Supporting Information

Experimental details:

Wet-Ionic Liquid: IL obtained from Sigma Aldrich (>98%, CAS 174899-83-3) was equilibrated with equal volume of Milli-Q water in a stoppered glass tube for 30 minutes. After equilibration, the tube was centrifuge to separate the aqueous layer and IL layer. This water saturated IL was used throughout the present study. The water content of IL was calculated to be about 1 mol/L.

1-Butyl-3-methylimidazolium nitrate solution: Stock solution (0.5 mol/L) was prepared by dissolving appropriate amount of 1-Butyl-3-methylimidazolium nitrate salt (Sigma Aldrich, CAS 179075-88-8) in IL.

Lanthanide salts: $Nd(NTF_2)_3$ and $Eu(NTf_2)_3$ salts were prepared by reaction of their oxides with $HNTF_2$ (Sigma Aldrich, CAS 82113-65-3). 5 g $HNTF_2$ was dissolved in 10 mL Milli-Q water. Stoichiometric amounts of Eu_2O_3 or Nd_2O_3 solids were dissolved in $HNTF_2$ solution by stirring for 1 hour at room temperature. The solution was filtered, evaporated to dryness, and finally vacuum dried to get pink powder of $Nd(NTF_2)_3$ and white powder of $Eu(NTf_2)_3$. Stock solutions of $Nd(NTF_2)_3$ and $Eu(NTf_2)_3$ were prepared by dissolving appropriated amount of their salts in IL.

Absorbance Spectroscopy: Optical absorption spectra of Nd(III) in IL were collected over the wavelength range from 550 nm to 650 nm (0.2 nm interval) on Varian Cary-5G Spectrophotometer. The temperature of the sample and reference cell holders was controlled by water circulation from a constant-temperature water bath.

Luminescence Spectroscopy: Luminescence emission spectra and the lifetime of Eu(III) were recorded on HORIBA Jobin Yvon IBH FluoroLog-3 fluorometer adapted for time resolved measurements. The luminescence emission spectra were obtained in the wavelength region of 570–710 nm (0.5 nm/step, 2.0 nm bandwidth, 0.5 s integration time) by excitation at 394 nm (10 nm bandwidth). Signals were acquired using an IBH Data Station Hub, and were analyzed using DAS 6 decay analysis software.

Microcalorimetry: Microcalorimetric titrations were performed on an isothermal titration microcalorimeter (TAM-III) which measures the heat flow between the reaction vessel, reference vessel, and a heat sink maintained at a constant temperature. The gain factors were calibrated by the instrument before each experiment. The system was allowed to equilibrate for sufficient time before making a baseline measurement. The reaction cup initially contained 750 μL of the titrand which was stirred with a gold propeller maintained at 80 rpm. The injections of titrant were made through a Hamilton 250 μL syringe. When the system reached thermal equilibrium, 5 μL of titrant were injected into the reaction vessel and the heat flow was recorded. About 50 titration data were obtained for each experiment, and the data were analyzed by Nano Analyzer Software.

Electrospray Ionization Mass Spectrometry: The ESI-MS experiments were performed using an Agilent 6340 quadrupole ion trap mass spectrometer with a micro-ESI source. The

acetonitrile solution containing ionic liquid, Eu^{3+} and nitrate were directly injected into the ESI capillary at a flow rate of 1 μL/min. Typical concentrations of analyte in the spray solution were: ~5.5 μmol/L Eu^{3+}, ~17 μmol/L NTF_2^-, ~50 μmol/L $C_4mim{\cdot}NO_3$.

Table and Figures

Table S1: Life time of Eu(III) and number of coordinated water molecules

$R_{nitrate/Eu}$	τ_{H2O} (ms)	N_{H2O}
0	0.105	9.3
1	0.127	7.6
2	0.170	5.5
3	0.246	3.6
4	0.446	1.6
5	0.803	0.60
6	0.863	0.52
7	0.893	0.47
8	0.911	0.45

Note: Number of water molecules were calculated as: $N_{H2O} = 1.05/\tau - 0.70$, where τ is the fluorescence life time in ms

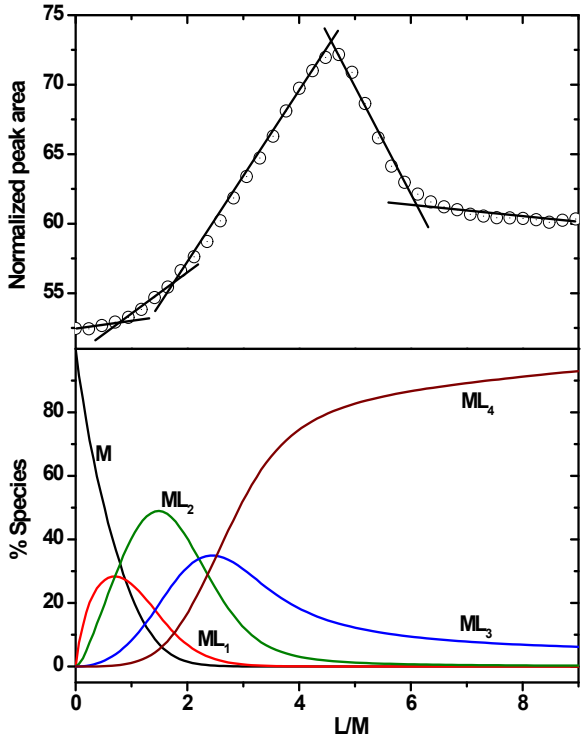

Fig. S1. Total peak area of the normalized absorption band ($^4I_{9/2} \rightarrow {}^4G_{5/2}$, $^2G_{7/2}$) between 560 – 600 nm versus nitrate concentration. The bottom figure shows the distribution of various species (ML, ML_2, ML_3 and ML_4, where M refers to Nd, and L refers to nitrate) as a function of titrant added. L/M ratio refers to C_{NO3}/C_{Nd} in the solution.

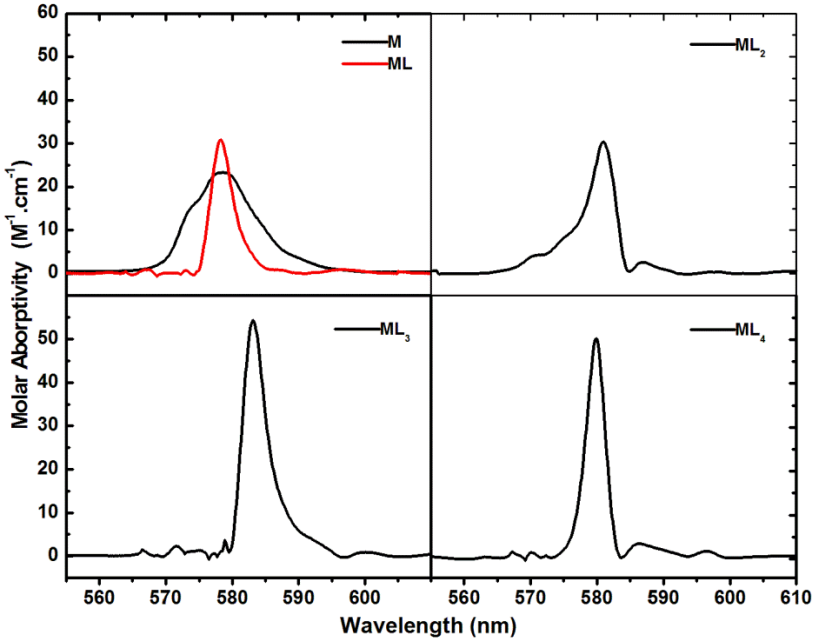

Fig. S2. Molar absorptivities of Nd(III)-nitrate complexes calculated from Figure 1 of the manuscript. M, ML, ML_2, ML_3 and ML_4 refers to Nd^{3+}, $Nd(NO_3)^{2+}$, $Nd(NO_3)_2^{+}$, $Nd(NO_3)_3$, and $Nd(NO_3)_4^{-}$, respectively.