## Supporting Information

**Table S1** Spectrophotometric titration conditions

| Ligand | Titr. # | Initial solution in cuvette | | | | Titrant solution | | | $pC_H$ range |
|---|---|---|---|---|---|---|---|---|---|
| | | $V^0$ mL | $n_{Np}^0$ μmol | $n_H^0$ μmol | $n_L^0$ μmol | $C_L$ mmol·L$^{-1}$ | $C_H$ or $C_{OH}$* mmol·L$^{-1}$ | $V_{add}$ mL | |
| HEDTA | 1 | 2.10 | 0.537 | 0.620 | 0.0 | 1.51 | 0.395 | 1.35 | 3.5 – 8.5 |
| | 2 | 2.10 | 0.528 | 0.610 | 0.0 | 51.3 | 80.0 | 1.30 | 3.5 – 5.5 |
| | 3 | 2.10 | 0.534 | 0.618 | 0.0 | 4.90 | -4.45 | 2.00 | 3.5 – 11 |
| | 4 | 2.13 | 0.536 | 4.37 | 1.25 | 0.0 | -10.0 | 1.30 | 3.0 – 11 |
| | 5 | 2.15 | 0.536 | 8.11 | 2.50 | 0.0 | -15.0 | 1.25 | 3.0 – 11 |
| NTA | 1 | 2.10 | 0.649 | 0.750 | 0 | 97.5 | 91.9 | 0.50 | 3.5 – 7.0 |
| | 2 | 2.60 | 0.649 | 47.5 | 48.6 | 0.0 | 10.4 | 0.70 | 7.0 – 3.5 |

*Positive and negative values refer to the concentrations of $C_H$ and $C_{OH}$, respectively.

**Table S2** Calorimetric titration conditions of Np(V)/HEDTA

| Titr. # | Initial solution in cuvette | | | | Titrant solution | | | $pC_H$ range |
|---|---|---|---|---|---|---|---|---|
| | $V^0$ mL | $n_{Np}^0$ μmol | $n_H^0$ μmol | $n_L^0$ μmol | $C_L$ mmol·L$^{-1}$ | $C_H$ or $C_{OH}$* mmol·L$^{-1}$ | $V_{add}$ mL | |
| 1 | 0.9 | 0.204 | 0.230 | 0.502 | 0.0 | 4.77 | 0.20 | 8.5 – 3.5 |
| 2 | 0.9 | 0.227 | 0.260 | 0.502 | 0.0 | 4.77 | 0.20 | 8.5 – 3.5 |
| 3 | 0.9 | 0.227 | 1.69 | 0.502 | 0.0 | -9.70 | 0.23 | 3.5 – 10.5 |

*Positive and negative values refer to the concentrations of $C_H$ and $C_{OH}$, respectively.

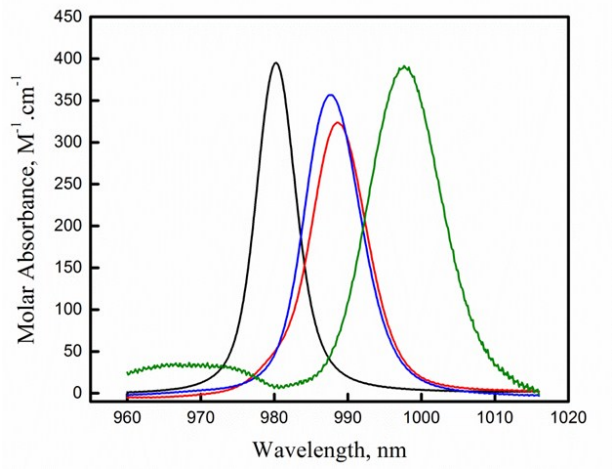



Fig. S1. Resolved molar absorptivities of individual Np(V) species for the Np(V)/HEDTA system. $NpO_2^+$ (black), $NpO_2L^{2-}$ (blue), $NpO_2HL^-$ (red), and $(NpO_2)_2(OH)_2L_2^{6-}$ (green).

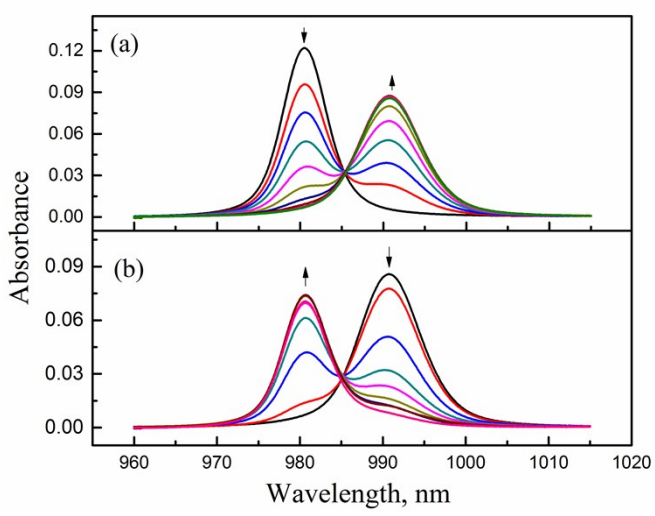
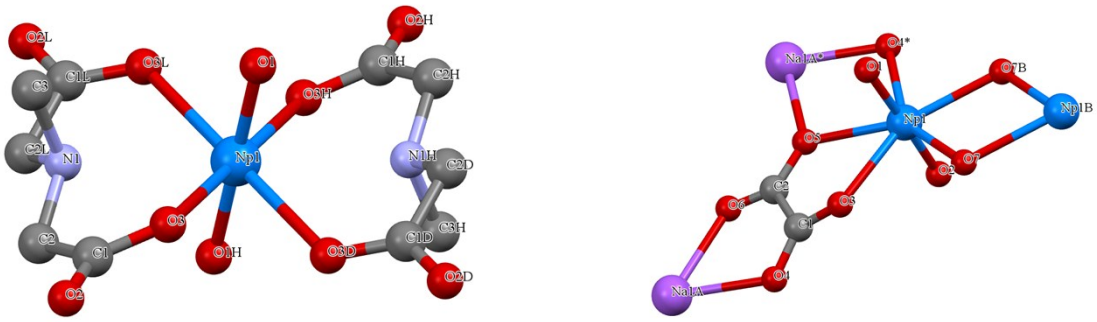



Fig. S2. Spectrophotometric titrations of Np(V)/NTA complexation at $I$ = 1.0 mol·L$^{-1}$ $NaClO_4$, $t$ = 25 °C. Experimental conditions are provided in Table S1: (a) titration # 1, (b) titration # 2.




(a) Compound A (b) Compound B

Fig. S3. Crystal structures of two Np(V) compounds. Compound A: Tris(guanidinium) bis(n-methyliminodiacetato)-dioxo-neptunium(v); Compound B: catena-(($\mu_6$-Oxalato)-($\mu_2$-aqua)-($\mu_2$-hydroxo)-neptunium(v)-di-sodium).

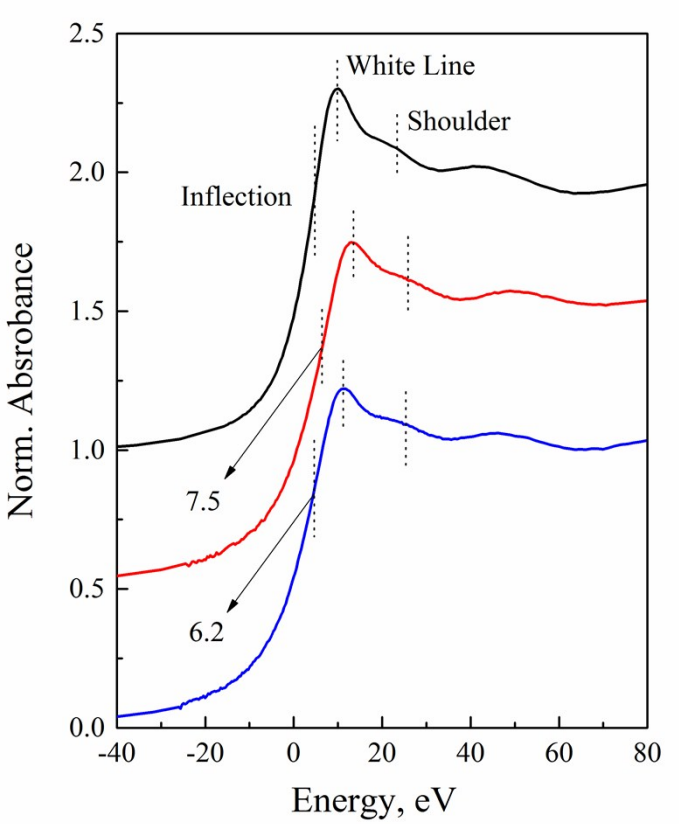



Fig. S4. XANES spectra of three Np(V) solutions. Black line- solution I, red – solution II, blue – solution III. Solution conditions refer to the caption of Figure 7.