

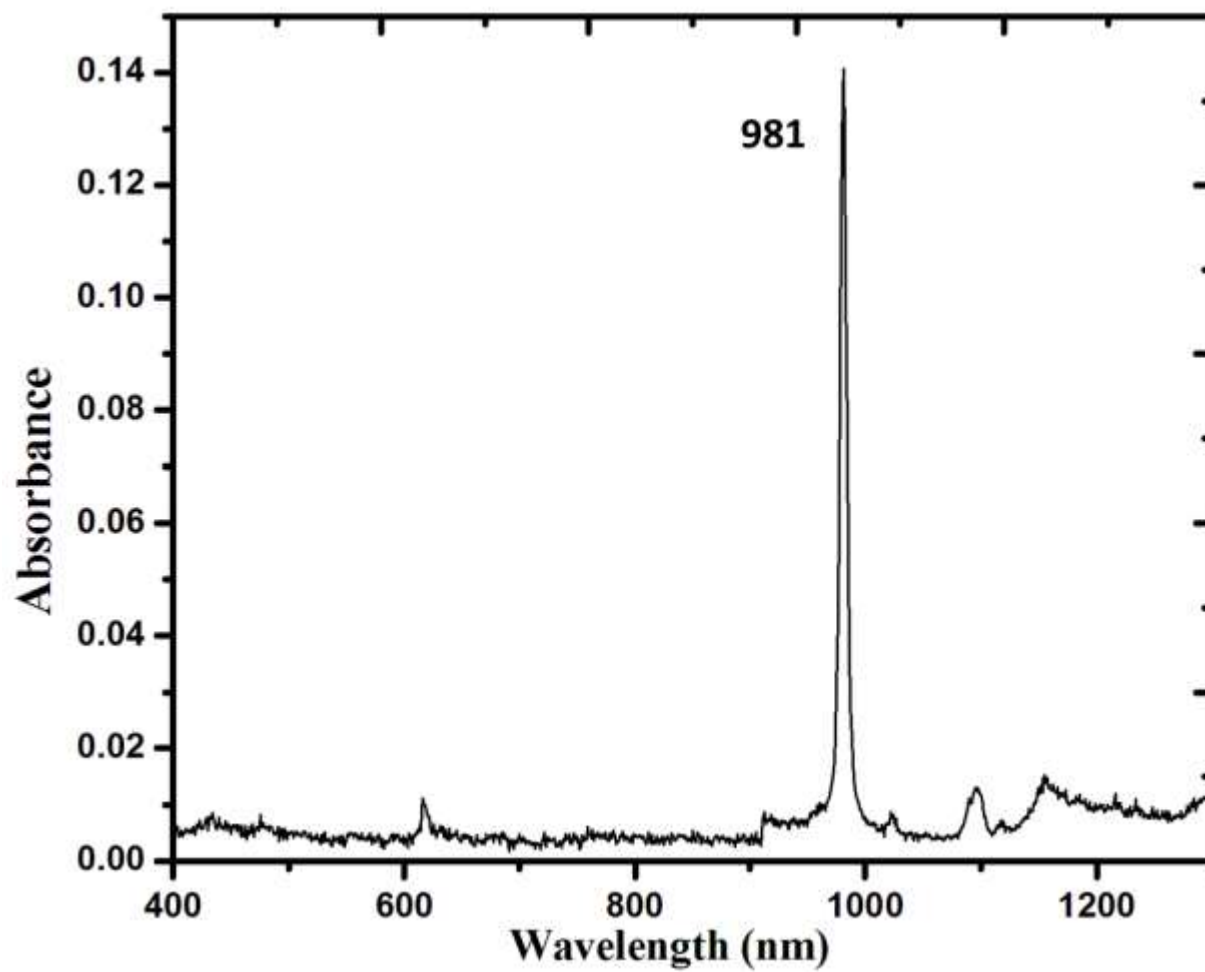
# **Three-Dimensional Network of Cation–Cation-Bound Neptunyl(V) Squares: Synthesis and in Situ Raman Spectroscopy Studies**

Geng Bang Jin\*

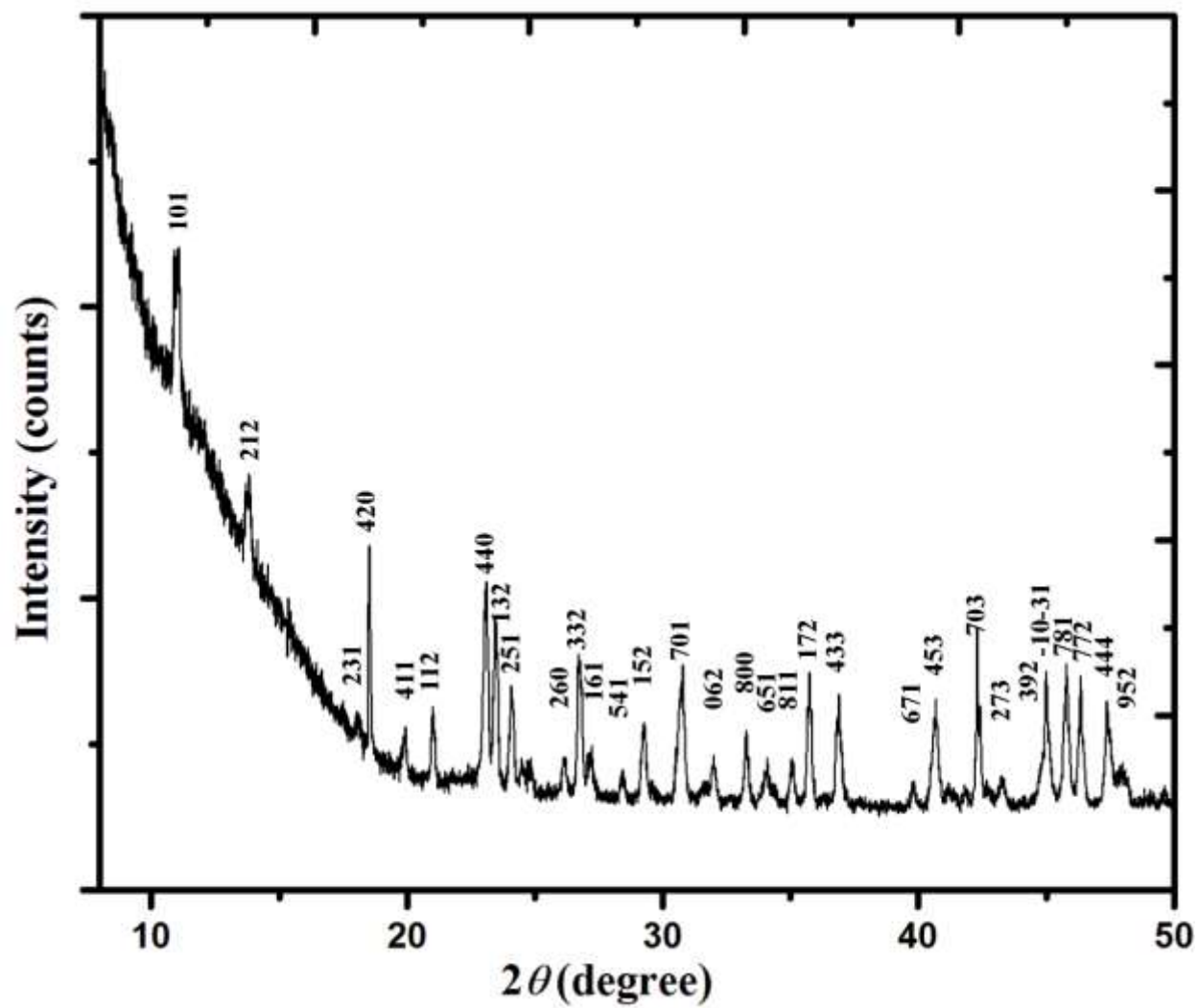
Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, Illinois  
60439, United States

**Supporting Information**

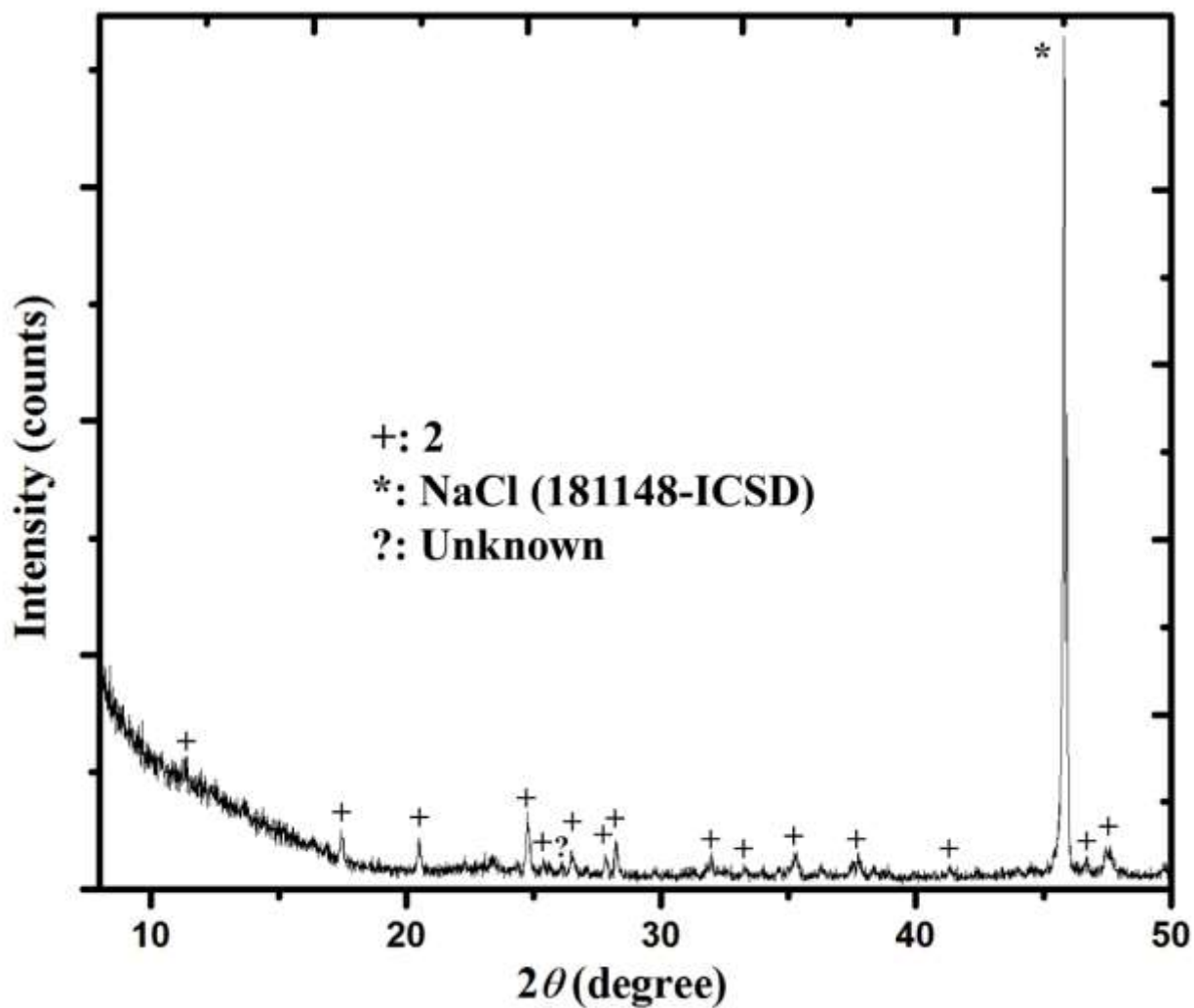
**Figure S1.** An absorption spectrum of a 0.120 M Np(V) (in ~1 M HCl) stock solution.



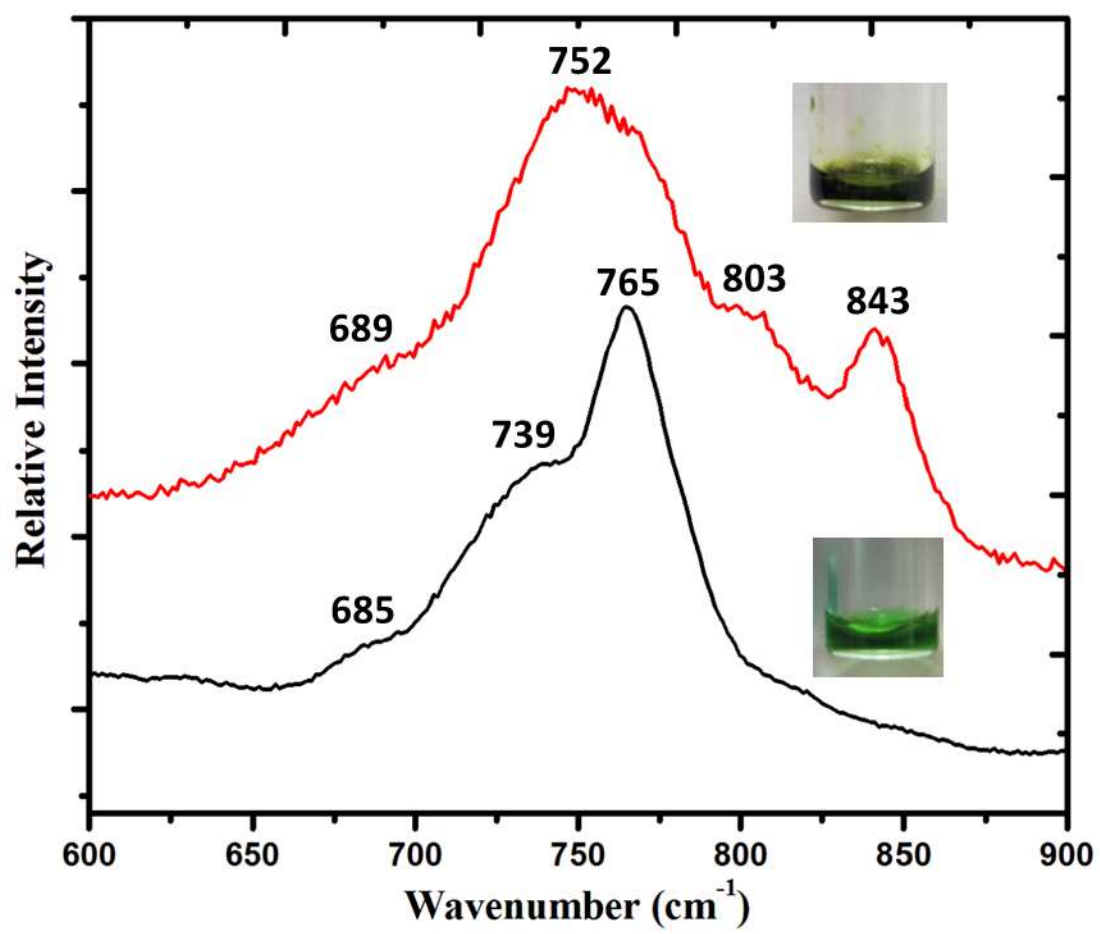
**Figure S2:** Powder X-ray diffraction pattern of  $(\text{NpO}_2)\text{Cl}(\text{H}_2\text{O})_2$  (**1**) after manually removing the colorless salts.



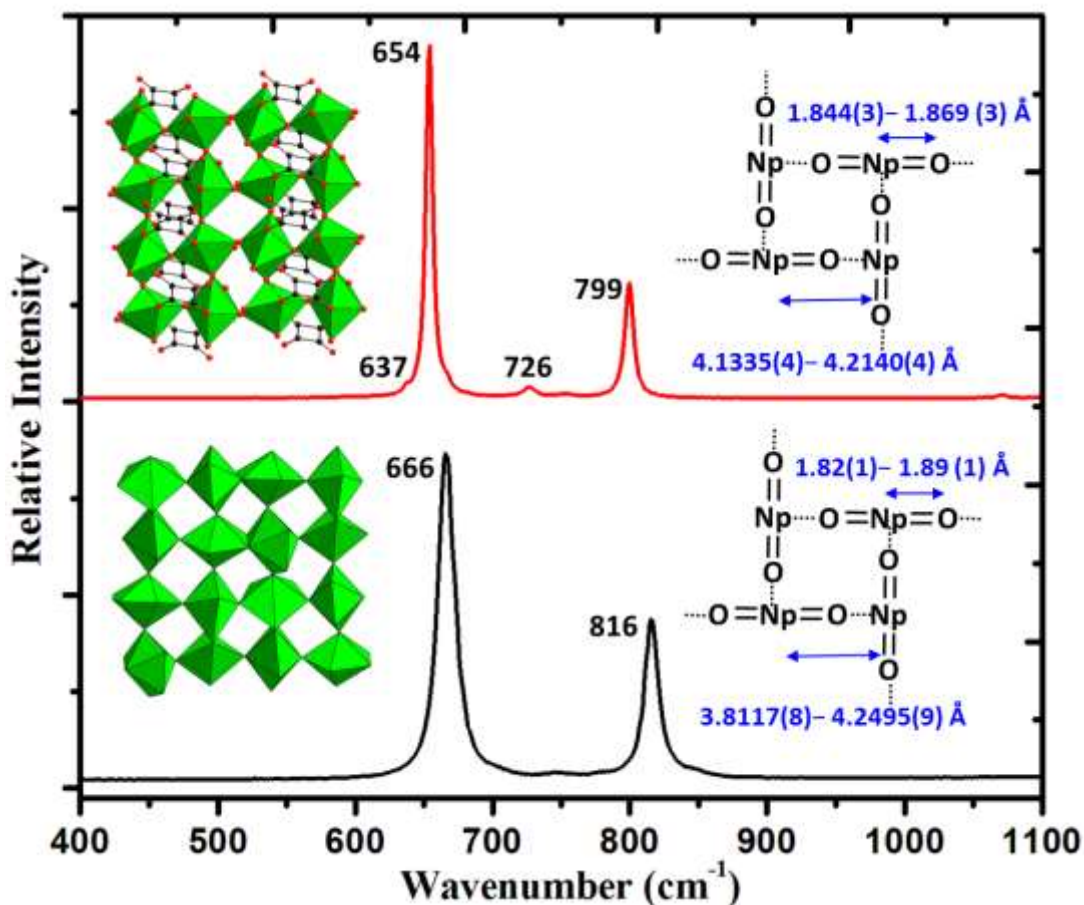
**Figure S3:** Powder X-ray diffraction pattern of the solid mixture of green  $(\text{Na}_x\text{Np}(\text{NpO}_2)_6(\text{OH})_{1+x}\text{Cl}_9(\text{H}_2\text{O})_{8-x})$  ( $0 < x \leq 1$ ) (**2**) and **4**) and colorless products from one of rapid evaporation experiments.



**Figure S4:** Raman spectra of a  $\sim 1.0$  (black) and a  $\sim 1.5$  M (red) Np(V) solutions.



**Figure S5:** Raman spectra of  $(\text{NpO}_2)_2(\text{C}_4\text{O}_4)(\text{H}_2\text{O})^{\text{a}}$  (red) and  $(\text{NpO}_2)_4\text{Cl}_4(\text{H}_2\text{O})_6 \cdot (\text{H}_2\text{O})_3^{\text{b}}$  (black) with 2-D cationic CCI square sheets of neptunyl(V) pentagonal bipyramids. 654 and 666  $\text{cm}^{-1}$ , 799 and 816  $\text{cm}^{-1}$  peaks are attributed to  $\nu_1$  and  $\nu_3$  modes of  $\text{NpO}_2^+$  units, respectively. 637 and 726  $\text{cm}^{-1}$  peaks are attributed to the vibrational modes of  $[\text{C}_4\text{O}_4]^{2-}$  anions.<sup>1</sup>

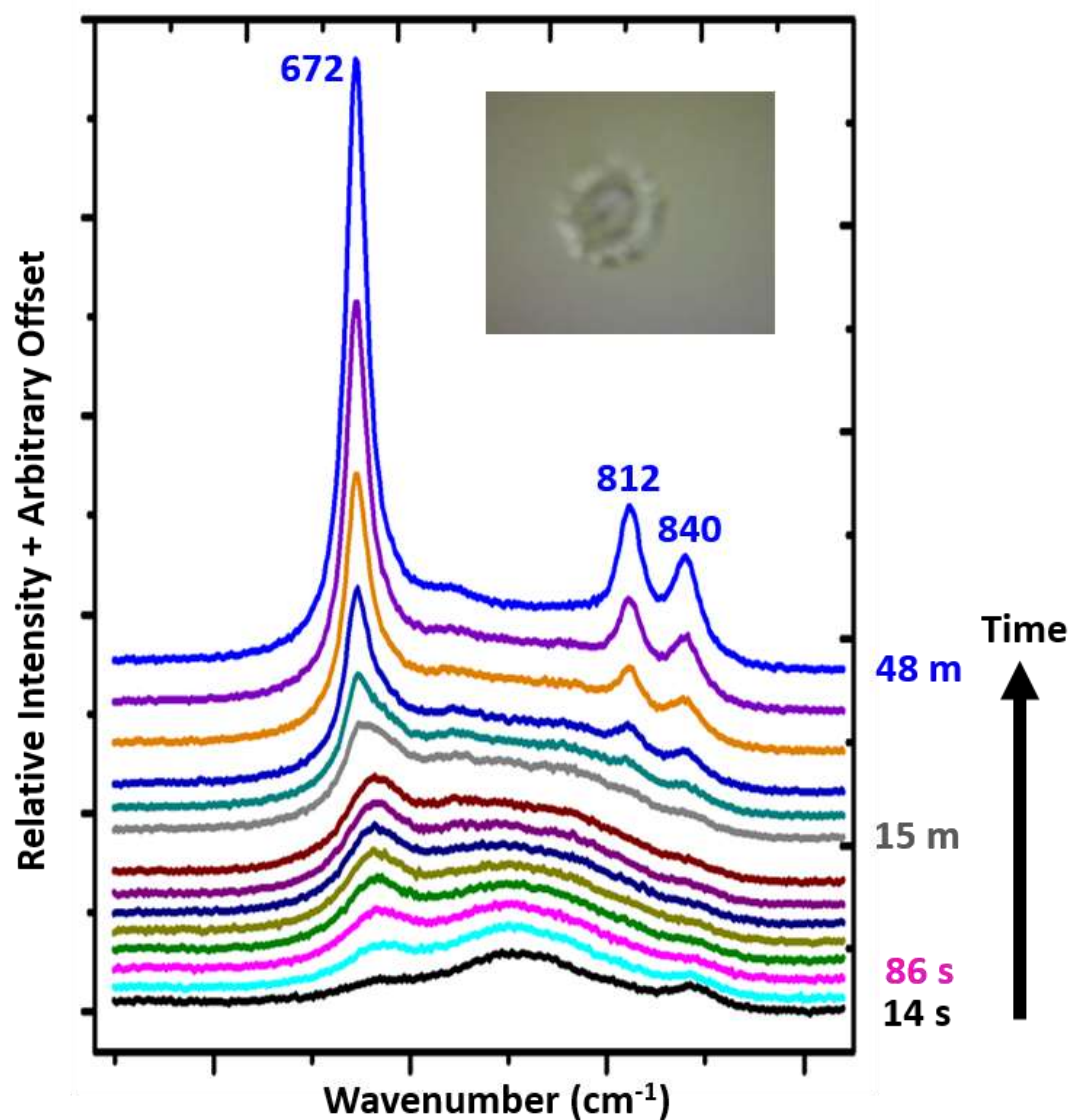


<sup>a</sup>Green prisms of  $(\text{NpO}_2)_2(\text{C}_4\text{O}_4)(\text{H}_2\text{O})$  were obtained from a hydrothermal treatment of a mixture of 0.080 mL of a 0.162 M neptunium(V) stock solution (in  $\sim 1 \text{ M HCl}$ ), 2.4 mg of  $\text{C}_4\text{H}_2\text{O}_4$ , 0.160 mL of a 1 M KOH solution, and 0.760 mL  $\text{H}_2\text{O}$  at 150  $^\circ\text{C}$  for 3 days. Crystallographic data: triclinic,  $P\bar{1}$ ,  $a = 7.5696(7)$ ,  $b = 8.1919(8) \text{ \AA}$ ,  $c = 8.2955(8) \text{ \AA}$ ,  $\alpha = 90.218(1)^\circ$ ,  $\beta = 101.397(1)^\circ$ ,  $\gamma = 113.251(1)^\circ$ ,  $V = 461.39(8) \text{ \AA}^3$ ,  $Z = 2$ ,  $\rho_{\text{calcd}} = 4.506 \text{ g cm}^{-3}$ ,  $\mu = 224.03 \text{ cm}^{-1}$ ,  $R1 = 0.0136$ ,  $wR2 = 0.0354$ .

<sup>b</sup>Green plate-like crystals of  $(\text{NpO}_2)_4\text{Cl}_4(\text{H}_2\text{O})_6 \cdot (\text{H}_2\text{O})_3$  were obtained from an evaporation experiment of a mixed Np(V) solution for several weeks in a similar fashion as **1**. The reactants include 0.250 mL of a 0.120 M Np(V) stock solution (in  $\sim 1 \text{ M HCl}$ ), 5.8 mg of NaCl, 0.250 mL of a concentrated HCl (12 M), and 0.250 mL  $\text{H}_2\text{O}$ . The accuracy of crystallographic data and structural refinement results suffer severely from crystal twinning; nevertheless the connectivity

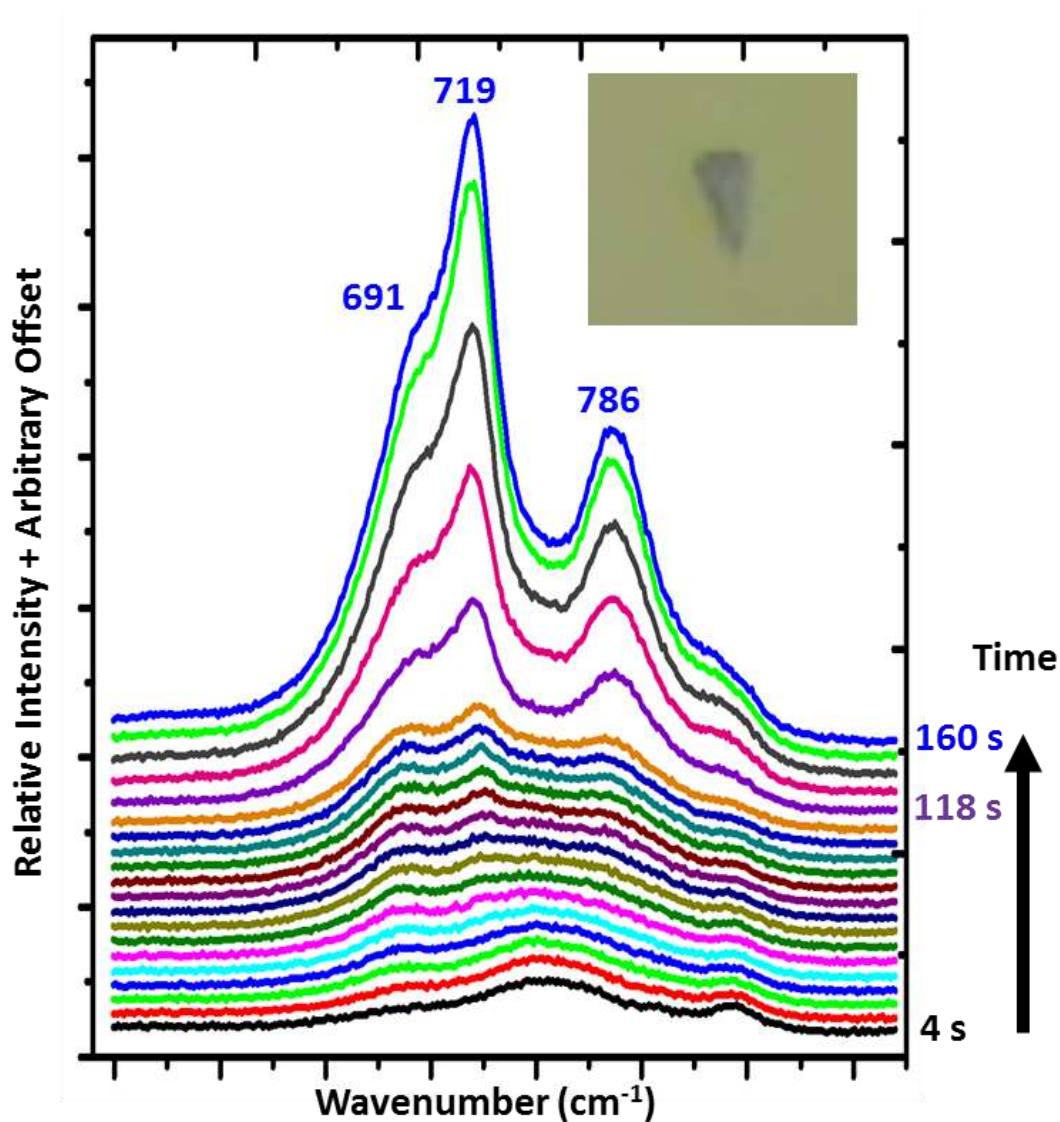
between heavier Np atoms can be determined unambiguously from the X-ray diffraction experiments. The most reliable crystallographic data from numerous data collections: monoclinic,  $Cc$ ,  $a = 16.128(1)$ ,  $b = 16.149(1)$  Å,  $c = 16.787(1)$  Å,  $\beta = 99.188(1)^\circ$ ,  $V = 4316.3(5)$  Å<sup>3</sup>,  $Z = 8$ ,  $\rho_{\text{calcd}} = 4.191$  g cm<sup>-3</sup>,  $\mu = 196.59$  cm<sup>-1</sup>,  $R1 = 0.0384$ ,  $wR2 = 0.1180$ .

**Figure S6:** Portion of the in situ Raman spectra of a evaporation process of a 1.5 M Np(V) solution using 10% laser power and 20% laser focus in less than an hour. The formation of green solid (5) is shown in the picture, which was obtained right after the experiment.

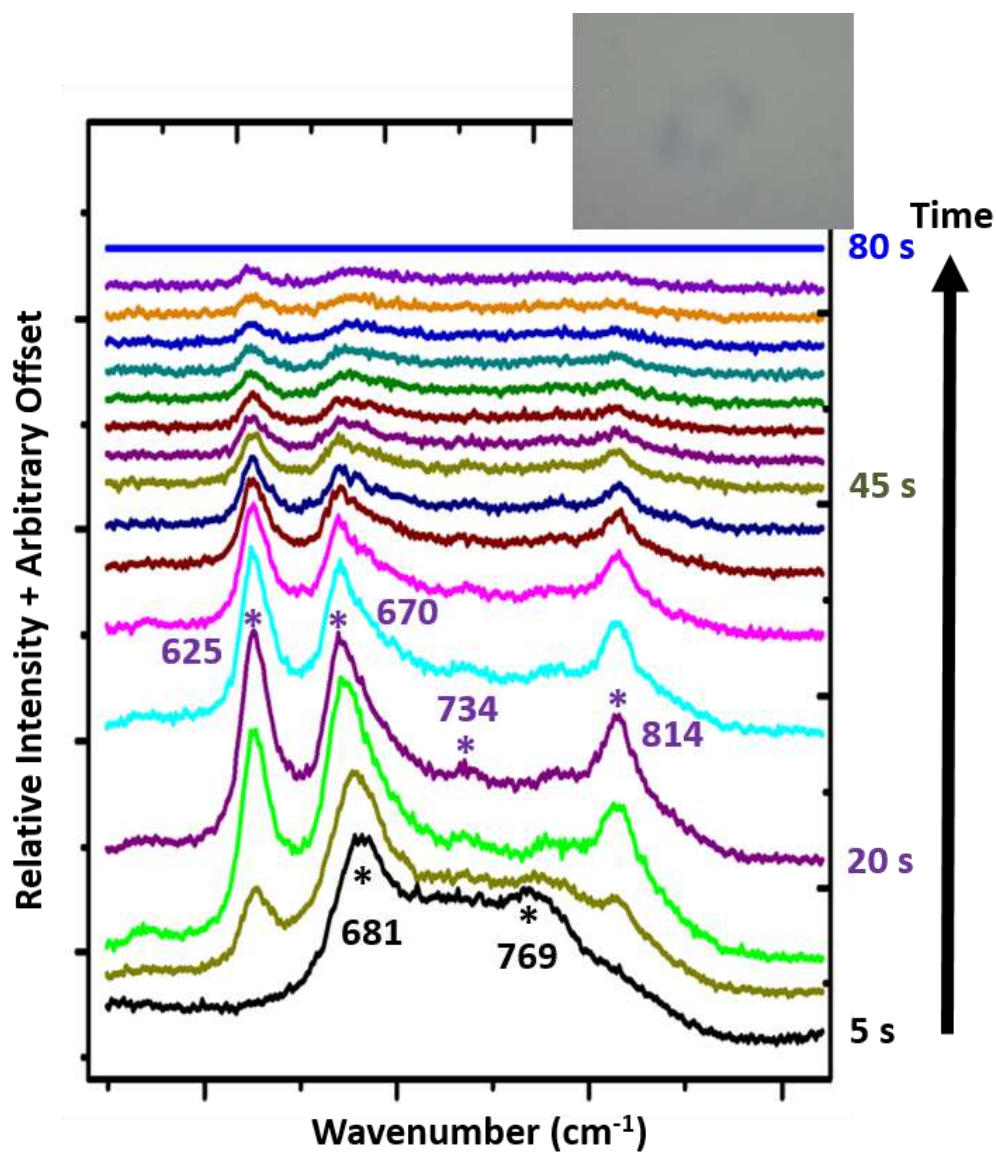




**Figure S7:** In situ Raman spectra of a evaporation process of a 1.5 M Np(V) solution using 10% laser power and 0% laser focus in a few minutes. The formation of green  $\text{Na}_x\text{Np}^{\text{IV}}(\text{Np}^{\text{V}}\text{O}_2)_6(\text{OH})_{1+x}\text{Cl}_9(\text{H}_2\text{O})_{8-x}$  ( $0 < x \leq 1$ ) (2) solid is shown in the picture, which was obtained right after the experiment.



**Figure S8:** In situ Raman spectra of a evaporation process of a 1.0 M Np(V) solution using 50% laser power and 0% laser focus in approximately one minute. The green solid (6) formed in the middle of the evaporation is mostly disappeared at the end of the experiment as shown in the picture.



**References:**

- (1) Nakashima, S.; Balkanski, M. *Solid State Commun.* **1976**, *19*, 1225-1228.