Electronic Supplementary Information (ESI) for:

Extraction of Lanthanides Using 1-hydroxy-6-N-octylcarboxamido-2(1H)-pyridinone as an Extractant via Competitive Ligand Complexations Between Aqueous and Organic Phases

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Methods

Solvents, reagents, and chemicals were purchased from commercial vendors and used without further purification. ^{1}H and ^{13}C NMR spectra were recorded at ambient temperature on a Varian VNMRS 500 MHz narrow-bore broadband system. ^{1}H and ^{13}C NMR chemical shifts were referenced to the residual solvent. Mass spectrometry analyses were performed using a JEOL AccuTOF-D time-of-flight (TOF) mass spectrometer with a DART (direct analysis in real time) ionization source from JEOL USA, Inc. (Peabody, MA).
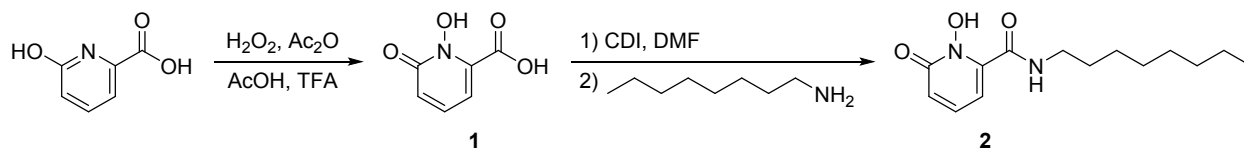
Fig. S1. Synthesis scheme for 1-hydroxy-6-*N*-octylcarboxamido-2(1*H*)-pyridinone (octyl-HOPO, **2**).

Synthesis of 6-carboxy-1-hydroxy-2(1*H*)-pyridinone (1). This compound was prepared following a reported procedure.[1] A mixture of acetic anhydride (30 mL) and a 30% aqueous hydrogen peroxide solution (10 mL) was stirred in an ice bath for 4 h to form a peracetic acid solution. A separate solution was prepared by dissolving 6-hydroxypicolinic acid (5.03 g, 35.10 mmol) in a mixture of trifluoroacetic acid (30 mL) and glacial acetic acid (10 mL). After stirring at room temperature for 10 min, this 6-hydroxypicolinic acid solution was added to the peracetic acid solution. The reaction mixture was then stirred at 80 °C overnight, yielding a white precipitate after cooling to room temperature. The precipitate was filtered, washed with cold methanol, and dried under vacuum. A 10% w/w aqueous KOH solution (90 mL) was then added to the precipitate, and the mixture was stirred at 70 °C overnight. After cooling to room temperature, the mixture was cooled in an ice bath, and the product was precipitated by adding cold concentrated HCl (30 mL). The precipitate was filtered and washed with a 0.1 M aqueous HCl solution, cold methanol, and cold water in succession. The product was dried under vacuum to yield an off-white solid (2.54 g, 47%).

^{1}H NMR (DMSO-d_6, 500 MHz) δ 11.33 (s, 1H), 7.45 (dd, J = 9.0, 7.0 Hz, 1H), 6.73 (dd, J = 9.0, 1.5 Hz, 1H), 6.65 (dd, J = 7.0, 1.5 Hz, 1H). ^{13}C NMR (DMSO-d_6, 126 MHz) δ 161.9, 157.2,

139.0, 136.8, 120.3, 106.4. HRMS (DART-TOF) *m/z*: [M−H]⁻ calcd for $C_6H_4NO_4$: 154.0140; found: 154.0142.

Synthesis of 1-hydroxy-6-*N*-octylcarboxamido-2(1*H*)-pyridinone (octyl-HOPO) (2). This compound was synthesized according to a modified literature procedure.[2] 6-Carboxy-1-hydroxy-2(1*H*)-pyridinone (**1**) (1.01 g, 6.51 mmol) and *N,N'*-carbonyl diimidazole (CDI) (1.27 g, 7.81 mmol) were stirred in dry DMF (40 mL) at room temperature under N_2 for 2 h. Then, *n*-octylamine (1.18 mL, 7.17 mmol) was added, and the mixture continued stirring at room temperature under N_2 overnight. Afterwards, the solvent was removed by rotary evaporation, and the crude residue was taken up in dichloromethane (50 mL). The solution was extracted with 0.1 M NaOH (2 × 25 mL), and the combined aqueous layers were reduced to about 20 mL in volume by rotary evaporation. The concentrated aqueous solution was acidified with 2 M HCl to pH 2, upon which white precipitates formed. The solids were collected by filtration, washed with cold water, and dried under vacuum to give the product as an off-white solid (1.16 g, 67%).
¹H NMR (CDCl₃, 500 MHz) δ 9.56 (s, 1H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.49–7.43 (m, 1H), 7.03 (d, *J* = 8.6 Hz, 1H), 3.51–3.44 (m, 2H), 1.68–1.60 (m, 2H), 1.43–1.35 (m, 2H), 1.35–1.22 (m, 8H), 0.87 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (CDCl₃, 126 MHz) δ 158.8, 156.6, 137.2, 133.2, 115.2, 114.0, 40.3, 32.0, 29.4, 27.2, 22.8, 14.3. HRMS (DART-TOF) *m/z*: [M+H]⁺ calcd for $C_{14}H_{23}N_2O_3$: 267.1709; found: 267.1706.

Materials for Distribution studies: Extraction studies were carried out using 1,3-diisopropylbenzene obtained from Sigma Aldrich and was used as received with out further purification. Aqueous phases solutions used distilled, deionized water from a Millipore filtration system (resistivity 18.2 $M\Omega$ cm⁻¹). The ¹⁵²/¹⁵⁴Eu radioisotope was obtained from Isotope Products, Burbank, CA and the Radiochemical and Engineering Research Center of Oak Ridge National Laboratory provided the ²⁴¹Am radioisotope. The lanthanides were obtained as 10,000 ppm (4% HNO₃) standardized solutions from High-Purity Standards, Charleston, SC. The DTPA used was obtained as the penta-sodium salt from Acros Organics as a 40% w/w aqueous solution. All other chemicals were obtained from Fisher Scientific and were used as received without further purification.

Distribution Studies. The extraction experiments of the lanthanides and europium/americium (Eu/Am) separation experiments were carried out in a similar manner. The aqueous solutions for both sets of experiments were the same with the exception that the Eu/Am experiments were spiked with a small quantity of a $^{152/154}$Eu/^{241}Am radiotracer mixture prior to mixing. An aqueous solution containing 0.7 mmol of each lanthanide (with the exception of Pm) was made using analytical ICP standards. To this mixture was added one or more of the following; Citric Acid and/or DTPA at the concentrations indicated in Table 2 article. For the studies involving Eu/Am separation the citric acid was replaced with lactic acid to allow for a direct comparison to the initial work done by Boyd and Weaver.[3] The octyl-HOPO and DEHPA were dissolved in 1,3-diisopropylbenzene (DIPB) at the concentrations indicated. Extraction studies were preformed by pipetting 0.500 mL of the organic phase and 0.500 mL of the aqueous phase in a 2 mL eppendorf centrifuge tube. The solutions were mixed using a rugged rotating wheel set at 60 rpm in a temperature controlled air–box (25 $\pm$ 0.2 °C) for 3 hrs. After 3 hrs, the tubes were centrifuged at 3000 rom for 5 mins to ensure complete phase disengagement. A this point the two types of experiments utilized different methods for determining the distribution ratios (or values) (*D*), the *D* values were determined using Eq. 1.

$$D_{Ln} = \frac{[Ln]_{org}}{[Ln]_{aq}}$$

(**1**)

To determine the D_{Ln} for the adjacent lanthanide separations the organic phase was removed via pipette then the aqueous phase was subsampled and diluted 10x, then was diluted further 901x prior to injecting the sample into the inductively–coupled plasma mass spectrometer (ICP–MS). The concentrations of the lanthanides in the samples determined via ICP–MS were subtracted from the initial concentrations of the lanthanides, which were also determined by ICP–MS, to determine the concentrations of each lanthanide in the organic phase. Eq. 2 was used to determine the organic phase concentration. In Eq. 2 the initial aqueous [Ln] is subtracted from the experimentally determined [Ln] post mixing, this equation assumes that there was on film or third phase formations.

$$[Ln]_{org} = [Ln]_{aq(init.)} - [Ln]_{aq(mixed)} \quad (2)$$

The experiments used to determine the separation of Eu/Am utilizing radiotracers were simpler compared to the adjacent lanthanide separation experiments. Both organic and aqueous phases were subsampled by 0.250 mL for each phase and placing them in polypropylene culture tubes that were sealed and placed in a germanium spectrometer. The germanium spectrometer is used to measure the amount of disintegrations/counts in each sample over a set time period. The total amount of counts over a time period is normalized to give CPM, which is then used to determine the D value using CPM in each phase in place of concentration. The D values of the ^{152}Eu and ^{241}Am are used in Eq. 3 to calculate the separation factor (*SF*).

$$SF_{Eu/Am} = \frac{D_{Eu}}{D_{Am}} \quad (3)$$

Instrumentation: The $^{152/154}$Eu and ^{241}Am in the organic and aqueous solutions were counted using Canberra Analyst pure Ge Gamma counter. The counting times were of a sufficient duration to ensure that the counting error would not affect the precision of the distribution ratios, when combined the volumetric, replicate and counting errors would be less then ±5%. The lanthanide concentrations in the aqueous solutions were measured using a Thermo Scientific X-Series II ICP-MS. The ICP-MS method and instrument set up are the same as previously report in the literature.[4]

References

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