Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electrodeposition of neodymium and dysprosium from organic electrolytes

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Electronic Supplementary Information (ESI)

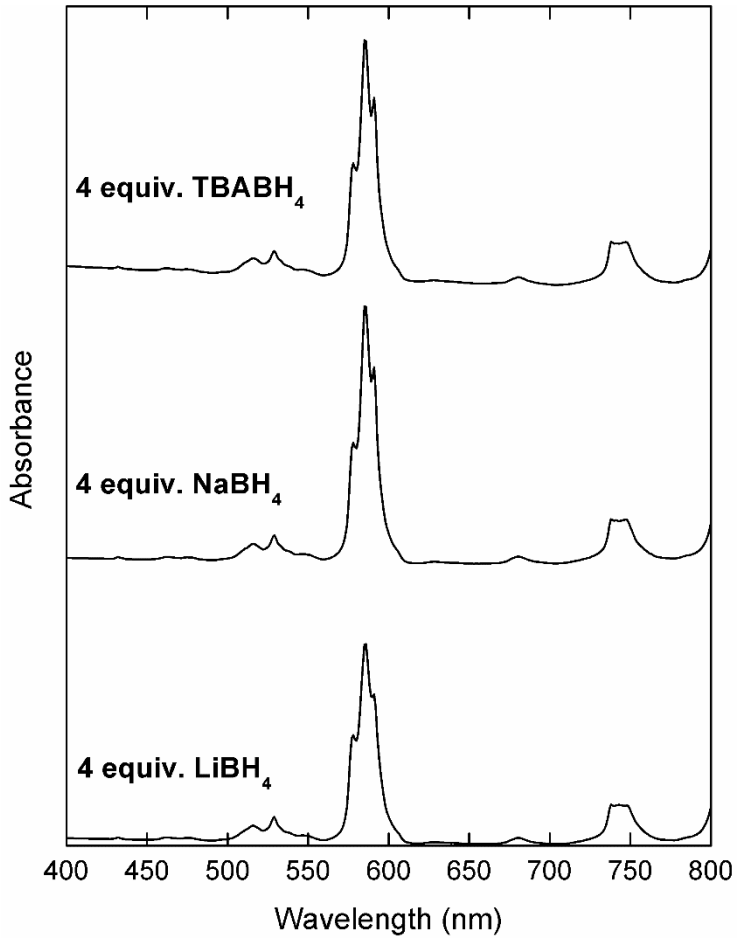

Figure S1. UV-Vis absorption spectra of 0.1 mol L^{-1} $Nd(Tf_2N)_3$, and 4 molar equivalents of $TBABH_4$ (top), $NaBH_4$ (middle), and $LiBH_4$ (bottom) in DME..

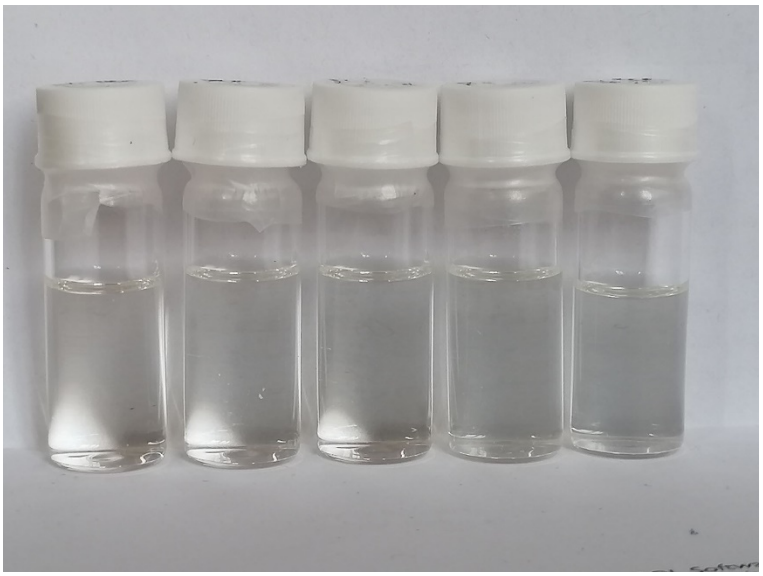

Figure S2. Solutions of 0.1 mol L^{-1} $Dy(Tf_2N)_3$ and, from left to right 0, 1, 2, 3, 4 molar equivalents of $TBABH_4$ in DME.

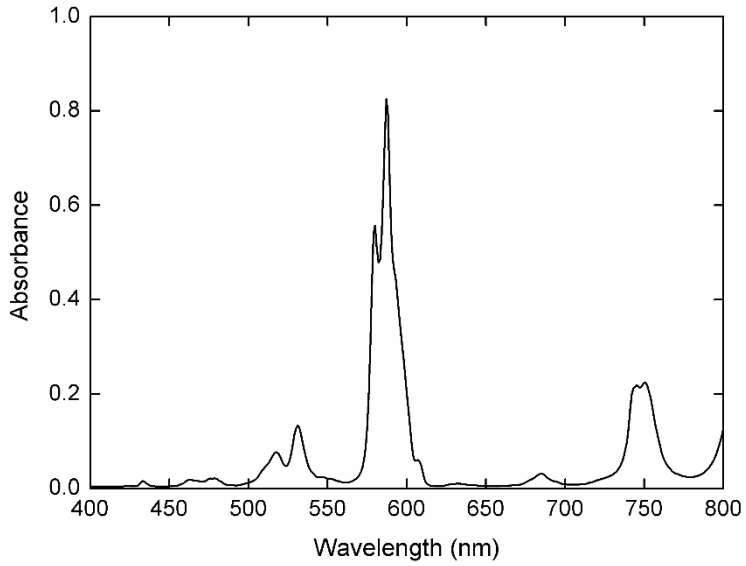

Figure S3. UV-Vis absorption spectrum of 0.1 mol L^{-1} $Nd_2Cl_6(DME)_4$, and 4 molar equivalents of $LiBH_4$ in MeTHF.

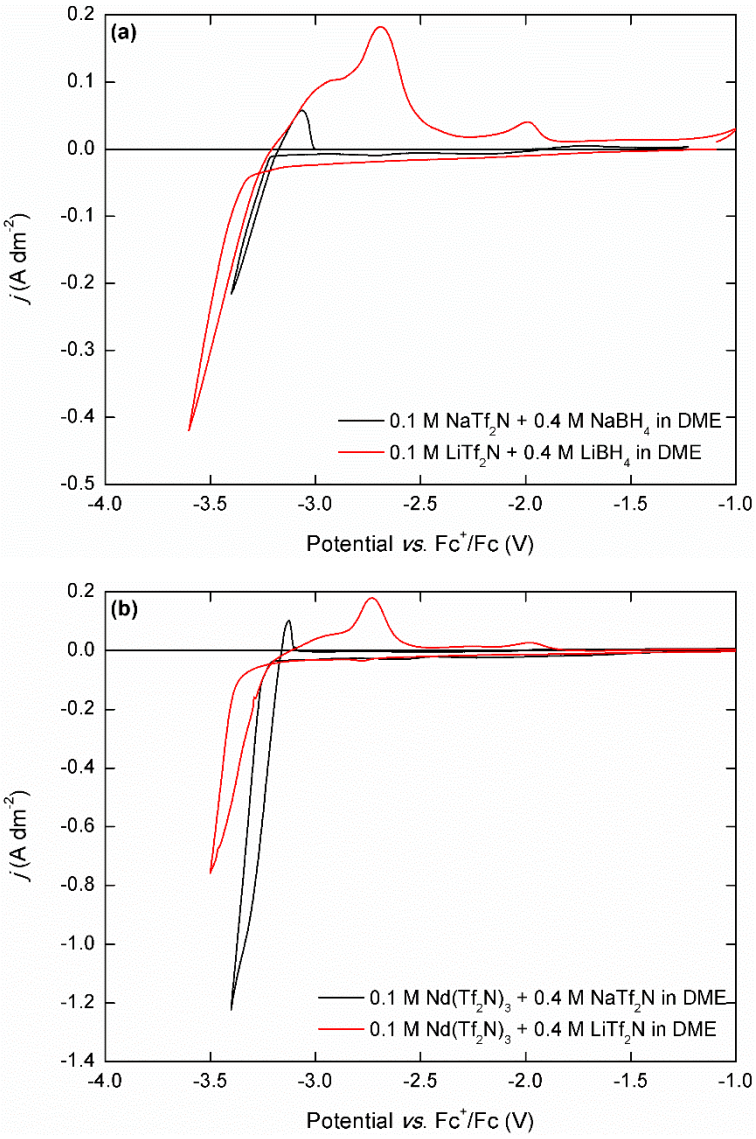

Figure S4. (a) CVs (first cycle) of 0.1 mol L^{-1} $NaTf_2N$ + 4 molar equivalents of $NaBH_4$ (black curve), and 0.1 M $Li(Tf_2N)$ + 4 molar equivalents of $LiBH_4$ (red curve) in DME. (b) CVs of 0.1 mol L^{-1} $Nd(Tf_2N)_3$ + 4 molar equivalents of $NaTf_2N$ (black curve), and 4 molar equivalents of $LiTf_2N$ (red curve). The working and counter electrodes were pieces of platinum-coated silicon wafers with a surface area of 0.003 dm^2 and 0.01 dm^2, respectively. The reference electrode was Fc^+/Fc (0.005 mol L^{-1} each) dissolved in [BMP][Tf_2N]. The scan rate was 10 mV s^{-1}.

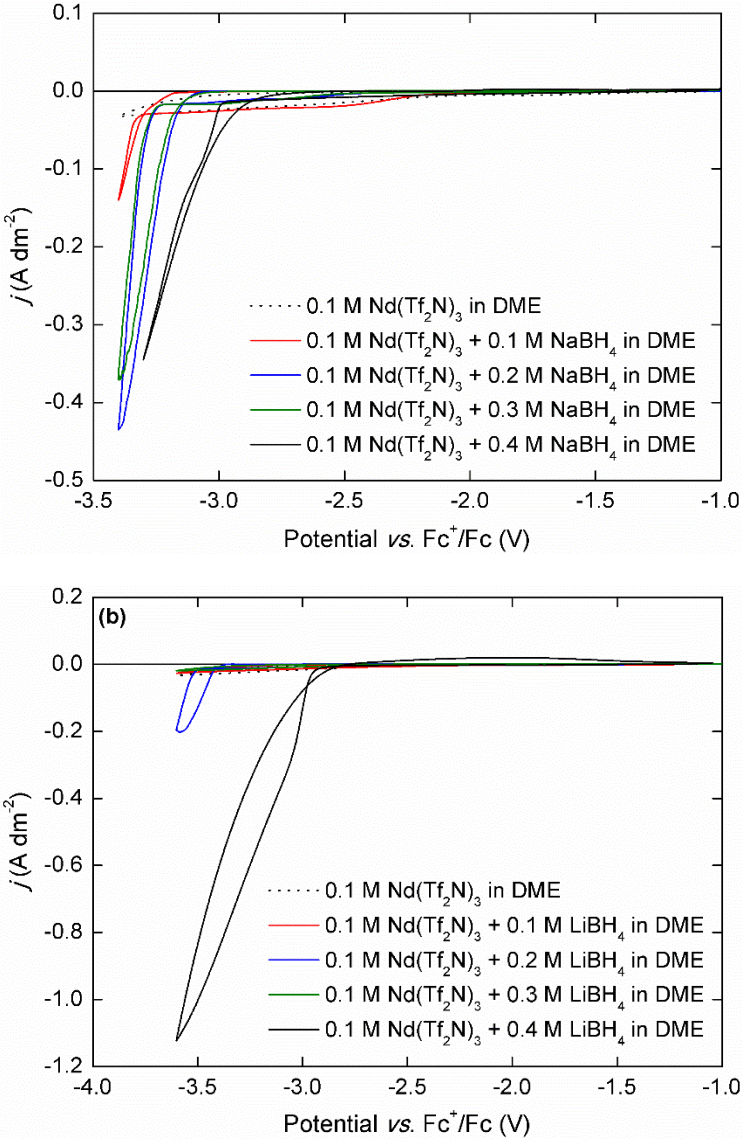

Figure S5. CVs (first cycle) of 0.1 mol L^{-1} $Nd(Tf_2N)_3$ + 0 to 4 molar equivalents of (a) $NaBH_4$, and (b) $LiBH_4$, recorded at a scan rate of 10 mV s^{-1}. The working and counter electrodes were pieces of platinum-coated silicon wafers with a surface area of 0.003 dm^2 and 0.01 dm^2, respectively. The reference electrode was Fc^+/Fc (0.005 mol L^{-1} each) dissolved in [BMP][Tf_2N].

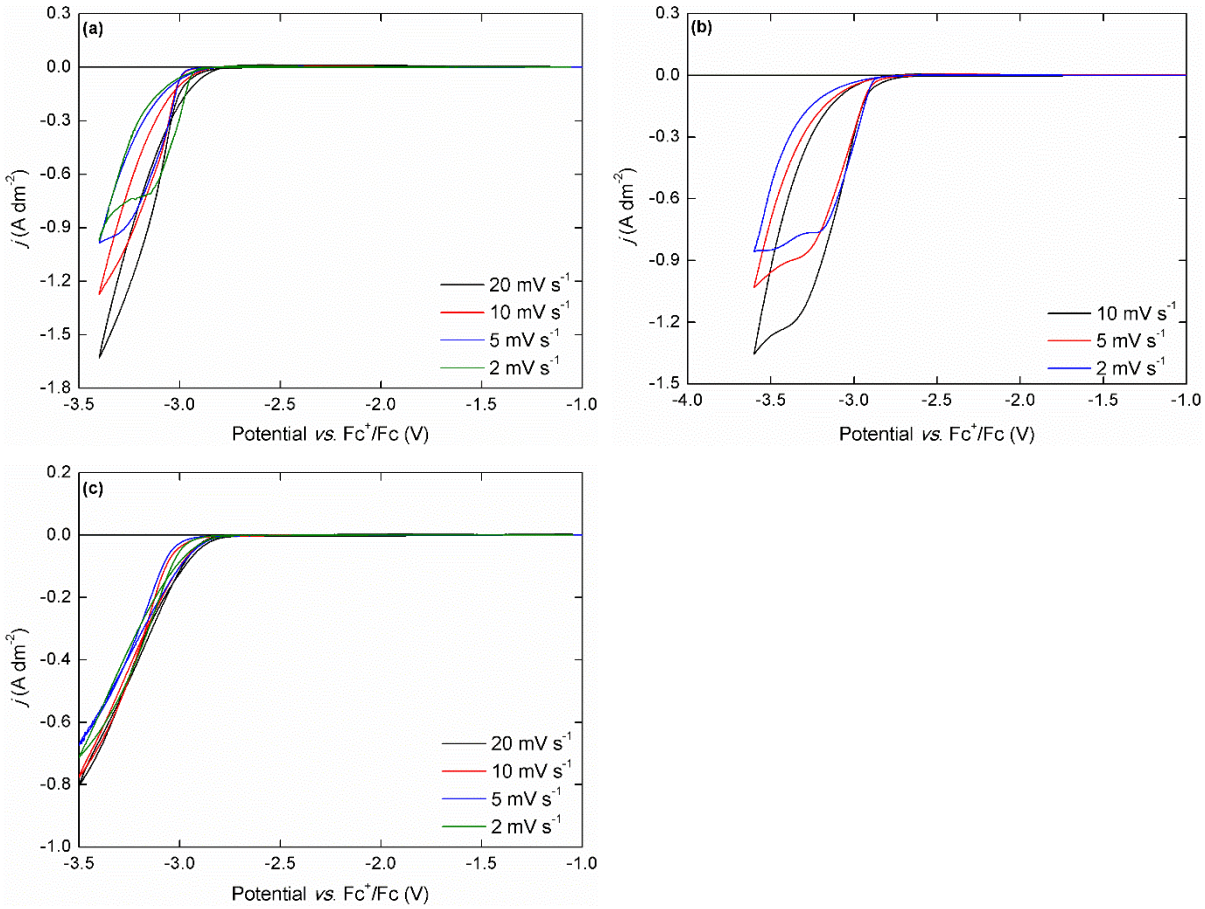

Figure S6. CVs (first cycle) of 0.1 mol L^{-1} $Dy(Tf_2N)_3$ + 4 molar equivalents of (a) $NaBH_4$, (b) $LiBH_4$, and (c) $TBABH_4$ recorded at varying scan rate. The working and counter electrodes were pieces of platinum-coated silicon wafers with a surface area of 0.003 dm^2 and 0.01 dm^2, respectively. The reference electrode was Fc^+/Fc (0.005 mol L^{-1} each) dissolved in [BMP][Tf_2N].

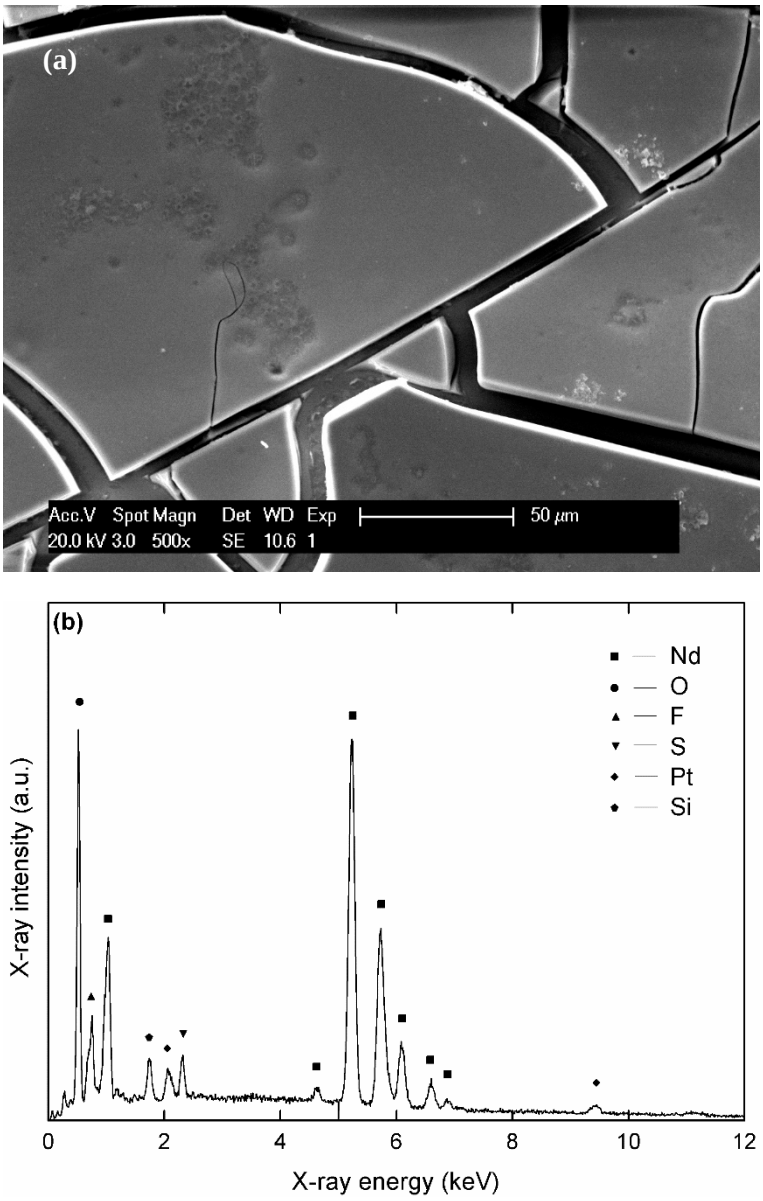

Figure S7. (a) Scanning electron micrograph of a deposit prepared at a constant potential of −3.1 V vs. Fc^{+}/Fc in a stirred solution of 0.1 mol L^{-1} $Nd(Tf_2N)_3$ + 4 molar equivalents of $NaBH_4$ in DME at X500 magnification. (c) EDX spectrum of the deposit in the energy range 0–12 keV, recorded at an acceleration voltage of 20 kV with assignment of the major lines.

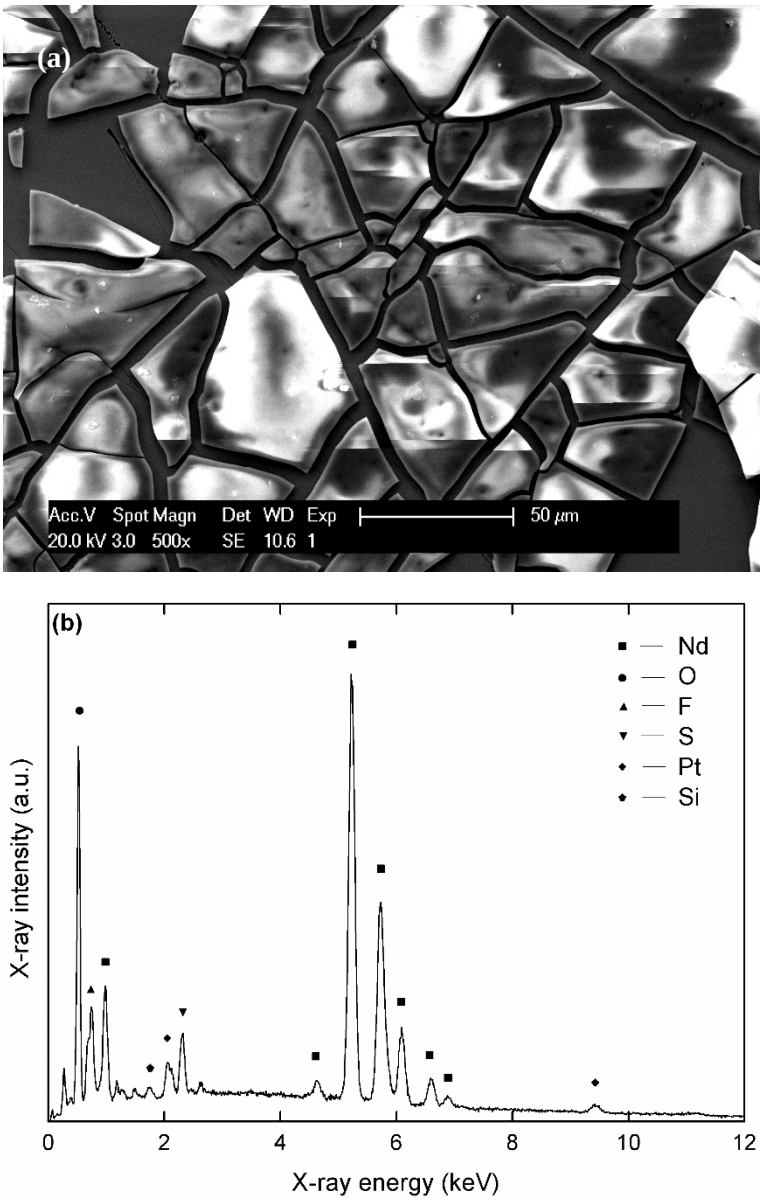

Figure S8. (a) Scanning electron micrograph of a deposit prepared at a constant potential of −3.1 V vs. Fc^{+}/Fc in a stirred solution of 0.1 mol L^{-1} $Nd(Tf_2N)_3$ + 4 molar equivalents of $LiBH_4$ in DME at X500 magnification. (c) EDX spectrum of the deposit in the energy range 0–12 keV, recorded at an acceleration voltage of 20 kV with assignment of the major lines.

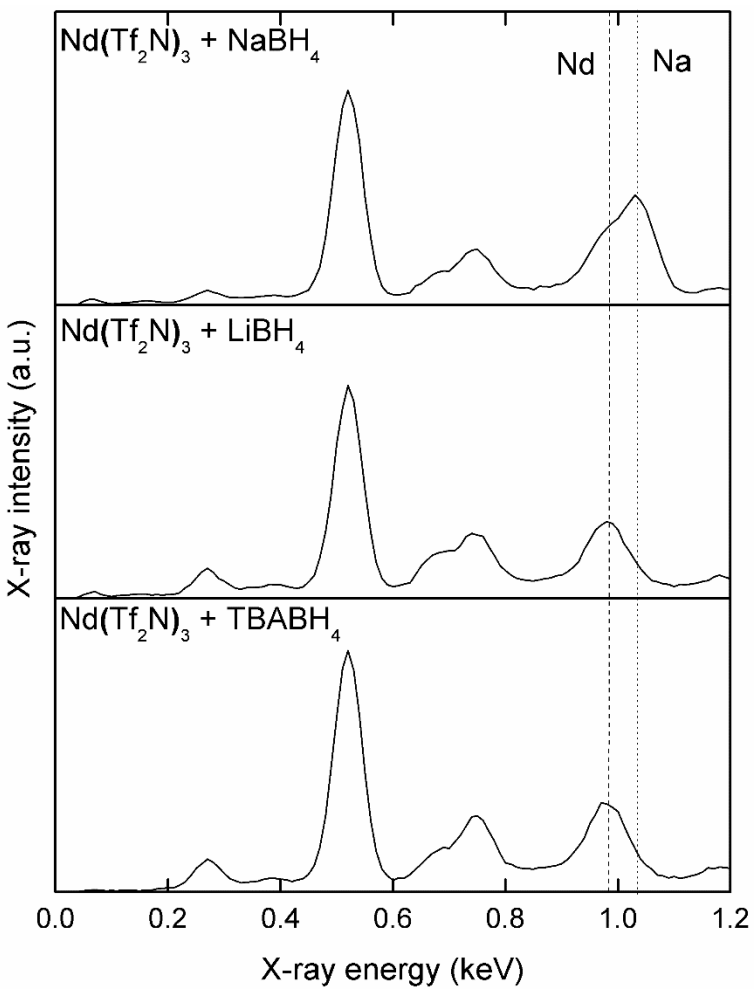

Figure S9. EDX spectra in the energy range 0–1.2 keV of neodymium deposits prepared in 0.1 mol L^{-1} $Nd(Tf_2N)_3$ + 4 molar equivalents of $NaBH_4$, $LiBH_4$, or $TBABH_4$, recorded at an acceleration voltage of 20 kV. The dashed and dotted lined indicate the characteristic X-ray lines of neodymium (Mα = 0.98 keV) and sodium (Kα = 1.04 keV), respectively.

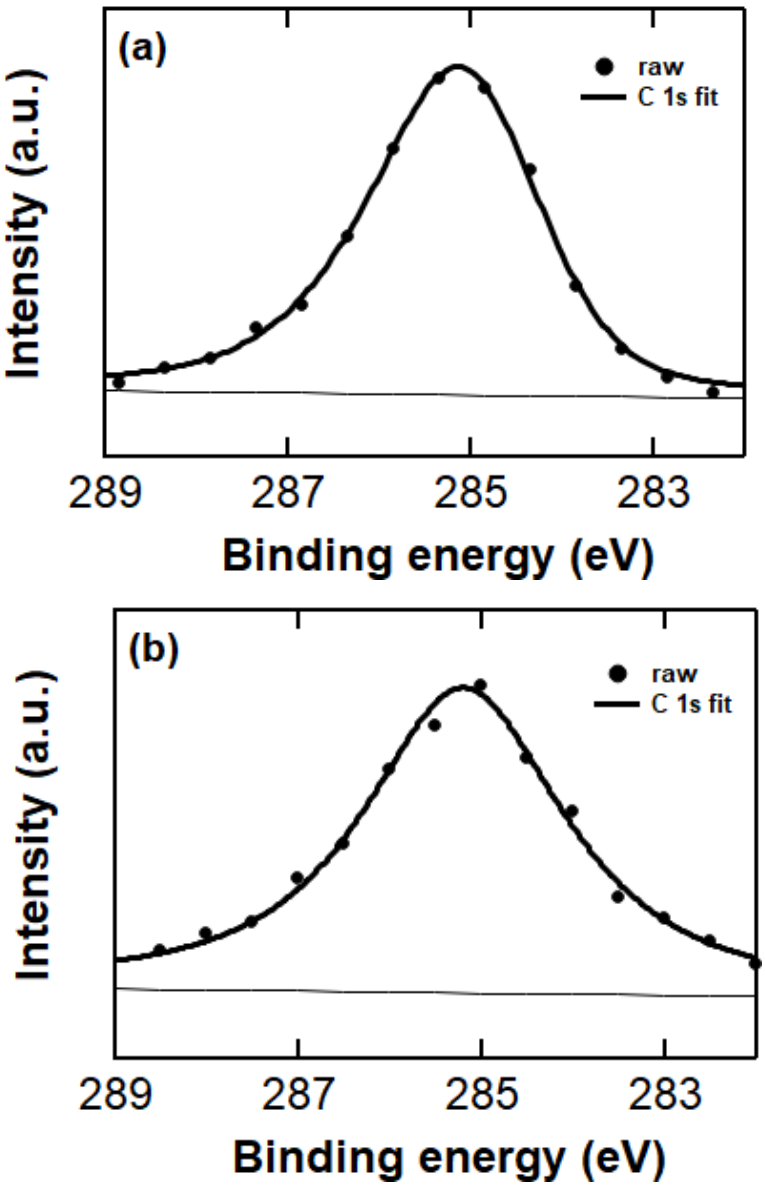

Figure S10. Curve-fitted C 1s XPS spectra (surface) from Nd (a) and Dy (b) deposits with a thickness of approx. 1 µm, obtained from potentiostatic deposition in $Nd(Tf_2N)_3$ or $Dy(Tf_2N)_3$ + $TBABH_4$ electrolytes at –3.4 V *vs.* Fc^+/Fc. The C 1s peak was shifted to 285.2 eV (mainly C–H bonds) for calibration of the spectra.

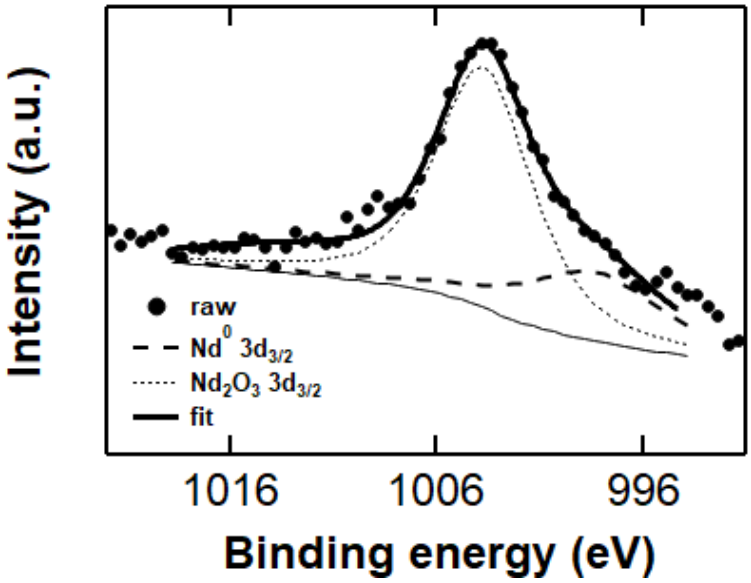

Figure S11. Curve-fitted Nd $3d_{3/2}$ XPS spectra (surface) from deposits with a thickness of approx. 1 µm, obtained from potentiostatic deposition in $Nd(Tf_2N)_3$ + $TBABH_4$ electrolytes at –3.4 V vs. Fc^+/Fc.

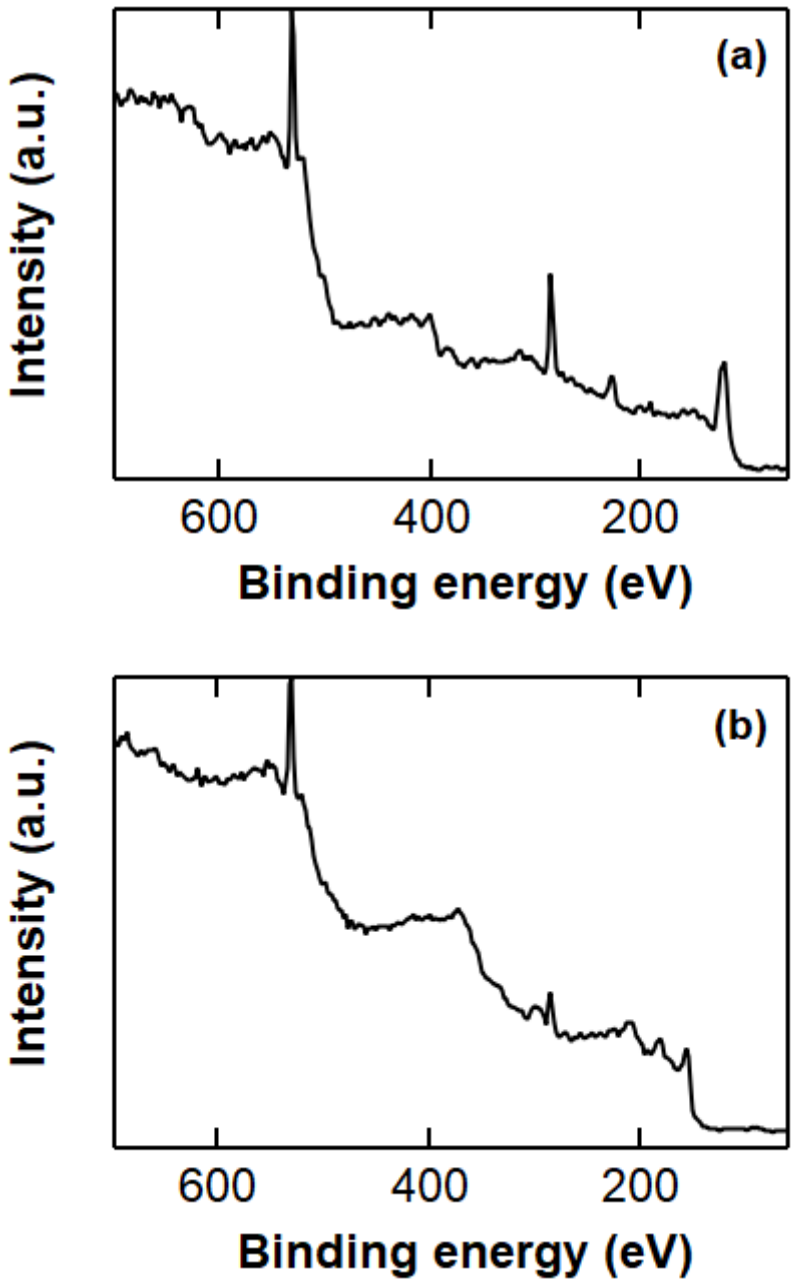

Figure S12. XPS survey scans in the range 60–700 eV, of Nd (a) and Dy (b) deposits with a thickness of approx. 1 µm, obtained from potentiostatic deposition in $Nd(Tf_2N)_3$ or $Dy(Tf_2N)_3$ + $TBABH_4$ electrolytes at –3.4 V *vs.* Fc^+/Fc.

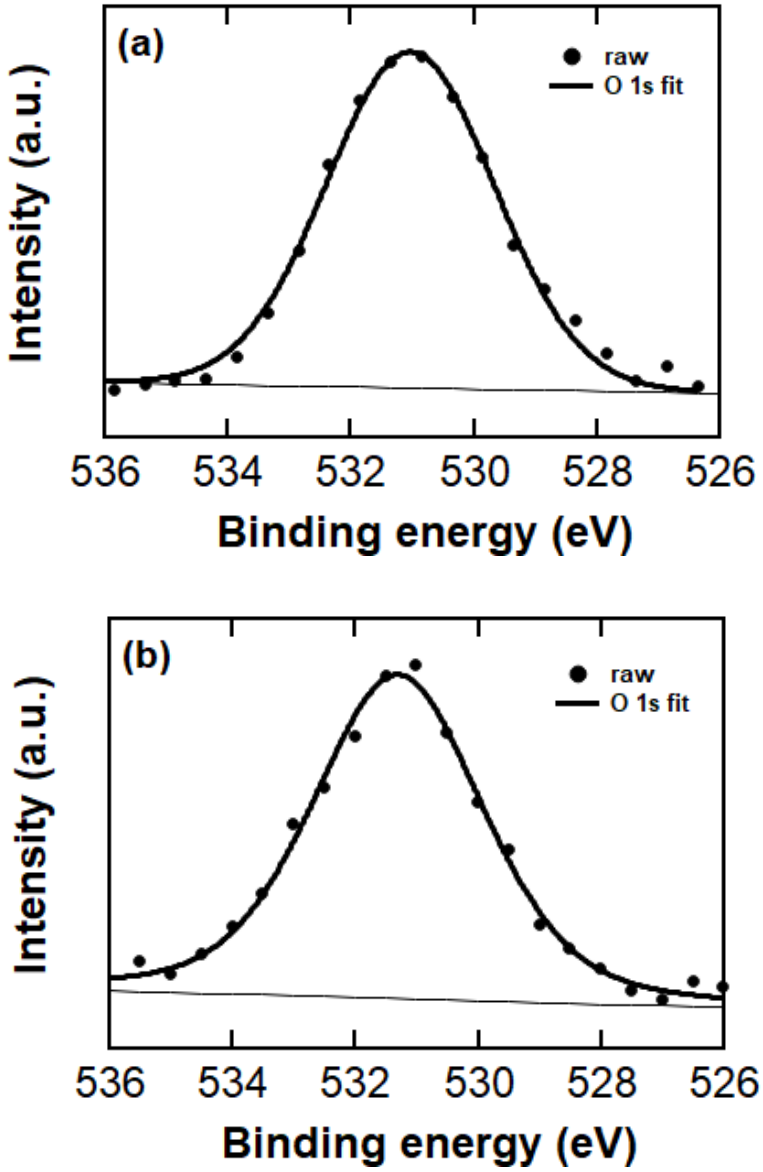

Figure S13. Curve-fitted O 1s XPS spectra (surface) from Nd (a) and Dy (b) deposits with a thickness of approx. 1 µm, obtained from potentiostatic deposition in $Nd(Tf_2N)_3$ or $Dy(Tf_2N)_3$ + $TBABH_4$ electrolytes at –3.4 V *vs.* Fc^+/Fc.