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## **Supplementary Information**



*igure S1*. Visible absorption spectra: **a**, **b**: Pu(IV) and Pu(VI) (both 6.2 mmol.L<sup>-1</sup>) in HNO<sub>3</sub> 5 mol.L<sup>-1</sup>. <sup>1</sup>. **c**, **d**: Pu(IV) and Pu(VI) in TBP-HNO<sub>3</sub> equilibrated with HNO<sub>3</sub> 5 mol.L<sup>-1</sup>.



**Figure S2**. CVs of Pu(IV) 6.11 mmol.L<sup>-1</sup> in TBP equilibrated with HNO<sub>3</sub> (5 mol.L<sup>-1</sup>) aqueous solution at a GCE electrode (area 0.007 cm<sup>2</sup>). Scan rate v = 750 mV.s<sup>-1</sup>. Dotted line: uncompensated from ohmic drop. Solid line: 10 k $\Omega$  positive feedback compensation (corresponding to 85% of total resistance).



U 0.2 0.4 0.6 0.8 Figure S3. CVs with different cathodic potential limit of Pu(VI) 5.72 mmol.L<sup>-1</sup> in TBP equilibrated with HNO<sub>3</sub> (3 mol.L<sup>-1</sup>) aqueous solution at a GCE electrode (area 0.007 cm<sup>2</sup>). Ohmic drop correction. Scan rate v = 500 mV.s<sup>-1</sup>.