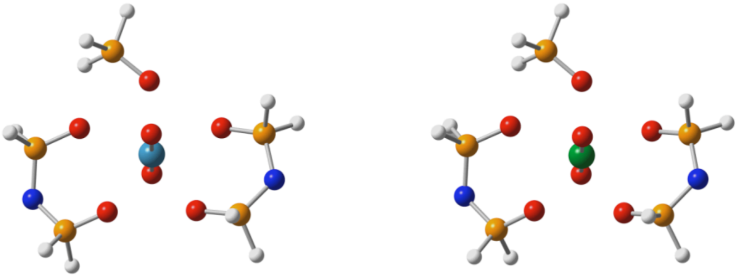

Figure S1. Simplified structures optimised in the presence of a continuum CH_2Cl_2 solvent. White, blue, red, orange, blue and green spheres represent hydrogen, nitrogen, oxygen, phosphorus, uranium and neptunium atoms, respectively.

Simplified [UO_2 TPIP$)_2$(H_3PO)] structure

U	-0.1811465	0.2442732	0.2198605
P	-0.2444916	-0.8065945	3.6774391
P	2.6101868	2.4413439	0.0430597
P	-2.5405264	-1.6068875	2.2486577
P	1.2638047	0.2571008	-3.1036503
P	-1.3352809	-0.8258012	-3.0219417
O	0.1499928	0.1383828	2.5514714
O	1.9331194	1.3246387	0.7953869
O	-2.1478259	-0.7075395	1.0855567
O	0.5598688	-1.3532891	0.0831859
O	1.0693009	0.9089834	-1.7399095
O	-0.8903804	1.8567827	0.3261708
O	-1.5534706	-0.2428203	-1.6341772
N	-0.0045356	-0.4086745	-3.7857363
N	-1.6473144	-1.5414624	3.5601647
H	-0.2231729	-0.0976804	4.8914792
H	0.7801678	-1.7597783	3.8479127
H	-2.6105273	-2.9377068	1.7891430
H	-3.8704746	-1.3256136	2.6081122
H	-1.4235652	-2.2309736	-2.9457210
H	-2.4254396	-0.4808824	-3.8388817
H	2.3126040	-0.6811964	-3.0065085
H	1.7779635	1.2153390	-3.9948147
H	3.5180122	2.0335513	-0.9448793
H	1.7482907	3.3353572	-0.6086639
H	3.3748400	3.2511477	0.8972836

Simplified [NpO_2(TPIP$)_2$(H_3PO)] structure

Np	-0.0335322	-0.1929715	0.2299477
P	-0.4262365	-0.4817068	3.7296967
P	2.8597260	1.9687343	0.0278870
P	-2.5745531	-1.5577202	2.2770820

P	0.8657848	0.9390773	-3.1458365
P	-1.0731701	-1.0790697	-3.0367056
O	0.4653892	-0.5386304	2.4958985
O	1.9733778	1.0571753	0.8324926
O	-1.7216332	-1.5999454	1.0144332
O	0.9418486	-1.5553366	-0.2348346
O	0.8819692	1.0878556	-1.6303047
O	-1.0175226	1.1651923	0.6948074
O	-1.4094074	-0.6344576	-1.6197278
N	0.1354653	-0.3330162	-3.7556351
N	-1.8344977	-1.2155680	3.6420456
H	-0.5992616	0.8686097	4.1001191
H	0.2684625	-1.0273182	4.8220144
H	-3.2118733	-2.7993836	2.4367162
H	-3.6483125	-0.6683143	2.0647604
H	-0.8023562	-2.4600507	-3.0569788
H	-2.2386236	-0.9690384	-3.8187082
H	2.1849869	0.9245557	-3.6356886
H	0.3434655	2.1308122	-3.6899000
H	3.5170163	1.3810446	-1.0629245
H	2.2474008	3.1153531	-0.4970427
H	3.9060872	2.4741176	0.8163862

Spectroscopic Data

Compound 1, $[NpO_2(TPIP)_2(Ph_3PO)]$

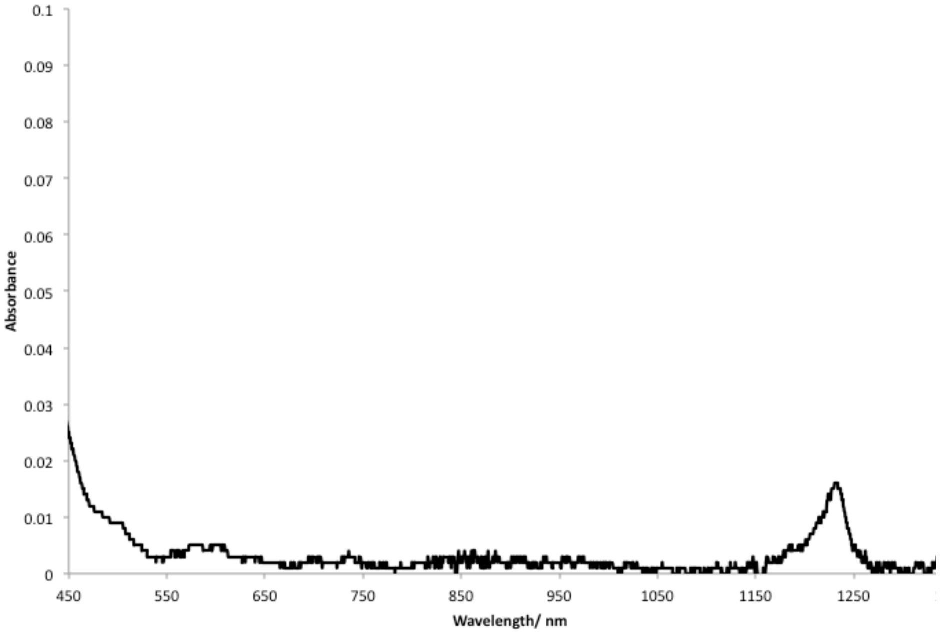

Figure S2. Vis-nIR spectrum of **1** recorded in CH_2Cl_2 at room temperature

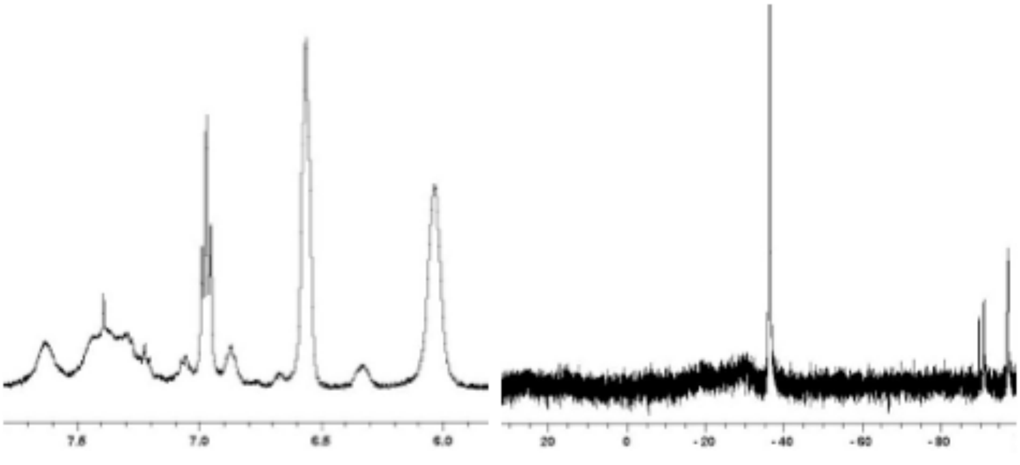

Figure S3. *Left*: ^1H NMR spectrum and *right:* $^{31}P\{^1H\}$ NMR spectrum of **1** recorded in CD_2Cl_2 at 295 K.

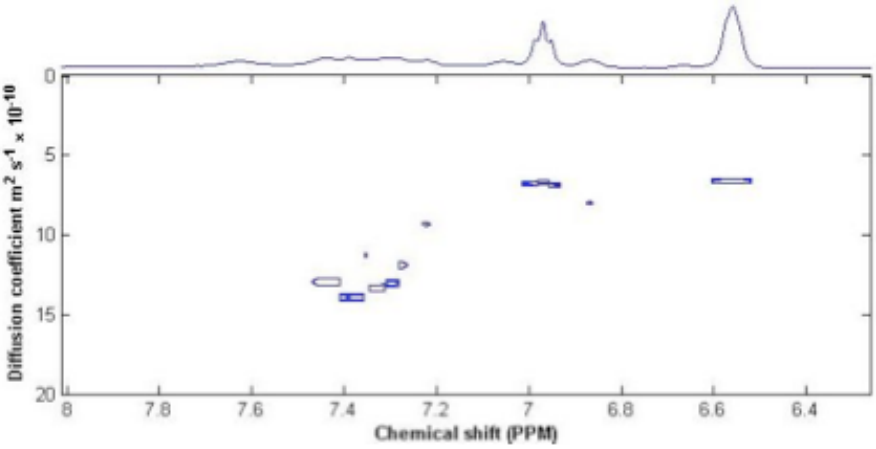

Figure S4. The ^{1}H DOSY NMR spectrum of the aromatic resonances in **1** recorded in CD_2Cl_2 at 295 K.

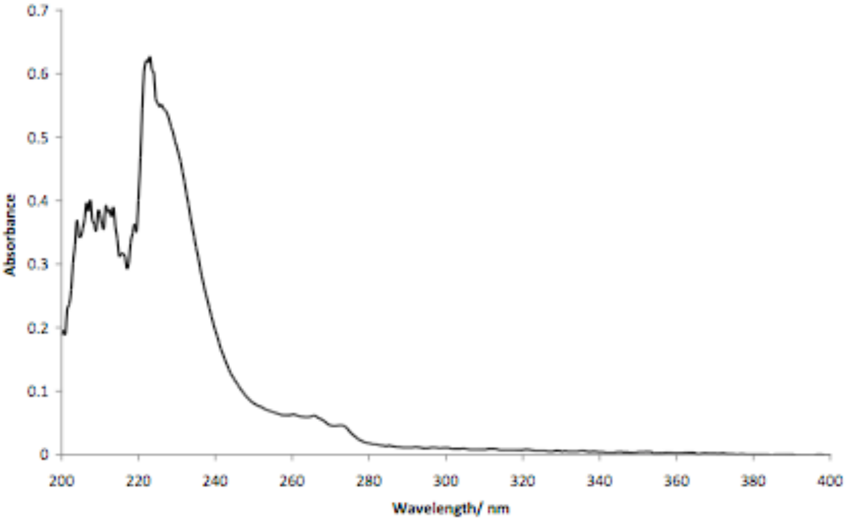

Figure S5. UV-vis spectrum of **1** in CH_2Cl_2 recorded at room temperature. Note the low intensity absorption tail at > 300 nm, which extends into the visible region.

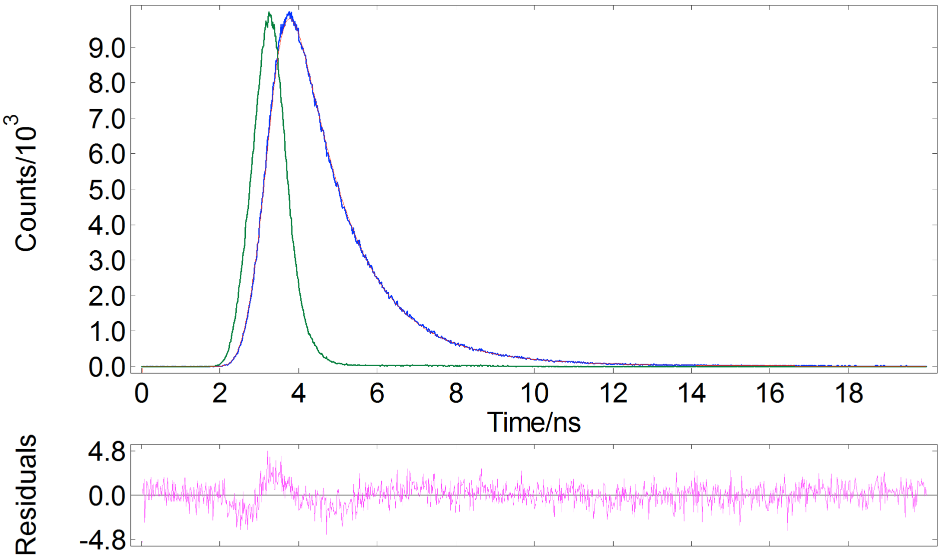

Figure S6. Fitted kinetic trace of **1** recorded in CH_2Cl_2 at 295 K following 405 nm laser excitation with a picosecond pulsed diode laser

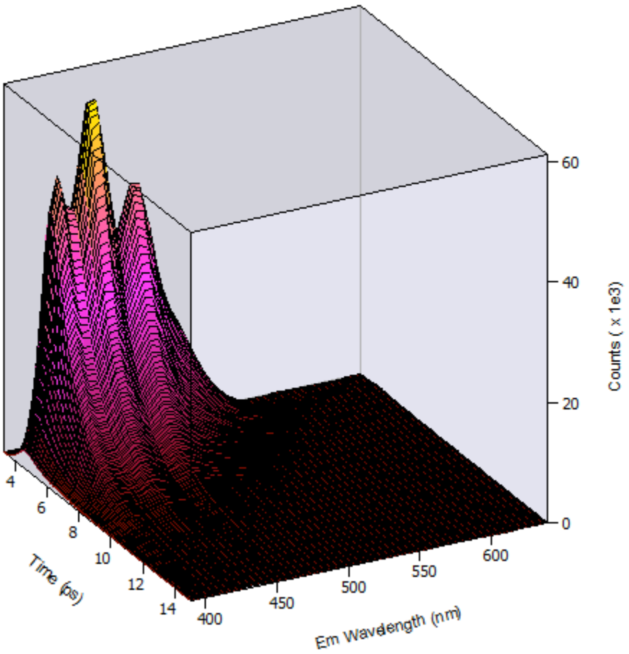

Figure S7. Time resolved emission spectrum of **1** recorded following 375 nm excitation with a picosecond pulsed diode laser in CH_2Cl_2 at 295 K.

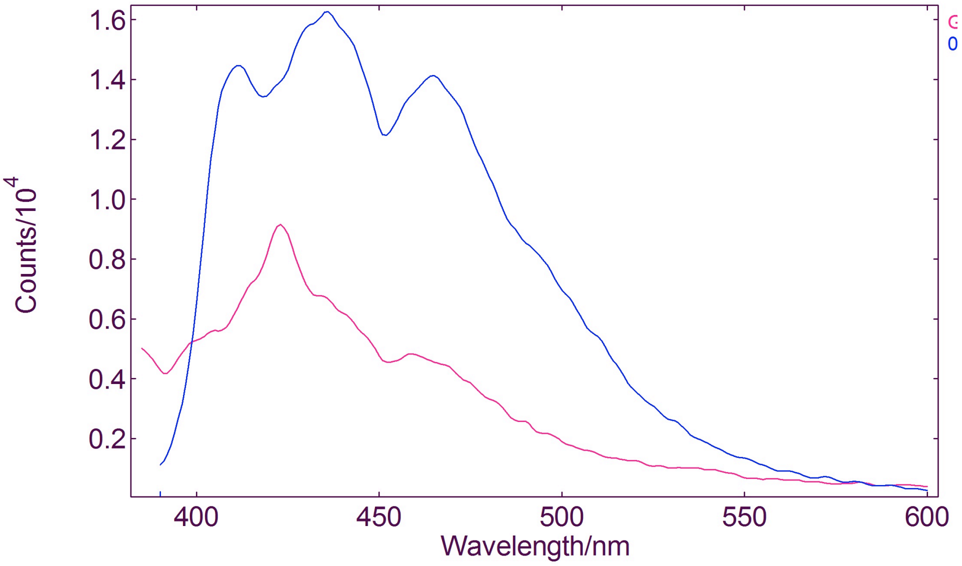

Figure S8. Steady state phosphorescence spectrum of [Gd(TPIP)$_3$] in a frozen CH_2Cl_2 glass at 77 K following 290 nm excitation (red trace) and steady state emission spectrum of **1** in fluid CH_2Cl_2 solution recorded at 295 K following 290 nm excitation (blue trace).

Compound 2, [UO$_2$(TPIP)$_2$(Ph$_3$PO)]

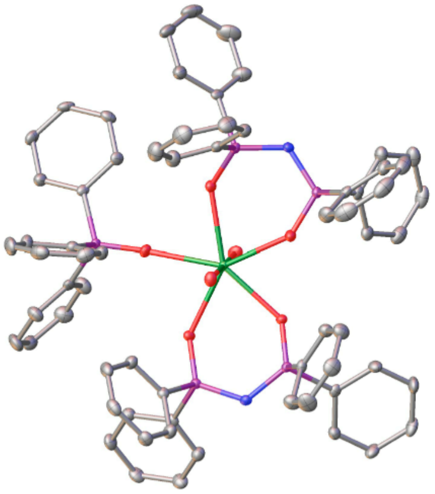

Figure S9. Solid state molecular structure of **2** with thermal ellipsoids set at the 50 % probability level; lattice solvent molecules and H atoms are omitted for clarity

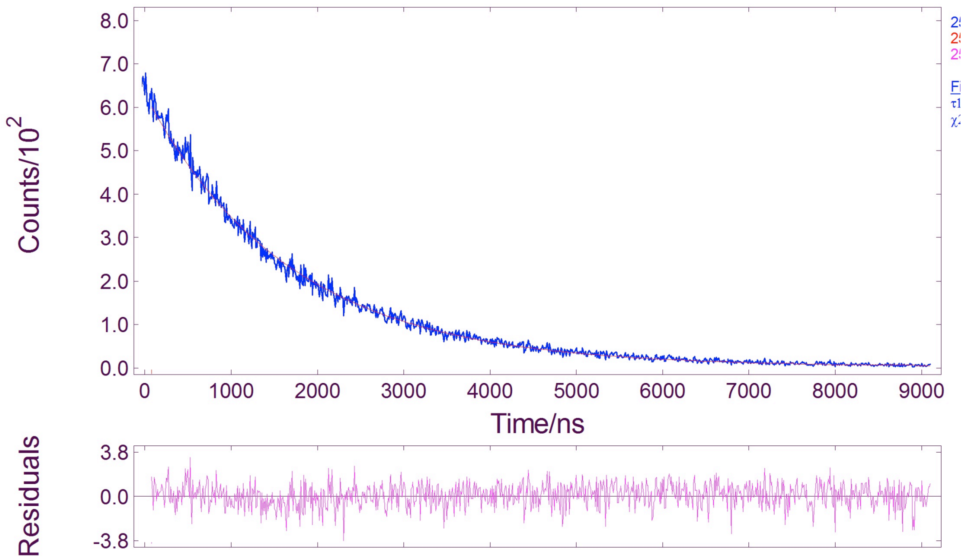

Figure S10. Fitted kinetic trace of **2** recorded in CH_2Cl_2 at 295 K following 405 nm laser excitation with a picosecond pulsed diode laser

Spectroscopic Data for Mixtures of 1 and 2

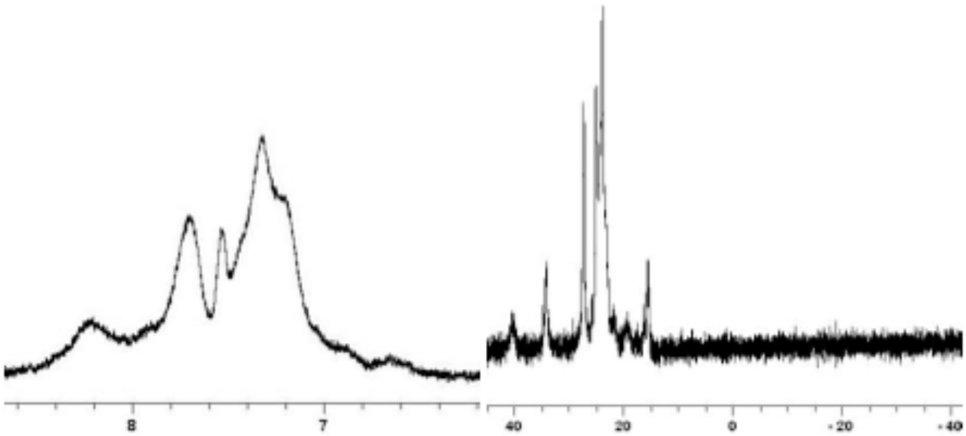

Figure S11. *Left*: ^1H NMR spectrum and *right:* $^{31}P\{^1H\}$ NMR spectrum of a mixture of **1** (1.47 mM) and **2** (0.87 mM) recorded in CD_2Cl_2 at 295 K.

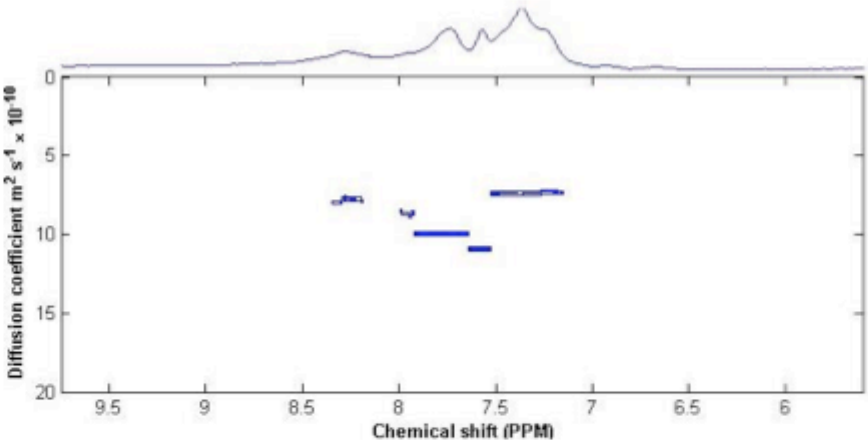

Figure S12. The ^{1}H DOSY NMR spectrum of the aromatic resonances of a mixture of **1** (1.47 mM) and **2** (0.87 mM) recorded in CD_2Cl_2 at 295 K.

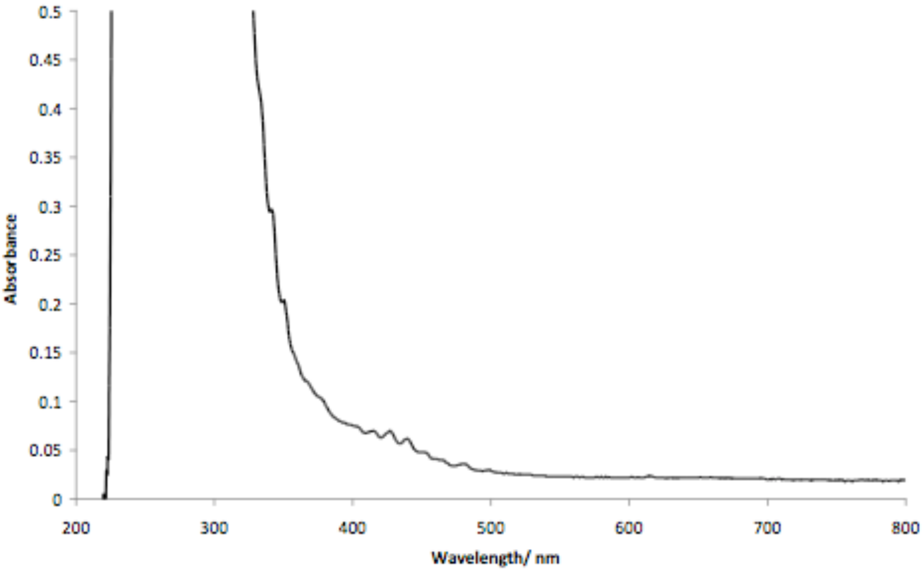

Figure S13. UV-vis spectrum of **1** (1.47 mM) and **2** (0.87 mM) in CH_2Cl_2 at room temperature expanded to highlight the vibrationally resolved uranyl(VI) $O_{yl} \rightarrow U$ LMCT absorption at ca. 420 nm.

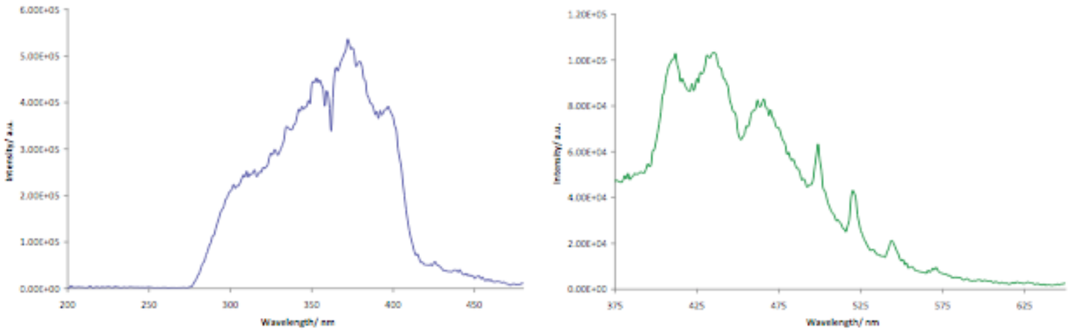

Figure S14. *Left*: excitation spectrum (emission wavelength = 500 nm) and *right:* emission spectrum (excitation wavelength = 330 nm) of a mixture of **1** (1.47 mM) and **2** (0.87 mM) recorded in CD_2Cl_2 at 295 K

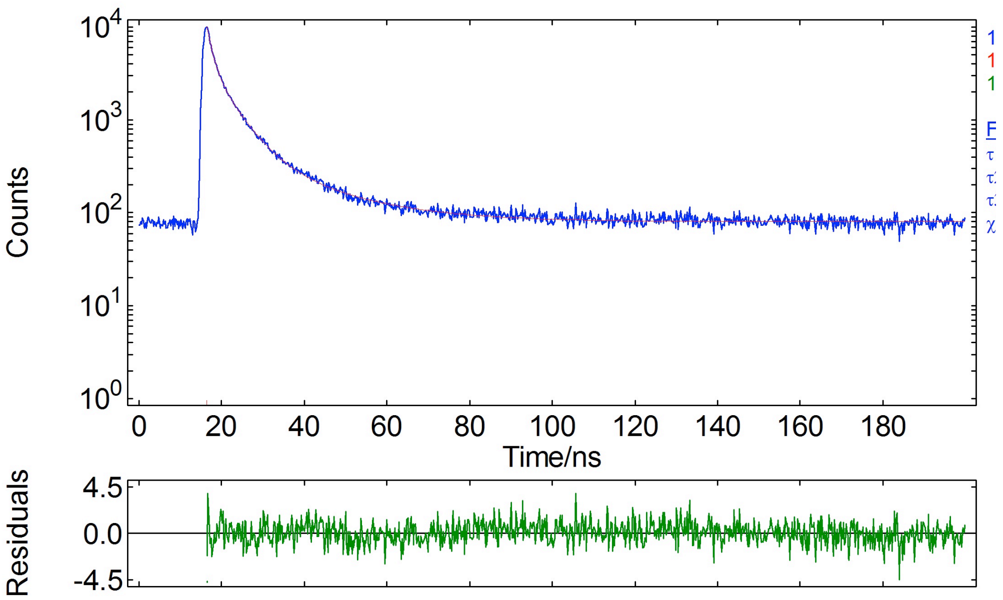

Figure S15. Fitted kinetic trace of a mixture of **1** (1.47 mM) and **2** (0.87 mM) recorded in CH_2Cl_2 at 295 K following 420 nm laser excitation with a picosecond pulsed Supercontinuum laser

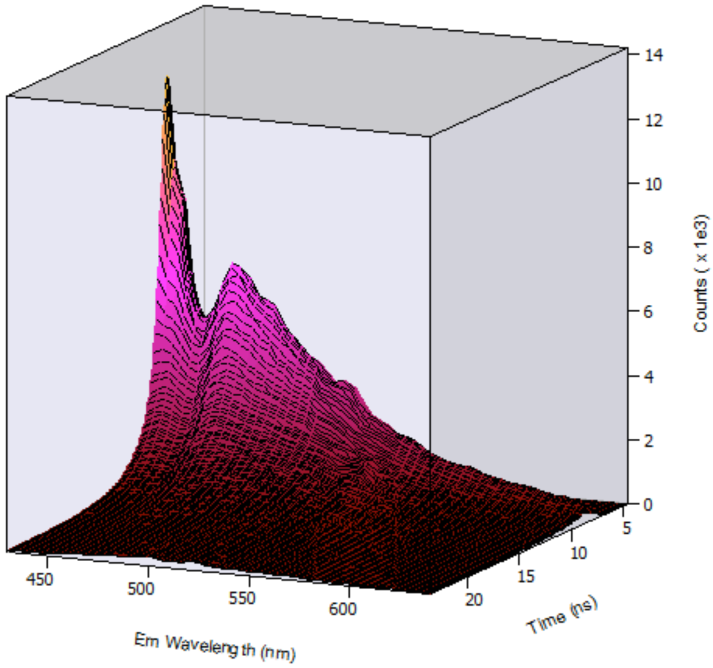

Figure S16. Time resolved emission spectrum of a mixture of **1** (1.47 mM) and **2** (0.87 mM) recorded in CH_2Cl_2 at 295 K following 420 nm laser excitation with a picosecond pulsed Supercontinuum laser

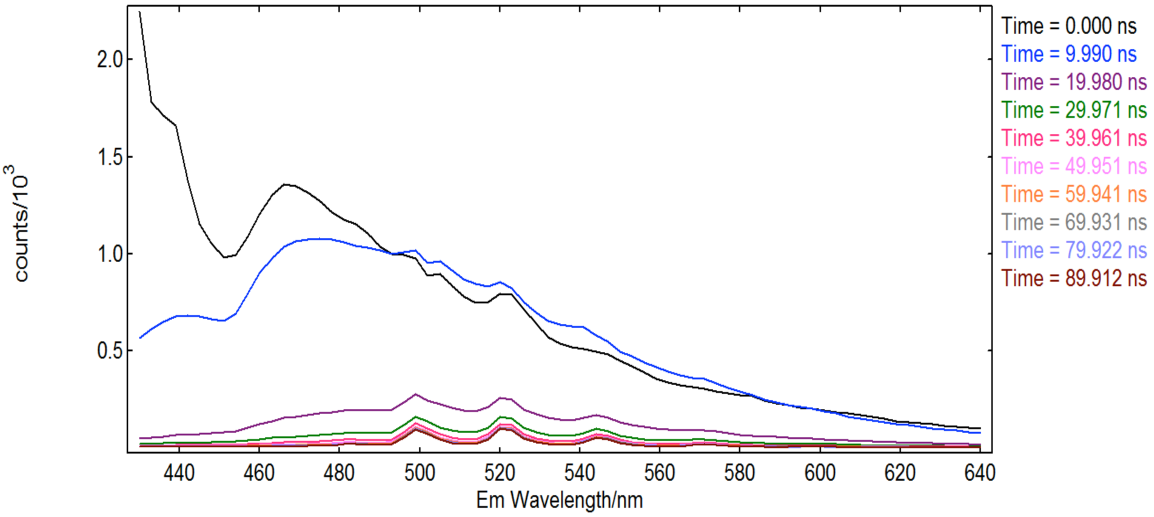

Figure S17. Emission spectra of mixture of **1** (1.47 mM) and **2** (0.87 mM) recorded in CH_2Cl_2 at 295 K following 420 nm laser excitation with a picosecond pulsed Supercontinuum laser at differing time intervals (10 data slices, 0 – 90 ns, 10 ns steps) showing the dominance of neptunyl(VI) based emission at short time delays and the dominance of uranyl(VI) based emission at longer time delays.

References

1. S.W. Magennis, S. Parsons and Z. Pikramenou*, Chem. Eur. J.*, 2002, **8**, 5761.
2. S.M. Cornet, L.J.L. Häller, M.J. Sarsfield, D. Collison, M. Helliwell, I. May and N. Kaltsoyannis, *Chem. Commun*., 2009, 917.
3. O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339.
4. R. Ahlrichs, M. Bär, M. Häser, H. Horn, and C. Kölmel, *Chem. Phys. Lett*., 1989, **162**, 165.