ELECTRONIC SUPPLEMENTARY INFORMATION

A Discrete Tetramic Neptunyl(V) Cluster Supported by A Schiff Base Ligand†

Roy Copping,[ab] Victor Mougel,[a] Christophe Den Auwer[bc], Claude Berthon,[b] Philippe Moisy,[b] and Marinella Mazzanti*[a]

[a] *Laboratoire de Reconnaissance Ionique et Chimie de Coordination, SCIB, (UMR-E 3 CEA-UJF)), INAC, CEA-Grenoble, 17 rue des Martyrs, 38054 Grenoble Cedex 09, France. Fax++33(4)38785090; Tel: ++33(4)38785090 ; E-mail: marinella.mazzanti@cea.fr*

[b] *CEA, Nuclear Energy Division, Radiochemistry & Processes Department, 30207 Bagnols sur Cèze, France*

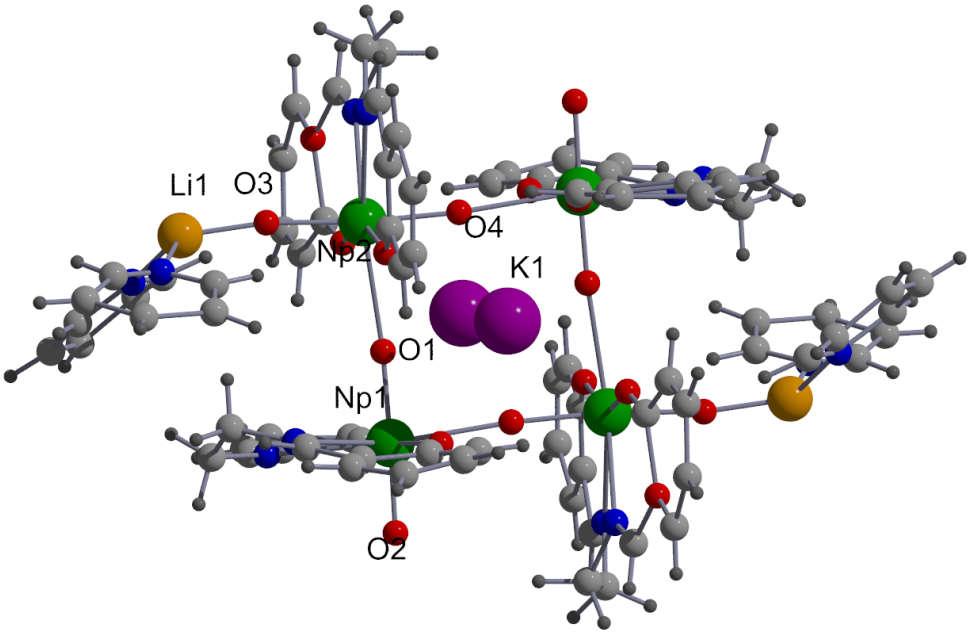
[c] *Nice Sophia Antipolis University, Chemistry Institute of Nice, 06108 Nice, France*

GENERAL

Experiments were performed under an argon atmosphere using a Schlenk line contained within a regular atmosphere negative pressure radiological containment glovebox. Strict radiological control and safety practices were observed during the manipulation of highly radioactive neptunium-237(half life 2.144 x 10^6 years). All solvents were anhydrous grade purchased from Sigma-Aldrich and used without further purification, pyridine-D_5 was dried over molecular sieves (4x). UV/Vis/nIR were recorded on a Varian Cary, Infra-red spectra were recorded on a Bruker Equinox Spectrometer and ^{1}H NMR were recorded on a Agilent DD2 400MHz spectrometer, equipped with a 5mm HCX indirect probe with z-gradient.

X-RAY DIFFRACTION

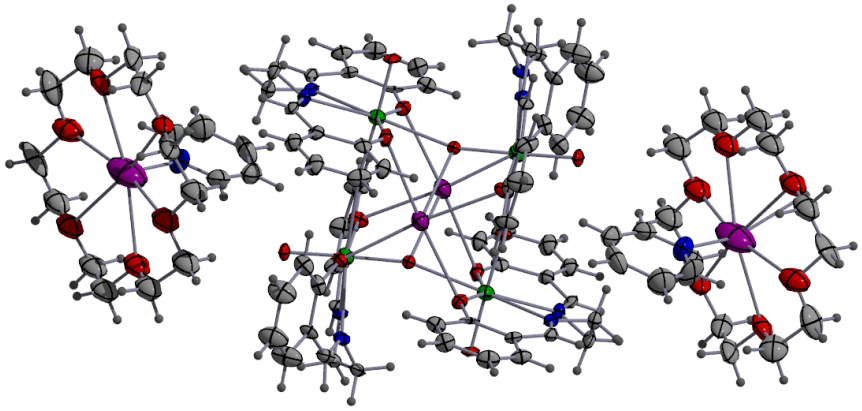
Figure S1. Ball and Stick Structures of the tetrameric unit $[\{NpO_2(salen)\}_4(\mu_8\text{-}K)_2][LiPy_2]_2$, **2**.



Crystal data for complex ***2***; $C_{84}H_{76}K_2Li_2N_{12}O_{16}Np_4$, M = 2549.65, monoclinic, a = 16.766(10), b = 14.812(9), c = 23.441(14) Å, β = 96.680(6)°, V = 5732(4) Å^3, T = 205(2) K, space group $P2_1/n$, Z = 2, D_c = 1.477 g cm^{-3}, Mo-K radiation (λ = 0.71073 Å), μ = 3.722 mm^{-1}, yellow prismatic crystal with dimensions 0.05 × 0.04 × 0.03 mm,

11300 reflections measured, 5533 unique reflections (R_{int} = 0.0906), 2936 reflections with I > 2σ(I). Final R (I > 2σ(I)), R_1 = 0.1446, wR_2 = 0.2208. Final R (all data), R_1 = 0.3153, wR_2 = 0.3537

Figure S2. ORTEP (50% probability ellipsoids) view of 1 displaying the two $[K(18C6)Py]^+$ groups.



IR Spectra

Figure S3. Infrared spectra of the yellow solid obtained from the reaction of salenK_2 and $[(NpO_2Py_5)(KI_2Py_2)]_n$ in pyridine before dissolution with 18-C-6 (green) and of crystals of **1**, $[\{NpO_2(salen)\}_4(\mu_8\text{-}K)_2][K(18C6)Py]_2$ (blue).

(Green); stretches at 986, 951, 931, 907, 887, 854, 793, 779, 764, 750, 709, 691, 663, 634, 622, 644 and 601cm^{-1}

(Blue); stretches at 962, 910, 837, 827sh 791, 775, 756, 741, 703, 669, 655, 646, 638, 633,624 and 606 cm^{-1}

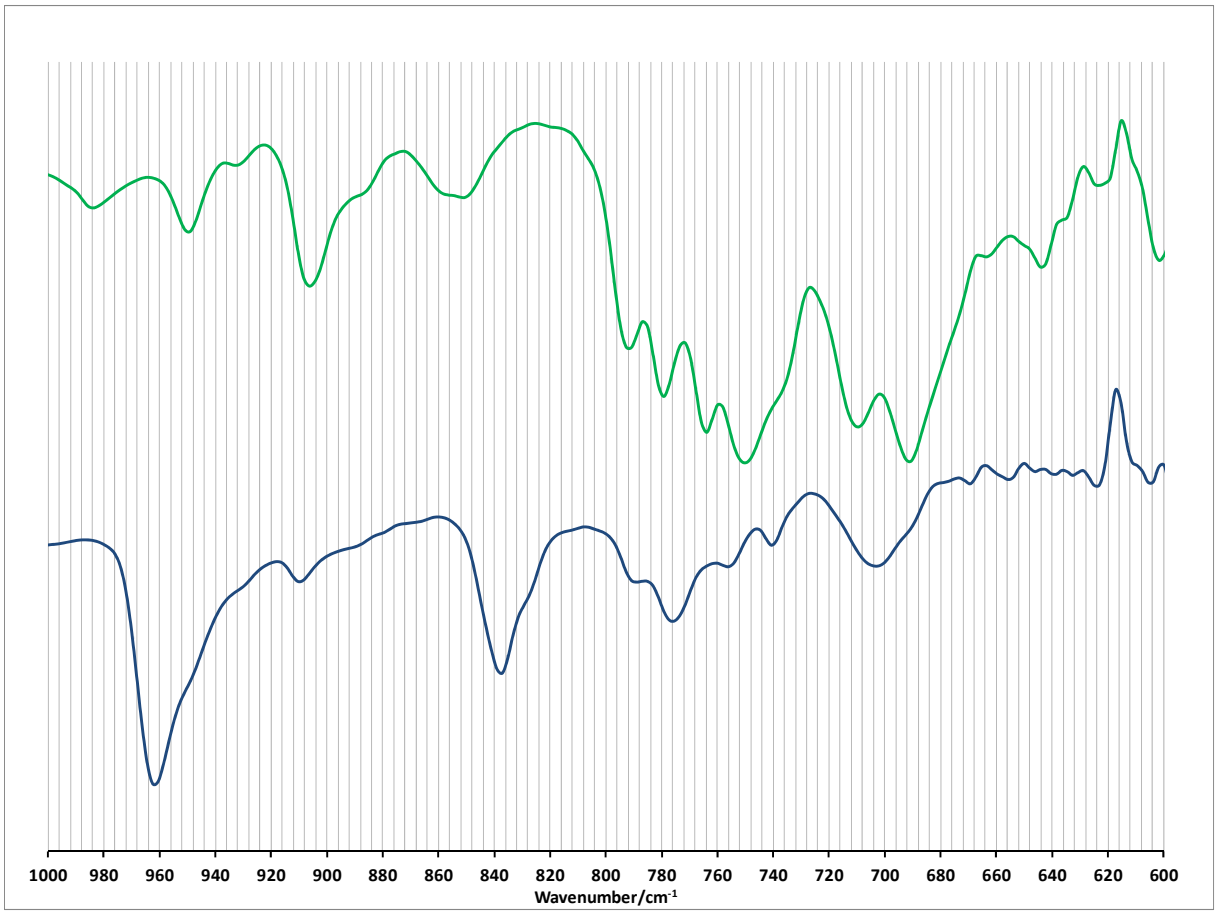


Figure S4. Infrared spectra of [(NpO2Py$_5$)(KI$_2$Py$_2$)]n (Purple) and of **1**, [{NpO$_2$(salen)}$_4$(μ$_8$-K)$_2$][K(18C6)Py]$_2$ crystals (Blue).

(Purple); stretches at 989, 951, 885, 875, 808, 750, 698, 677, 654, 642, 623 and 606 cm^{-1}

(Blue); stretches at 962, 910, 837, 827sh 791, 775, 756, 741, 703, 669, 655, 646, 638, 633,624 and 606 cm^{-1}

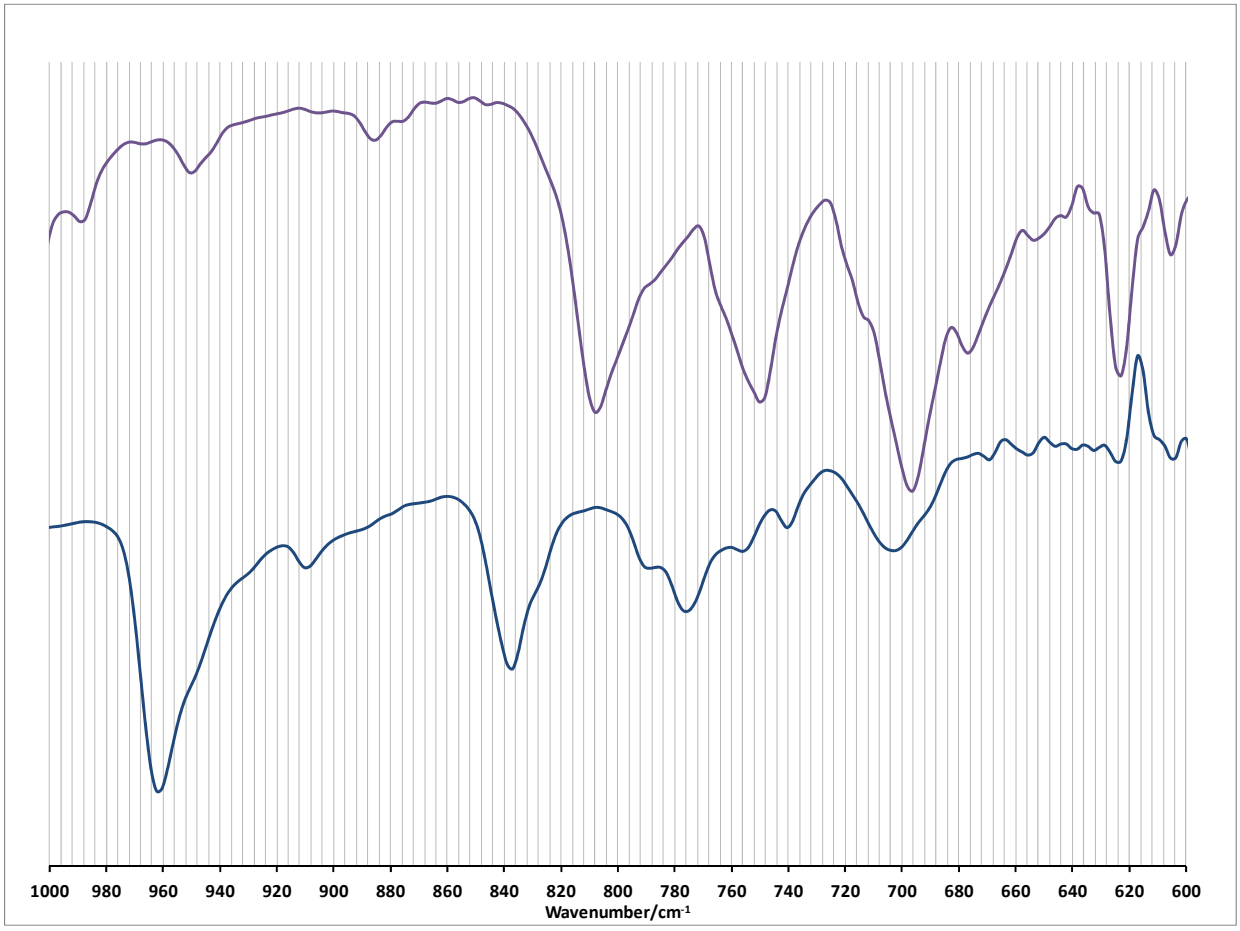
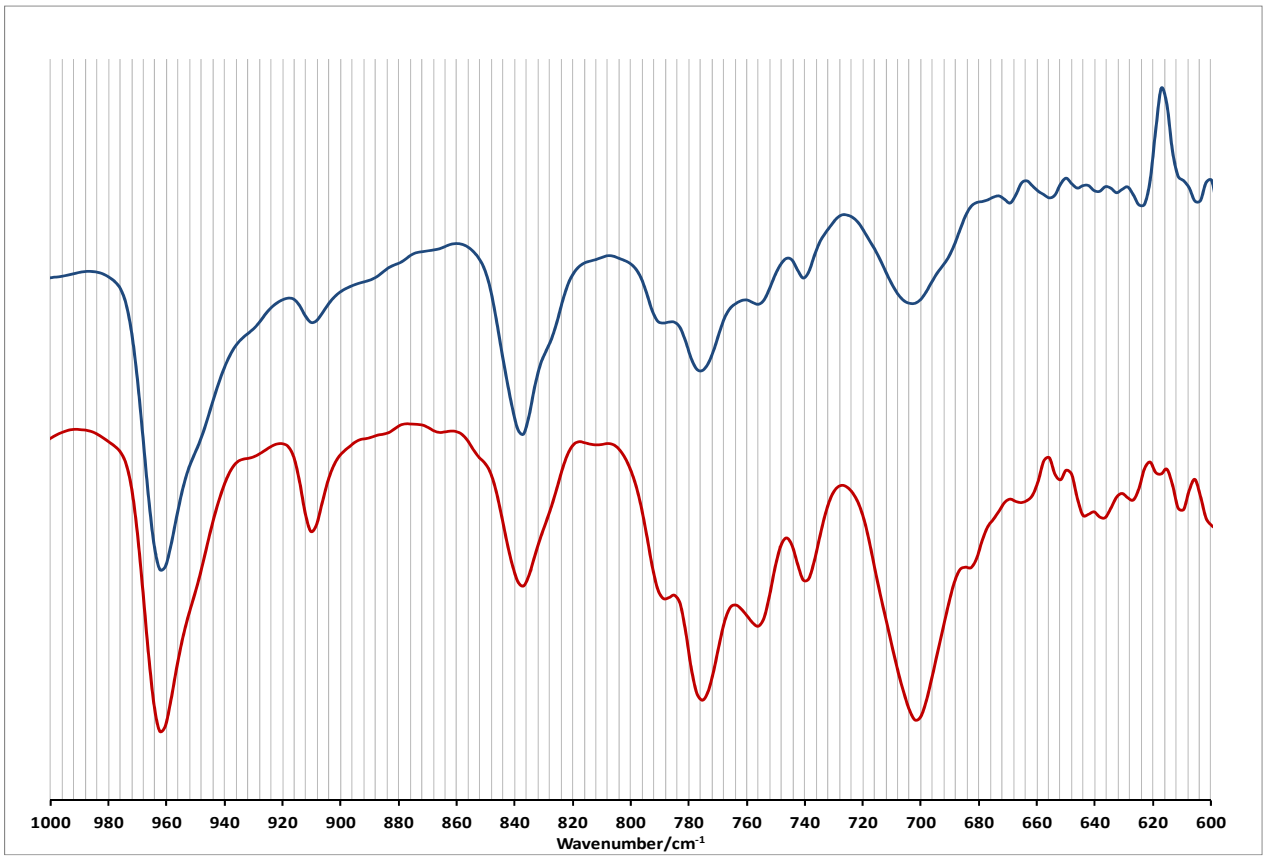


Figure S5. Infrared spectra of the X-ray quality crystals of **1**, $[\{NpO_2(salen)\}_4(\mu_8\text{-}K)_2][K(18C6)Py]_2$ (blue) and of the bulk precipitate of **1** (red).

(Blue); stretches at 962, 910, 837, 827sh 791, 775, 756, 741, 703, 669, 655, 646, 638, 633,624 and 606 cm^{-1}

(Red); stretches at 962, 910, 837, 789, 756, 741, 702, 683, 665, 652, 644, 636, 627, 617, and 611 cm^{-1}



Spherical hydrodynamic radius

The spherical hydrodynamic radius (called Stokes radius) of the molecule was calculated from the Stokes-Einstein equation and compared to the value obtained from the solid state structure and with a similar reference compound in the same solvent:

$$r_{sph} = \frac{k_B.T}{6\pi.\eta.D}$$

η (Pa.s) = viscosity of the medium ; k_B ($m^2.kg.s^{-2}.K^{-1}$) = Boltzmann constant.

T : absolute temperature (K); D : diffusion coefficient ($m^2.s^{-1}$)

The hydrodynamic radii calculated from the measured coefficient diffusion values are in good agreement with the spherical radii were evaluated from the crystal structure by considering the volume of the ellipsoid determined by the three main dimensions and calculating the radius of a sphere of the same volume.

Table S6. Diffusion coefficient values and estimated spherical radii.

Solvent	**Compound**	**D [$m^2.s^{-1}$]**	**r_{sph} [Å]$_{exp}$**	**r_{sph} [Å] (evaluated from crystal structure)**
Pyridine η=0.879 mPa.s (298K)	**tetramer**	4.40 x 10^{-10} ± 0.2x10^{-10}	5.7	5.9 for {[NpO_2(salen)]$_2$[μ_8-K]}$_2^{2-}$

Figure S7. **^{1}HNMR** of **1** in Pyridine-D_5 at 60°C and 400 MHz(integration included).

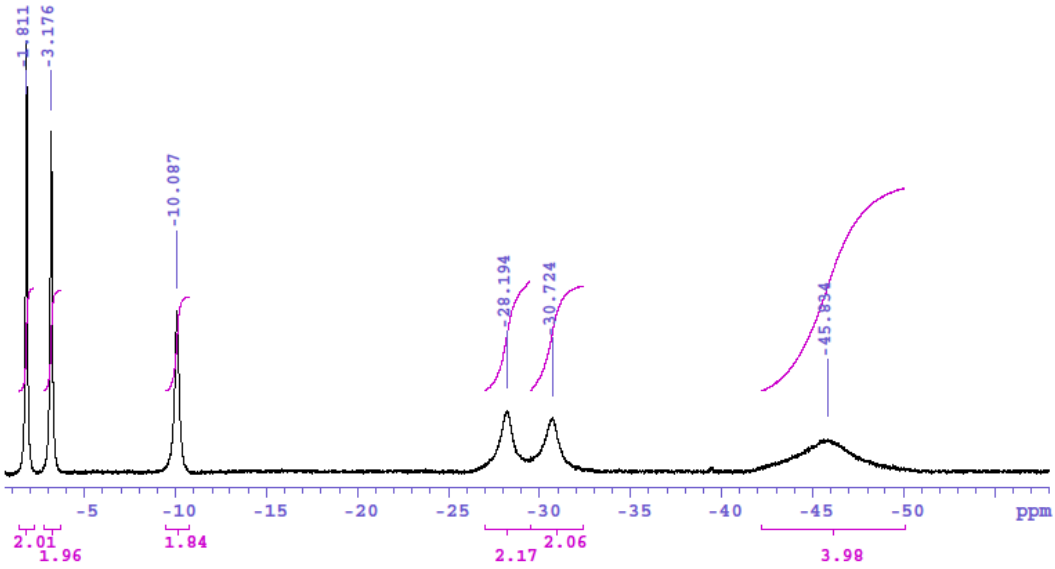


Figure S8. **^{1}H NMR** of **1** in Pyridine-D_5 at 60°C and 400 MHz (Full Spectrum).

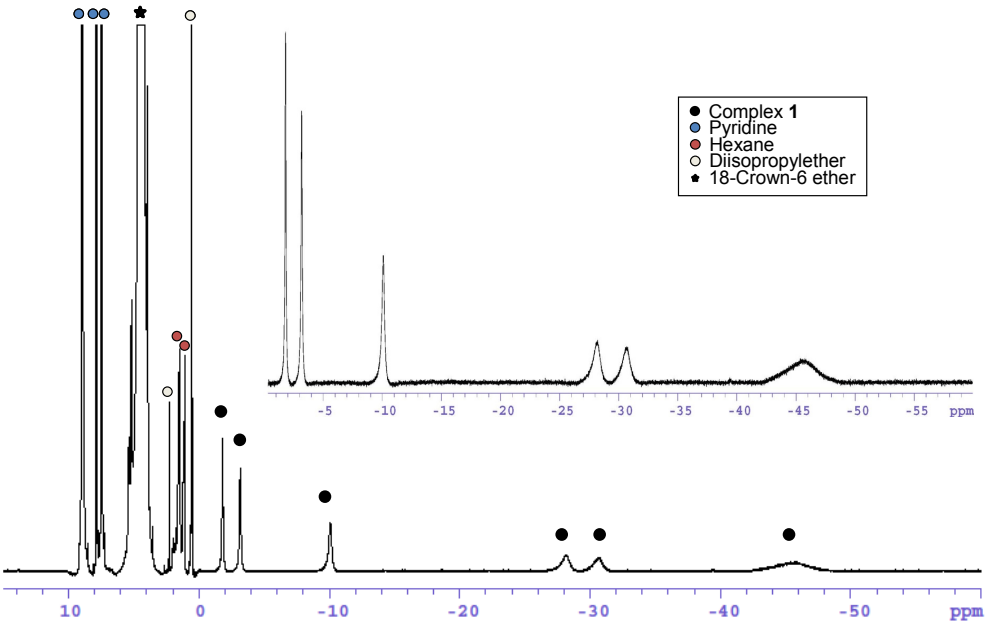


Figure S9. **^{1}HNMR** of **1** in Pyridine-D_5 at 25^{o}C and 400 MHz (Negative Region).

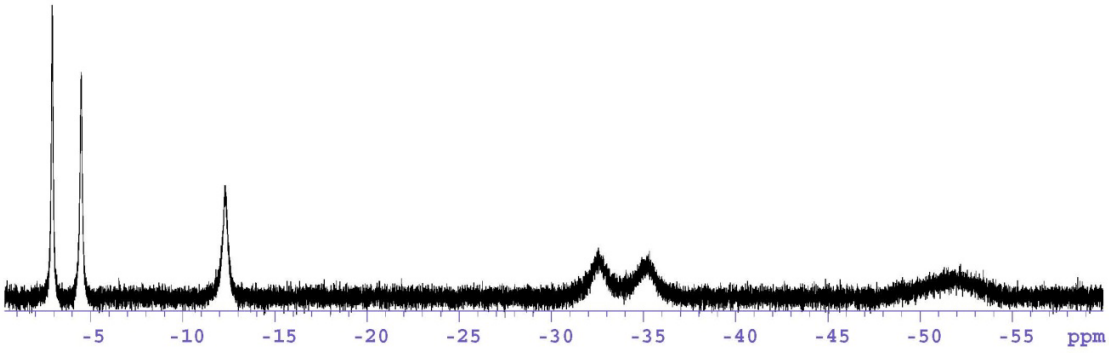


Figure S10. Near infra-red region of the electronic absorption spectra for NpO_2^+ species; Red: **1** in pyridine, (Np concentration 0.81 mM), Blue: $[(NpO_2Py_5)(KI_2Py_2)]_n$ in pyridine (Np concentration 0.46 mM).