Supplementary information for

Highly efficient extraction system for Am(III)-Cm(III) pair separation in spent nuclear fuel reprocessing

By

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Computational details

The geometries of molecules were fully optimized by DFT using PRIRODA code written by Laikov [1]. In calculations were used first-principles GGA PBE functional [2], scalar-relativistic theory with four-component spin-free Hamiltonian [3], and full electron DZ basis sets in which the numbers of contracted and primitive functions are {2,1}/{6,2} for H, {3,2,1}/{10,7,3} for C, N, and O, {4,3,1}/{15,11,3} for Cl, {10, 9, 7, 4, 1}/{34,33,24,18, 6} for Am, and Cm, respectively [4,5]. Stationary points on the potential energy surface (PES) were identified by analyzing Hessians. The thermodynamic functions (Gibbs energies, G) at 298.15 K were calculated using an approximation of restricted rotator and harmonic oscillator. The atomic charges were calculated according to Hirschfeld [6]. The topological analysis was performed in the frame of Bader theory [7].

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Synthesis

Experimental section

Materials

Chemical reagents such as ethylenediaminetetraacetic acid (EDTA), 1,1'-bis(diphenylphosphino)ferrocene (dppf) and other reagents and solvents were of analytical grade. Pd_2dba_3•$CHCl_3$ (tris(dibenzylideneacetone)dipalladium(0)-chloroform) was synthesized by the method described in [1]. Dimethylacetamide (DMAA) was purified by vacuum distillation over

phosphorus oxide (P_2O_5). All syntheses were performed in an argon inert atmosphere. Hexane and ethyl acetate for the synthesis were purified following the known procedures. Deuterated solvent toluene-d_8 for NMR spectra registration was purchased from commercial sources and used without further purification. DAPhenCl for synthesis of DAPhenCN may be prepared according to knowing procedures[2].

Methods

NMR spectra were recorded using standard 5 mm sample tubes on Agilent 400-MR spectrometer with operating frequencies of 400.1 MHz (^{1}H) and 100.6 MHz (^{13}C). IR spectra in the solid state were recorded on a Nicolet iS5 FTIR spectrometer (Thermo Scientific) using an internal reflectance attachment with diamond optical element−attenuated total reflection (ATR) with a 45° angle of incidence. The resolution is 4 cm^{-1}; the number of scans is 32. Single crystals of DAPhenCN were obtained upon slow isothermal (25°C) recrystallization of corresponding substances from EtOH.

4,7-dicyano-*N*^{2},*N*^{9}-diethyl-*N*^{2},*N*^{9}-bis(4-hexylphenyl)-1,10-phenanthroline-2,9-dicarboxamide (DAPhenCN)

Synthesis was performed in an argon atmosphere. A mixture of dppf (0.68 mmol, 0.378g) and $Pd_2(dba)_3$ (0.39 mmol, 0.354g) in 35 ml of DMAA was stirred at ambient temperature for 15 min to give a homogeneous orange solution. Then to this solution the **DAPhenCl** (0.0171 mol, 11.225g), $Zn(CN)_2$ (0.02 mol, 2.411g) and Zn (0.0035 mol, 0.227g) was added. Resulted suspension was diluted by DMAA (100 ml). The reaction mixture was heated to 135°C and was stirred for 3 hours at this temperature. After that, the reaction mixture was allowed to cool to room temperature and a solution of EDTA (8.55 g) in distilled water (350 ml) was added dropwise. A precipitate was filtered, rinsed on a filter with distilled water (2×250 ml) and dried to a constant weight. The **DAPhenCN** was purified by column chromatography. Eluent Hexane:EtOAc 4:1, R_f 0.4 (Hexane:EtOAc 3:2). Yield 80% (9.47g), yellow powder. m.p. 160-162°C. ^{1}H NMR (400 MHz, toluene-d_8, 70°C) δ 7.68 (s, 2H, Phen), 7.48 (s, 2H, Phen), 7.11 (d, ^3J = 6.78 Hz, 4H, Ar), 6.88 (d, ^3J = 6.78 Hz, 4H, Ar), 3.97 (q, ^3J = 6.6 Hz, 4H, N-CH_2), 2.23 (m, 4H), 1.35-1.18 (m, 10H), 1.17-0.92 (m, 12H), 0.77 (t, ^3J = 6.97 Hz, 6H); ^{13}C NMR (100 MHz, toluene-d_8, 70°C) δ 166.5, 155.8, 144.6, 142.6, 140.4, 129.3, 126.9, 126.6, 125.7, 119.6, 114.8, 45.1, 35.4, 31.8, 31.2, 28.9, 19.8, 14.1, 13.4; IR (cm^{-1}): 2234 (C≡N), 1651, 1646 (C=O).

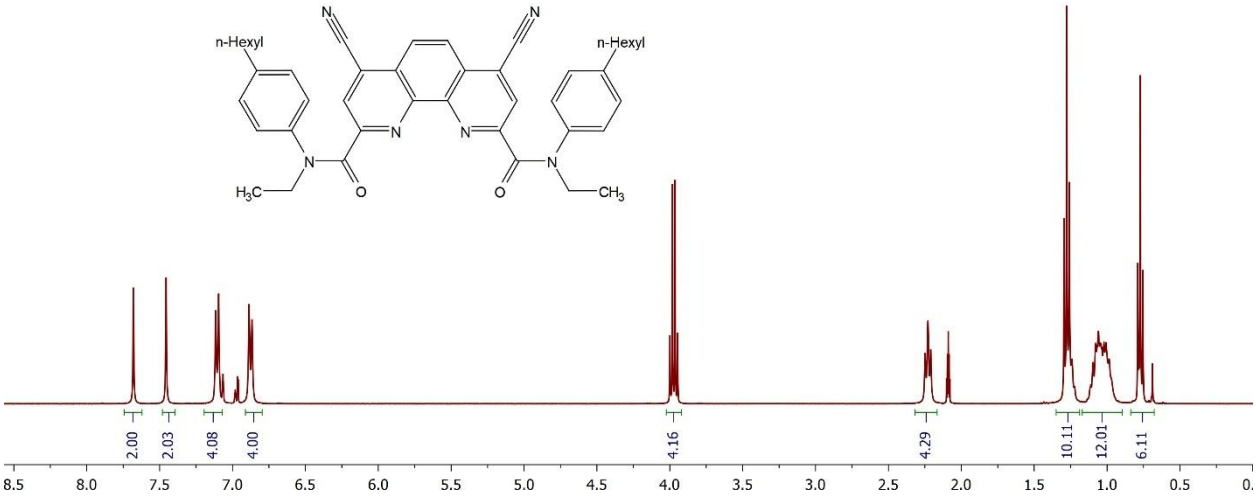

Figure S1. ^{1}H NMR spectrum of DAPhenCN in Toluene-d_8 at 70ºC.

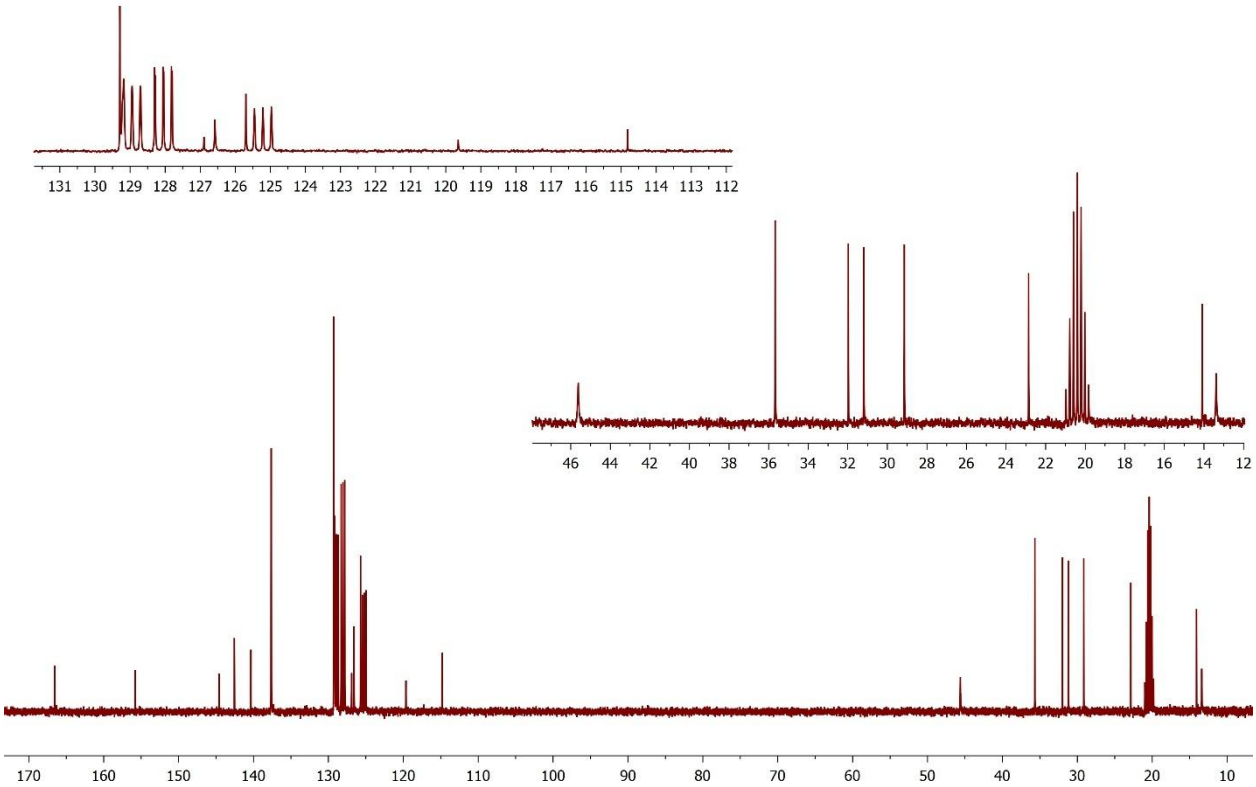

Figure S2. ^{13}C NMR spectrum of DAPhenCN in Toluene-d_8 at 70ºC.

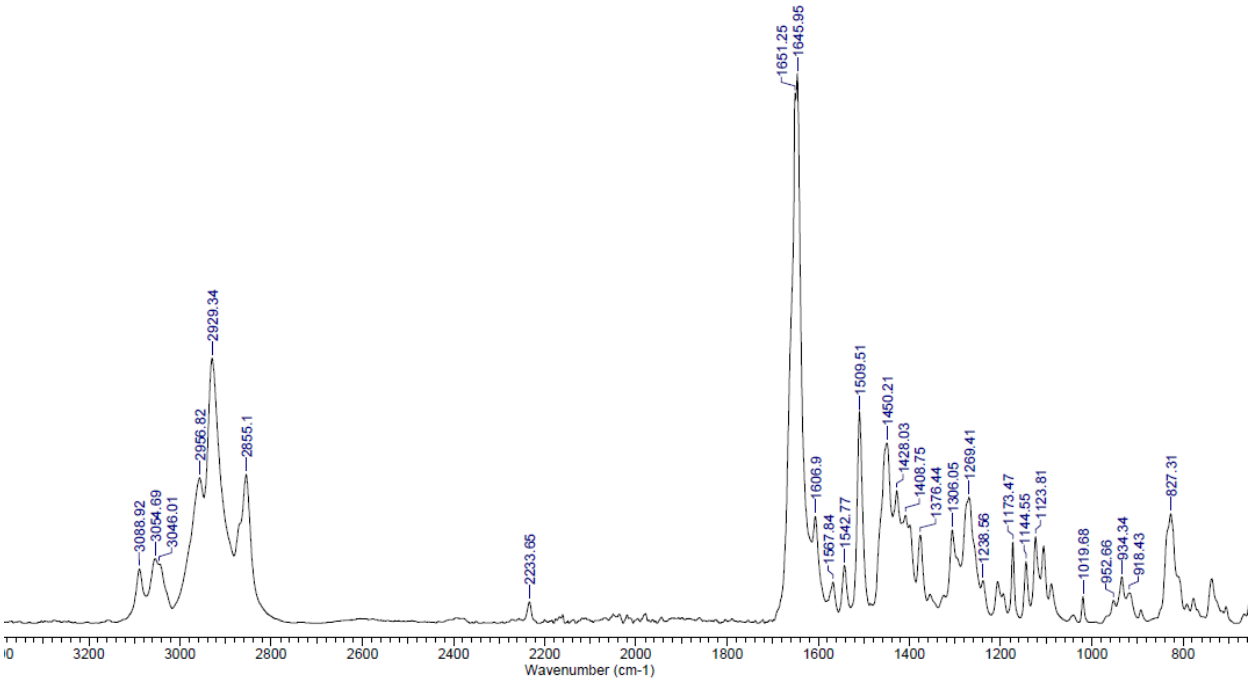

Figure S3. Solid-state IR spectrum of DAPhenCN at 25ºC.

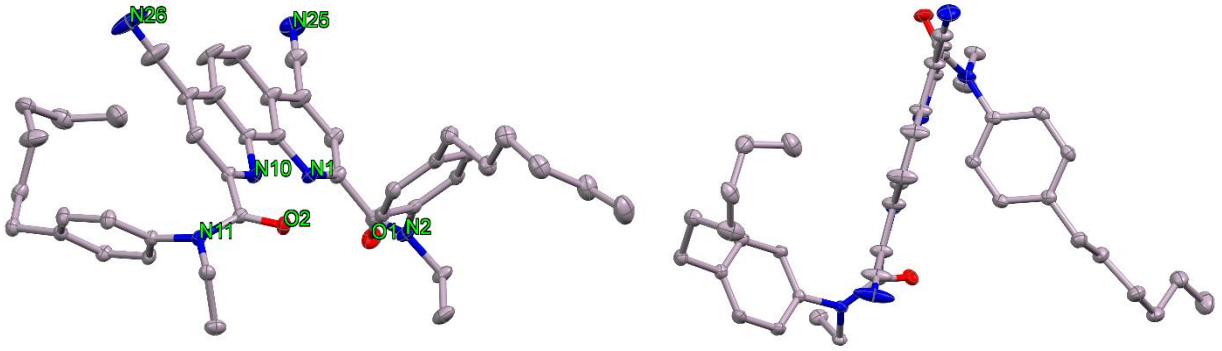

Figure S4. General view of the DAPhenCN in two projections. Hydrogen atoms are omitted, and other atoms are shown as thermal ellipsoids at a 50% probability level. Labels are given only for heteroatoms.

As follows from the diffraction X-ray data, the carboxyl groups of the **DAPhenCN** are on the opposite side of coordination site of the phenanthroline core. The length of the C=O bonds is 1.231(2)Å for C=O(1) and 1.219(2)Å for C=O(2). The crystal packing of **DAPhenCN** is dominated by parallel-displaced stacking interactions between the phenanthroline cores with the interplane angle of 0° and the intercentroid and shift distances of 4.034Å and 3.447Å, which produce infinite stacks along the crystallographic axis *c* (Figure S5, Table S1).

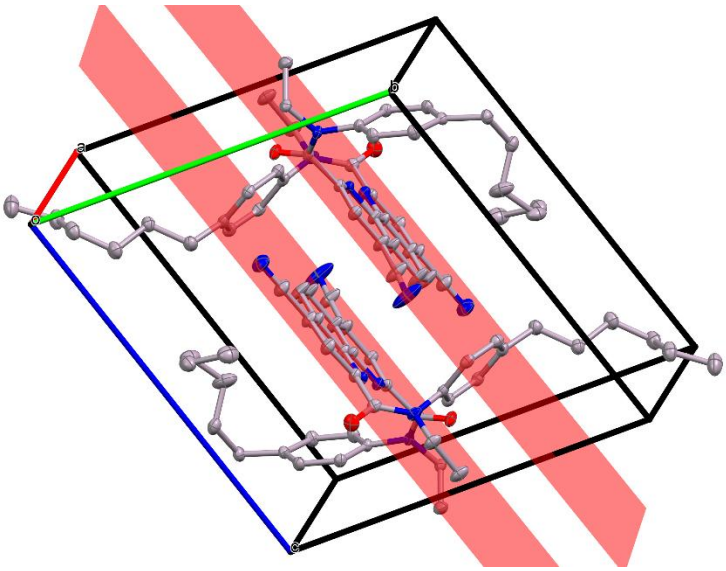

Figure S5. A fragment of the crystal packing in **DAPhenCN**, illustrating the formation of infinite stacks along the crystallographic axis *c*. Hydrogen atoms are omitted, other atoms are shown as thermal ellipsoids at a 50% probability level.

Table S1. Crystal data and structure refinement for **DAPhenCN**.

CCDC	2465953
Empirical formula	$C_{44}H_{48}N_6O_2$
Formula weight	692.88
Temperature/K	100
Crystal system	Triclinic
Space group	*P*-1
a/Å	11.3072(3)
b/Å	12.5366(4)
c/Å	15.2623(4)
α/°	73.418(1)
β/°	68.707(1)
γ/°	78.414(1)

Volume/Å^3	1920.49(10)
Z	2
ρ_{calc}, g/cm^3	1.198
μ/mm^{-1}	0.075
F(000)	740
Crystal size/mm^3	0.06 × 0.20 × 0.25
Radiation	Mo$K\alpha$ (λ = 0.71073)
2Θ range for data collection/°	2.443 to 30.638
Reflections collected	30820
Independent reflections	11758 [R_{int} = 0.0398, R_{sigma} = 0.0497]
Observed reflections with $I>2\sigma(I)$	8207
Data / restraints / parameters	11758 / 2 / 501
Goodness-of-fit on F^2	1.032
Final R indexes [$I>=2\sigma(I)$]	R_1 = 0.0515, wR_2 = 0.1197
Final R indexes [all data]	R_1 = 0.0814, wR_2 = 0.1364
T_{min} / T_{max}	0.972 / 0.981
Largest diff. peak / hole / eÅ^{-3}	0.379 / -0.386

Caution! *^{241}Am and ^{244}Cm, as well as all components of HLW are strongly radioactive and can pose serious health threats; all radioactive experiments were performed in specialized radiological facilities.*

Solvent extraction procedure

Solvent extraction experiments were carried out using 0.5 mL of an organic solution of the ligand in F-3 and 0.5 mL of an aqueous phase containing nitric acid along with radionuclides. The two phases were mixed in a 1.5 mL polypropylene vial using a vortex shaker for 30 minutes at 25 ± 1 °C. After mixing, the samples were centrifuged (5 min, 6000 rpm), and aliquots of aqueous phases were collected for radionuclide analysis. The content of ^{241}Am (Eα = 5637 keV) and ^{244}Cm (Eα = 5901 keV) were determined using alpha-spectrometry (Model 7401 with Si detectors, Canberra Ind.). The content of ^{241}Am and ^{244}Cm in the organic phase was estimated by the difference between the initial and equilibrium aqueous phase concentrations. Distribution ratios (D) were calculated as the ratio of the radionuclide content in the organic phase to that in the

aqueous phase. Separation factors (SF) were calculated as the ratio of distribution ratios for the two radionuclides.

During counter-current tests sample preparation was performed in heavy shielded five-section glove boxes PSB-02 and PSB-03 at the Radiochemical Analysis Laboratory of the Experimental Research Department. Alpha-emitting radionuclides (Pu, Am, Cm isotopes) were analyzed using an alpha spectrometer Canberra Model 7401. Gamma-spectrometric studies were conducted with a Canberra gamma spectrometer equipped with a cooled HPGe-detector.

Rare earth element (REE) concentrations were determined by ICP-OES using a Varian 725 spectrometer. The measurement error did not exceed 10%.

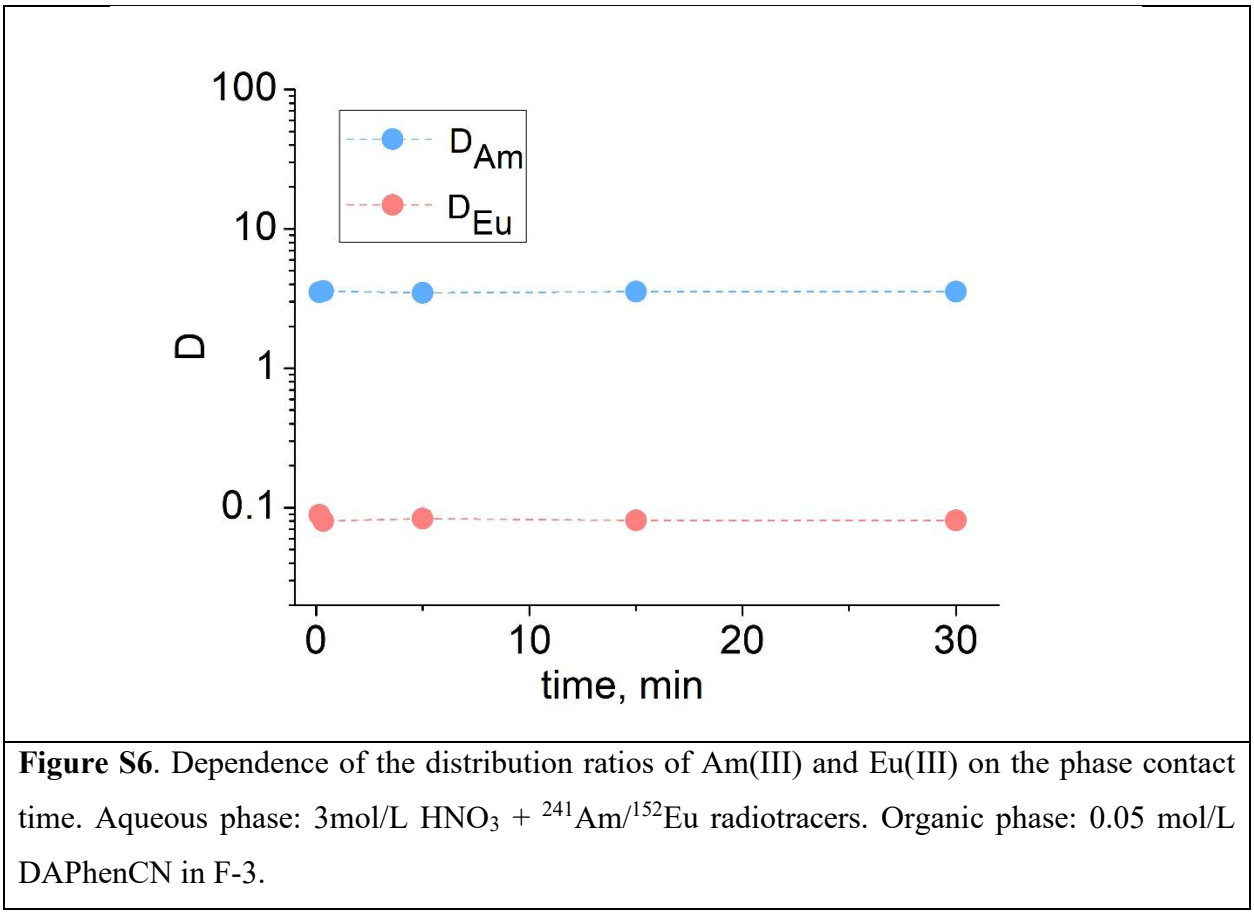

Figure S6. Dependence of the distribution ratios of Am(III) and Eu(III) on the phase contact time. Aqueous phase: 3mol/L HNO_3 + $^{241}Am/^{152}Eu$ radiotracers. Organic phase: 0.05 mol/L DAPhenCN in F-3.

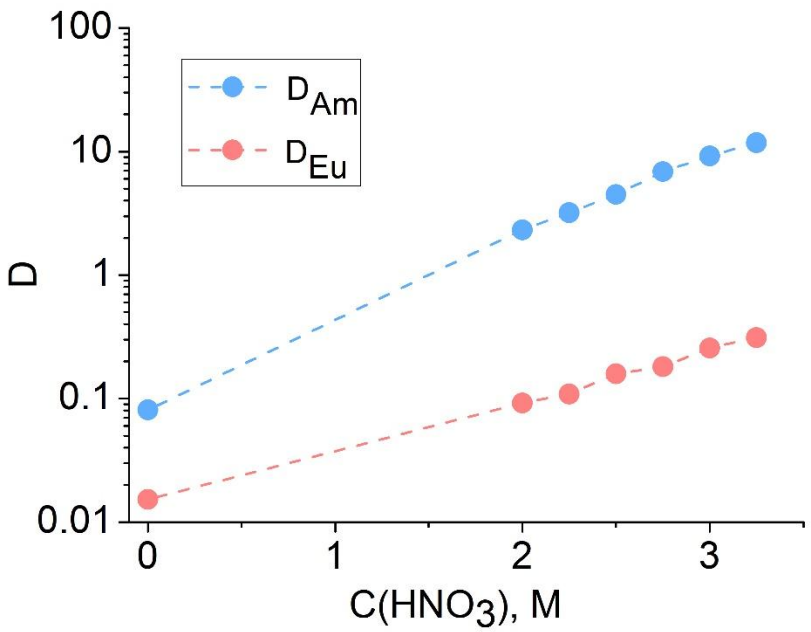

Figure S7. Effect of nitric acid concentration on the extraction of Am(III) and Eu(III) in the presence of NH_4NO_3. Aqueous phase: 0-3.25 mol/L HNO_3 + 3 mol/L NH_4NO_3 + $^{241}Am/^{152}Eu$ radiotracers. Organic phase: 0.05 mol/L DAPhenCN in F-3. Contact time: 30 min.

Irradiation procedure

γ-irradiation of organic phases was performed using "GAMMA400" (Moscow State University) of cesium-137 gamma-source with dose rate of up to 1.8 Gy min^{-1}. Concentration of ligands was 0.05 M. Irradiation was carried out in glass tubes. The resulting dose (≈200 kGy) was accumulated over 77 days in the presence of a 3 mol/L nitric acid solution."

Electron beam irradiation was carried out on the ILU-14 accelerator produced by the Budker Institute of Nuclear Physics of the Siberian Branch Russian Academy of Sciences in electronic mode. The electron energy was 7.6 MeV, and the dose rate was 20 kGy/min. Dosimetric monitoring was carried out using films of a standard sample of absorbed photon and electron radiation doses (SSAD(Ph) 5/50; VNIIFTRI).

In both cases irradiated organic phases were taken for solvent extraction experiments to assess the value of D(Am) according to solvent extraction experiment

In this regard, the properties of the synthesized extractant were studied under gamma and electron irradiation, during prolonged contact with americium-241 (alpha radiation), and during extended contact with aqueous nitric acid solutions.

To investigate radiolytic stability, systems consisting of "0.05 mol/L Phen-CN in diluent F-3 – 3 mol/L nitric acid" were studied. These biphasic systems were prepared in borosilicate glass test tubes. The volume ratio of the contacting phases was 3 mL to 3 mL. Each phase was prepared

in duplicate to conduct parallel experiments for the assessment of radiolytic and hydrolytic stability. Prior to the experiments, the phases were brought into contact and thoroughly mixed to establish phase equilibrium in the systems.

To assess the stability of the organic phase under internal alpha irradiation, the following experiments were performed. First, the organic phase "0.05 mol/L Phen-CN in F-3" was saturated with an aqueous nitric acid solution of americium-241 nitrate at an initial Am-241 concentration of 1.5 g/L. The nitric acid concentration in the aqueous phase was 4.5 mol/L. Under these conditions, the distribution ratio in the extraction system is approximately 10, resulting in the transfer of about 91% of the initial americium into the organic phase. Saturation of 4 mL of the organic phase was carried out using an equivalent volume of the aqueous phase. Sample of the saturated organic phase was collected after 33 days. Due to the high americium content in the system, its concentration was measured spectrophotometrically (using a Shimadzu PC 3100 spectrophotometer, Japan) at a wavelength of 503 nm. After sampling the organic phase, back-extraction of americium was carried out using 0.05 mol/L nitric acid, followed by extraction from 3 mol/L nitric acid.

To assess hydrolytic stability, the samples were stored in the dark to prevent possible photochemical reactions. Sampling was conducted in parallel with the collection of aliquots during gamma irradiation (which had the longest duration under our experimental conditions). Irradiation to a dose of 100 kGy required 28 days.

X-ray crystallography

Table S2. Crystal data and structure refinement for Ce_DAPhenCN.

CCDC	2452985
Empirical formula	$C_{89}H_{99.5}Ce_2N_{19.5}O_{26}$
Formula weight	2138.61
Temperature/K	100

Crystal system	monoclinic
Space group	C2/c
a/Å	21.609(2)
b/Å	25.231(2)
c/Å	36.940(4)
α/°	90
β/°	90.092(3)
γ/°	90
Volume/Å^3	20140(3)
Z	8
ρ_{calc}g/cm^3	1.411
μ/mm^{-1}	0.974
F(000)	8752
Crystal size/mm^3	0.15 × 0.1 × 0.04
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.308 to 50.188
Reflections collected	68746
Independent reflections	17836 [R_{int} = 0.1039, R_{sigma} = 0.1068]
Data/restraints/parameters	17836/74/1240
Goodness-of-fit on F^2	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0720, wR_2 = 0.1704
Final R indexes [all data]	R_1 = 0.1027, wR_2 = 0.1879
Largest diff. peak/hole / e Å^{-3}	1.11/-2.19

Experimental

Crystallographic data for Ce_DAPhenCN were collected on a Bruker D8 Venture diffractometer at 100 K in *ω*-scan mode with monochromatized MoKα radiation (λ = 0.71073 Å). For cell refinement and data reduction the software SAINT (V8.38A, Bruker) was used. Absorption correction based on measurements of equivalent reflections (multi-scan) was applied (SADABS-2016/2, Bruker 2016/2). The structure was solved by direct methods (SHELXT2014)[3]

and refined by full matrix least-squares on F^2 (SHELXL2014)[4] with anisotropic displacement parameters for all non-hydrogen atoms. The hydrogen atoms were placed geometrically and refined within the riding model. The twinning in the structure was refined using a twin law resulting in twin individual mass fractions 0.8106(9) / 0.1894(9). The PLATON SQUEEZE[5] procedure was used to account the contribution of highly disordered solvent molecules (probably acetonitrile) to the structure factors. The molecular graphics were generated using Olex2 1.5[6].

References

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