Supplementary Information

Extraction and Complexation of Trivalent Americium and Lanthanides by an Asymmetric Picolinic Acid-derived Tridentate N,O-hybrid ligand

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Content

1. EXPERIMENTAL SECTION

1.1 Chemicals and materials

^{241}Am and ^{152,154}Eu as radioactive tracers used in solvent extraction experiments were provided by the Institute of Nuclear and New Energy Technology (INET), Tsinghua University. The asymmetric tridentate ligand DOAPA(colorless oil, 45.01%) was synthesized according to published procedures with a purity over 99%[1]. ^{1}H NMR (400 Hz, CD_3OD) δ 0.85-1.71 (m, 30H, ($-CH_2(CH_2)_5CH_3)_2$), δ 3.29 (m, 2H, 5-N-CH_2), δ 3.51 (m, 2H, 4-N-CH_2), δ 7.74 (dd, 1H, 1-Pyridine-H), δ 8.09 (t, 1H, 2-Pyridine-H), δ 8.20 (dd, 1H, 3-Pyridine-H) (**Figure S7**). ^{13}C NMR (400 Hz, CD_3OD) δ 31.61-22.23, 13.03, 13.01 (16C, -N-$((CH_2)_7CH_3)_2$), 125,25 (1C, 4-Pyridine-C), 125.86 (1C, 2-Pyridine-C), 138.61 (1C, 3-Pyridine-C), 147.15 (1C, 6-Pyridine-C), 154.61 (1C, 5-Pyridine-C), 165.92 (1C, N=CO-Pyridine), 168.61 (1C, Pyridine-COOH) (**Figure S8**). The rare earth nitrates $Ln(NO_3)_3\cdot 6H_2O$ (Ln = La, Nd, Eu), *n*-dodecane, *n*-hexane, CH_3OH and CD_3OD were purchased from Aladdin Reagent Company. Milli-Q water was used throughout the experiments. Tetramethylsilane (TMS) was the internal standard substance for ^{1}H NMR and ^{13}C NMR. Unless specifically noted, all the other reagents in this work were of analytical grade or higher and used without further purification. ***CAUTION:*** *Both ^{241}Am and ^{152,154}Eu pose serious health threats owing to their intense radioactivity. All the relevant experiments thus must be strictly performed in special radiological facilities dedicated to studies on radioactive elements*.

1.2 Solvent Extraction

The aqueous solutions with desired HNO_3 concentrations (0.01-1.0 M) were spiked with the radiotracers ^{241}Am(III) and ^{152,154}Eu(III). The organic solutions were DOAPA of different concentrations in *n*-dodecane. For the batch extraction experiments, each 1.0 mL of aqueous phase was contacted with equal volume of organic phase, and the mixture was vigorously agitated in a 5 mL stoppered glass tube at a specific temperature. After centrifugation for phase separation, 100 μL of each phase was sampled and mixed with 10 mL scintillation cocktail (Hisafe 3) in a 20 mL plastic bottle. The activities of ^{241}Am(III) and ^{152,154}Eu(III) in both phases were measured by the ultralow-background liquid scintillation spectrometer (Quantulus 1220, PerkinElmer). The counting rates (radioactivity counts per unit volume) of ^{241}Am and ^{152,154}Eu can be determined simultaneously through a previously reported method[2, 3]. The distribution

ratio (*D*) was defined as the ratio of the counting rates (cpm) in the organic phase to those in the aqueous phase. The separation factor (*SF*) for Am(III) over Eu(III) was calculated as the ratio of D_{Am} to D_{Eu}.

1.3 Spectrophotometry

The absorption spectra were collected on a Cary 6000i UV-vis-NIR spectrophotometer (Agilent Inc.) at 298.0 ± 0.1 K. Typically, 2.5 mL of 0.05 M HNO_3 solution containing 0.1 mM Am(III) or 5.0 mM Nd(III) was added in a 10 mm quartz cuvette for the determination of initial absorption spectra in the aqueous phase. Subsequently, the aqueous solution was transferred into a 10 mL stoppered glass tube and mixed with 2.5 mL 0.05 M DOAPA/*n*-dodecane organic solution for 30 min. After phase separation, 2.0 mL of aqueous solution or organic solution was sampled and added in a 10 mm quartz cuvette for the measurement of final absorption spectra in both phases. The absorption bands of Am(III) and Nd(III) were obtained in the wavelength ranges of 490-550 nm and 550-610 nm, respectively.

Luminescence emission spectra of Eu(III)-DOAPA extracted complexes in the organic phase were recorded on an Edinburgh FLS-1000 spectrophotometer equipped with a 450 W ozone-free xenon arc lamp. Specifically, 2.5 mL of 5.0 mM Eu(III)/HNO_3 solution with acidities from 0.05 - 0.5 M was mixed with equivalent 0.01-0.2 M DOAPA/*n*-dodecane organic solution for 30 min. Afterwards, 2.0 mL of the organic phase was separated and added into a 10 mm quartz cuvette. The luminescence emission spectra were collected ranging from 550 to 720 nm with an interval of 0.5 nm (2 nm bandwidth) by excitation at 394 nm (3 nm bandwidth). The lifetime decay curves were collected in the emission wavelength of 617 nm (1-2 nm bandwidth) by excitation at 394 nm (2-4 nm bandwidth).

1.4 NMR Titration

For NMR (Nuclear Magnetic Resonance) titration, the stock solutions of DOAPA and $La(NO_3)_3$ were prepared by dissolving the ligand or rare earth nitrate in CD_3OD for ^1H NMR and ^{13}C NMR spectra determination. An initial 0.5 mL of DOAPA solution was added into the NMR tube and the NMR spectra were collected on a Bruker Avance III Model 600 MHz instrument. Each 0.5 equivalent La(III)-containing solution was then added into the above-mentioned NMR tube and mixed for 3 min for subsequent measurement. The titration was

stopped until no obvious changes in peak shape could be observed or new signals appeared in the NMR spectra.

1.5 Mass Spectra Analysis

ESI-MS spectrum (Electro Spray Ionization-Mass Spectroscopy) was obtained with Bruker Amazon SL spectrometer (Bruker Inc., Switzerland). The sample for mass spectrum collection was prepared by solvent extraction. Specifically, 10 mL of 0.05 M DOAPA/*n*-hexane solution and equal volume 5.0 mM Eu(III)/HNO_3 solution were mixed for 30 min to obtain an Eu(III)-incorporated organic phase. Subsequently, the loaded organic solution was concentrated through rotary evaporation and diluted with CH_3OH and CH_3CN for further measurement. The mass spectrum was acquired in negative mode over a mass-to-charge ratio (m/z) in the range of 1200-1600. The simulated spectrum of the extracted complex was obtained through a Molecular-Weight-Calculator software.

1.6 Computational Details

All the theoretical calculations were performed with the density functional theory (DFT) method at the B3LYP level using the Gaussian 16 package. Geometry optimizations without symmetry restrictions were carried out independently in the gas phase. In consideration of the scalar quasi-relativistic effects, 60 and 52 core electrons were substituted by the chosen quasi-relativistic effective core potentials (RECPs) for Am and Eu, respectively[4, 5]. In addition, the affiliated segmented contraction scheme ECP60MWB-SEG[5, 6] and ECP52MWB-SEG[7] valence basis sets were applied for Am and Eu atoms, respectively. The standard Pople basis set 6-31G(d) was used for the optimization calculations of H, C, N and O atoms. Meanwhile, the natural atomic charges as well as Wiberg bond indices (WBI)[8] were analyzed based on natural bond orbital (NBO)[9, 10] theory. The Multiwfn 3.4 programs and Visual Molecular Dynamics (VMD) software[11] were subsequently utilized for the molecular electrostatic potential (ESP) map calculation.

2. Supplementary Figures (Figure S1 to Figure S8)

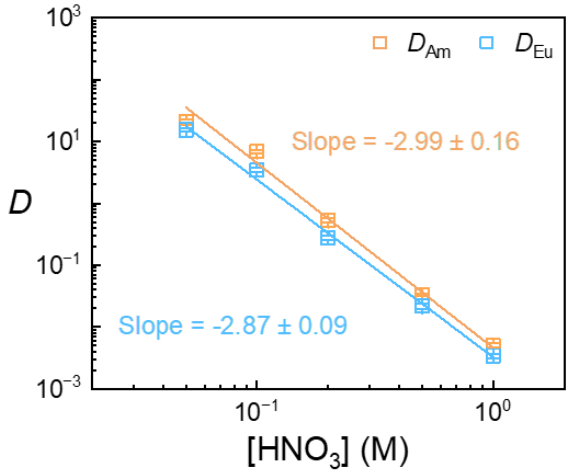

Figure S1. Linear fitting of *D* values at different concentrations of HNO_3.

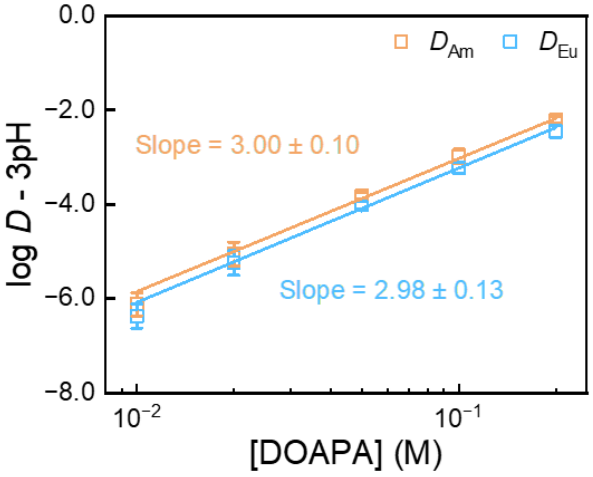

Figure S2. Linear fitting of log D - 3pH values at different concentrations of DOAPA.

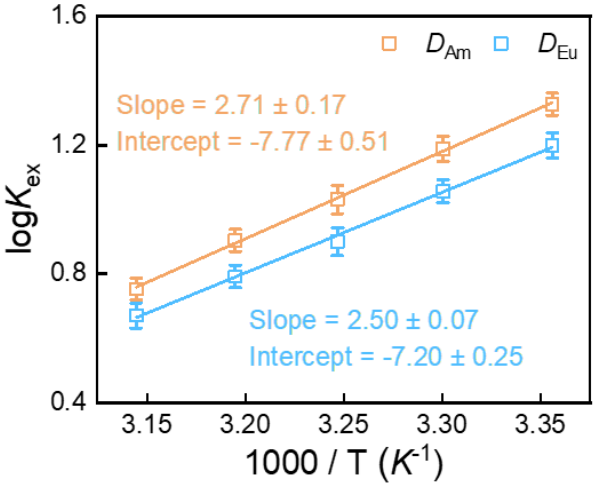

Figure S3. Linear fitting of log K_{ex} values at different temperatures.

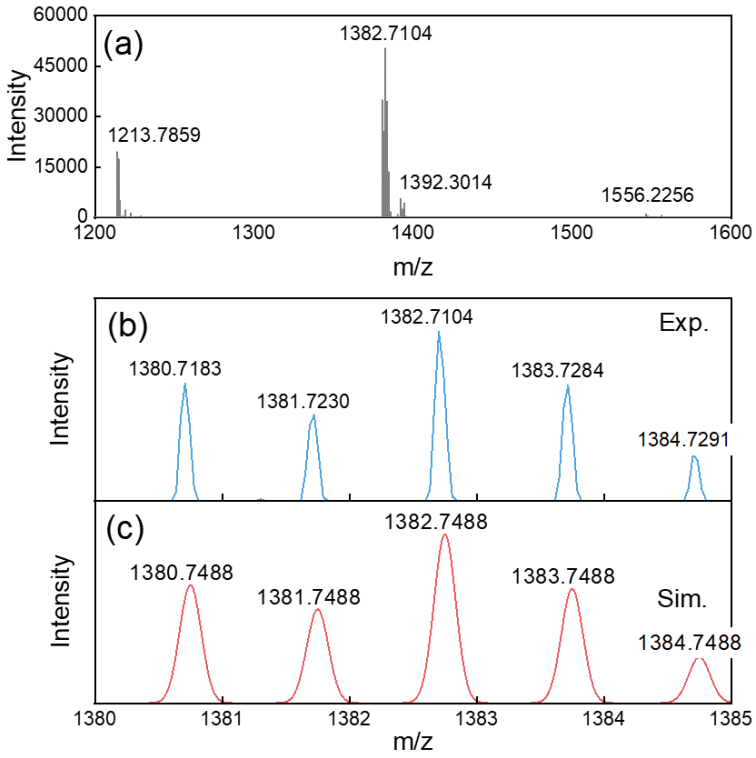

Figure S4. (a) The complete and (b) the partially enlarged negative mode mass spectrum of the Eu(III)-DOAPA extracted complex. (c) Simulated isotope distribution pattern of $[Eu^{3+}\text{-}(L^{-})_3\text{-}NO_3^{-}]^{-}$ complex, L represents dissociated DOAPA.

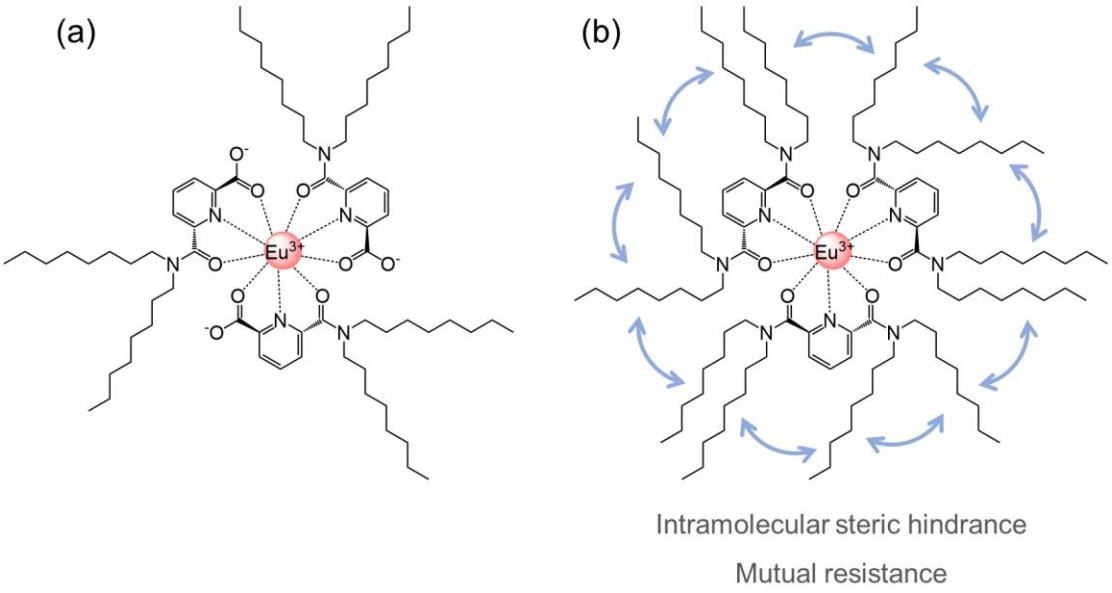

Figure S5. Diagram of supposed chemical structures of (a) Eu(III)-DOAPA complex and (b) Eu(III)-TOPDA complex.

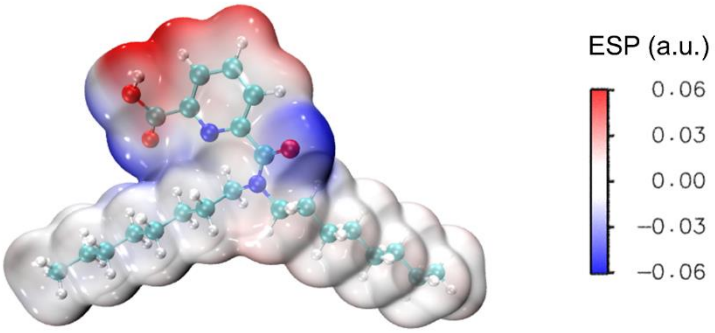

Figure S6. The map of ESP and the natural charges on N and O atoms of DOAPA at the B3LYP/6-311G(d) level of theory.

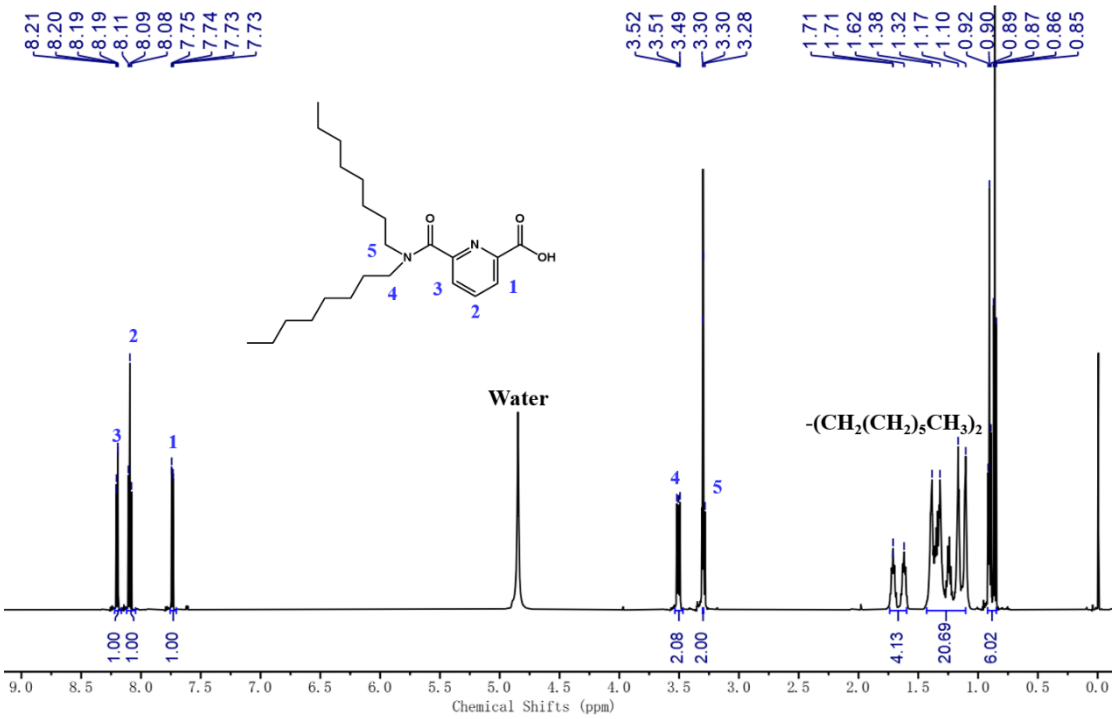

Figure S7. ^{1}H NMR spectrum of **DOAPA**.

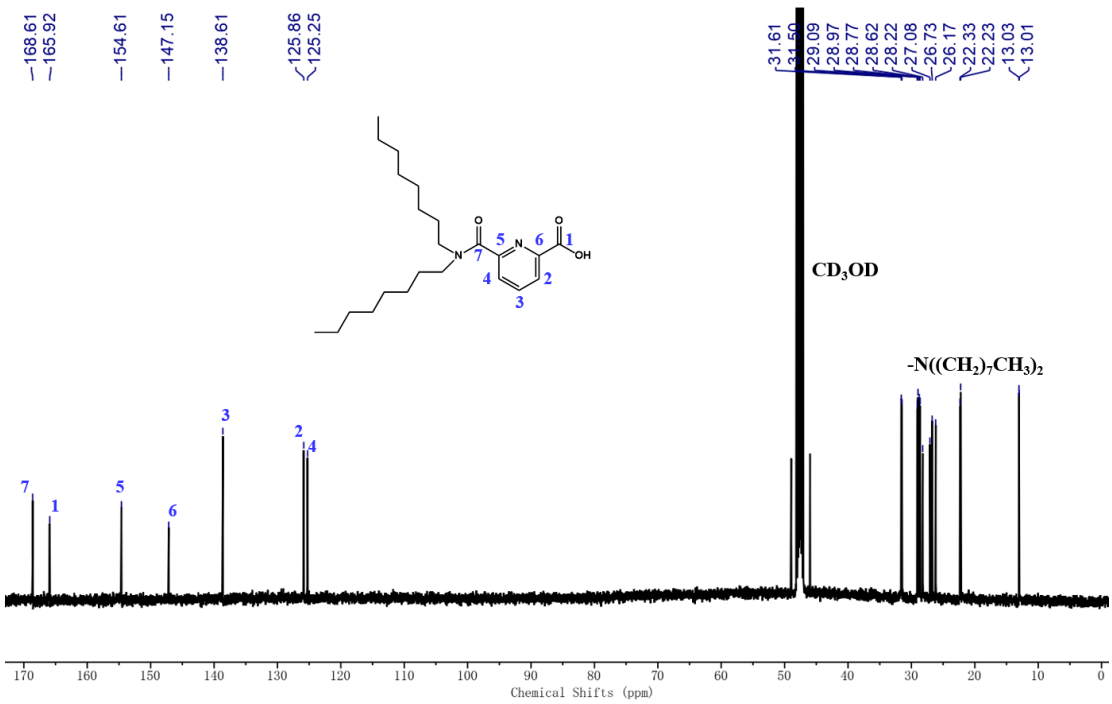

Figure S8. ^{13}C NMR spectrum of **DOAPA**.

3. Supplementary Tables (Table S1 to Table S4)

Table S1. Extraction equilibrium constants (log K_{ex}) of Am(III) and Eu(III) at different temperatures.

	logK_{ex}				
Temperature(K)	298	303	308	313	318
Am(III)	1.38	1.23	1.08	0.94	0.81
Eu(III)	1.26	1.12	0.98	0.85	0.73

Table S2. Calculated bond lengths (Å), Wiberg bond indices (WBI) and natural charges (Q) of the AmL_3 and EuL_3 complexes.

Bond parameters	Bonds	Complexes	
		AmL_3	EuL_3
Bond length (Å)	M-$N_{pyrindine}$	2.667	2.663
	M-$O_{carboxylate}$	2.533	2.545
	M-O_{amide}	2.369	2.381
WBI	M-$N_{pyrindine}$	0.231	0.228
	M-$O_{carboxylate}$	0.289	0.282
	M-O_{amide}	0.368	0.360

Table S3. Coordinates of the optimized Am(III) complex with DOAPA.

C	5.62105300	-2.86408200	1.57154800
N	4.66750400	-3.57517300	2.17815500
C	4.91554500	-4.82190700	2.60177900
C	6.14448200	-5.44060800	2.36450100
C	7.14445300	-4.70951400	1.71301900
C	6.89084700	-3.39770600	1.32561800
C	5.23172500	-1.45290600	1.12415200
O	6.07834700	-0.78373800	0.53663700
O	4.01518300	-1.13307900	1.41139200
C	3.68982200	-5.48527000	3.19148500
O	2.59971200	-5.24308100	2.63959800
N	3.80950500	-6.33315000	4.24447000
H	6.31338500	-6.47223300	2.65152500
H	8.10848700	-5.16961700	1.51248000
H	7.62284800	-2.77483200	0.82427300
C	1.07187300	0.08505900	0.29756100
N	1.49020000	-1.14723600	0.00586400
C	1.91093800	-1.45118600	-1.23119600
C	1.99971300	-0.47283200	-2.22387400
C	1.57189200	0.82582800	-1.92336100
C	1.07084500	1.10708800	-0.65850700
C	0.62782000	0.32822800	1.74213200
O	0.02494300	1.36793900	1.99008300
O	0.94683200	-0.62601800	2.55409800
C	2.36908200	-2.89019400	-1.32433500
O	2.75941100	-3.44062100	-0.27661200
N	2.37665100	-3.57850500	-2.49712200
H	2.42469600	-0.69245700	-3.19549600

H	1.64321400	1.60514300	-2.67711100
H	0.71297800	2.08798000	-0.36744400
Am	2.25847800	-2.51974800	2.13296300
C	0.63684200	-2.82352300	5.10225400
N	0.36739000	-3.23328700	3.86081600
C	-0.90061400	-3.41990200	3.46727900
C	-1.97415000	-3.09060300	4.29705700
C	-1.69994300	-2.63983400	5.59399100
C	-0.38041600	-2.54376700	6.02205500
C	2.12036700	-2.68333800	5.44874500
O	2.43021900	-2.69431900	6.64040900
O	2.89399600	-2.60550400	4.42140200
C	-0.97859800	-3.86169600	2.02355100
O	-0.07816200	-3.47557100	1.25655400
N	-2.00995000	-4.62106000	1.56178500
H	-2.99628100	-3.14340300	3.93899800
H	-2.51740900	-2.36412200	6.25439900
H	-0.10645000	-2.22666100	7.02175000
C	1.63255500	-3.21023600	-3.70939100
C	2.52985300	-2.91873700	-4.92168500
C	1.75123500	-2.46972100	-6.17023500
C	0.83817100	-3.54125700	-6.78618000
C	0.17581700	-3.08600300	-8.09373900
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C	4.47938800	-4.96305300	-2.45780000
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C	9.22782500	-9.34511900	-2.17840400
C	10.75929800	-9.38821500	-2.14558200
H	2.55859500	-5.47648300	-3.32885000
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H	6.76641000	-8.44581700	-3.14495400
H	6.73037200	-8.37128300	-1.38989000
H	9.02913100	-7.34219300	-1.38736900
H	9.06409300	-7.41605300	-3.14188500
H	8.86365500	-9.92157900	-3.04081500
H	8.82787600	-9.84873800	-1.28657200
H	11.15274600	-8.84939100	-1.27465000
H	11.18812800	-8.92329800	-3.04191600
H	11.13023400	-10.41834900	-2.09501500

Table S4. Coordinates of the optimized Eu(III) complex with DOAPA.

C	5.46581800	-2.26518300	2.42705000
N	4.45818900	-3.17617800	2.34778500
C	4.74230800	-4.42230100	2.91894700
C	6.13799600	-4.93470800	2.91051700
C	7.17198000	-4.00139400	2.89266600
C	6.86302100	-2.65310900	2.72350400
C	5.06314000	-0.94342100	2.11420500
O	5.85209700	0.09812200	2.03909400
O	3.84982500	-0.62784800	1.83619500
C	3.57378900	-5.11350800	3.41879500
O	2.44439000	-4.81192800	2.91524800
N	3.67807600	-6.12647800	4.34565000
H	6.32582600	-6.00128400	2.84809100
H	8.20845000	-4.32352600	2.94080400
H	7.63328700	-1.89053000	2.67128200
C	1.12865300	0.27368800	0.29073300
N	1.51403100	-0.97705400	0.03422400
C	1.95628800	-1.32388000	-1.18584300
C	2.09686800	-0.37227400	-2.19804400

C	1.70268000	0.94610800	-1.93540300
C	1.18565000	1.27290400	-0.68858600
C	0.65432800	0.56430400	1.72058400
O	0.14136400	1.66001400	1.93093300
O	0.85468700	-0.40852500	2.54037400
C	2.36944800	-2.77881700	-1.21906500
O	2.65391200	-3.31249400	-0.12797100
N	2.45795900	-3.49831000	-2.36671800
H	2.53308900	-0.62500900	-3.15625300
H	1.81208400	1.70419400	-2.70622000
H	0.85457100	2.27078300	-0.42485500
Eu	2.00878900	-2.42113500	2.18127200
C	0.24248100	-2.53158000	5.08839500
N	0.12739900	-3.04605300	3.81072400
C	-1.07808700	-3.42728300	3.36639200
C	-2.24582800	-3.27823100	4.11144400
C	-2.13552200	-2.74081400	5.43099600
C	-0.90543500	-2.38703500	5.92241400
C	1.55110800	-2.11899900	5.42226900
O	1.92272300	-1.59062100	6.56557800
O	2.55844600	-2.18250300	4.61580200
C	-1.00998300	-3.88296400	1.92878400
O	-0.09421800	-3.40997100	1.21390400
N	-1.91152600	-4.73701900	1.37928300
H	-3.21983400	-3.48933100	3.68844800
H	-3.03018200	-2.60227700	6.03089600
H	-0.79226200	-1.96430600	6.91646500
C	1.82282700	-3.14856700	-3.64491800
C	2.82197000	-2.89037300	-4.78256200
C	2.15398200	-2.46541100	-6.10184600
C	1.28038000	-3.54249800	-6.76358100
C	0.72397500	-3.10990200	-8.12703800
C	-0.15055400	-4.17714600	-8.79798000
C	-0.70361500	-3.74611600	-10.16289400
C	-1.57368500	-4.81830200	-10.82732000
C	-1.87997400	-4.88947800	-0.08804200
C	-2.53898500	-3.70829400	-0.81257000
C	-2.50502000	-3.87202400	-2.33772900
C	-3.16145700	-2.70434800	-3.08654000
C	-3.11397800	-2.85215200	-4.61317100
C	-3.77349800	-1.68700400	-5.36257700
C	-3.72081700	-1.82949500	-6.88950000
C	-4.38545900	-0.66330300	-7.62882200
C	-2.72181500	-5.71340800	2.12468000
C	-2.15236800	-7.14064400	2.07077200
C	-3.06000500	-8.14548300	2.79352100
C	-2.50783500	-9.57727800	2.78257200
C	-3.41348600	-10.58461900	3.50347700
C	-2.86497300	-12.01750300	3.49201200
C	-3.76920300	-13.02584200	4.21330800
C	-3.21425400	-14.45413100	4.19766600
C	2.49412400	-6.95979000	4.58501200
C	1.54483400	-6.44304900	5.67861200
C	0.29691600	-7.32172300	5.83360100
C	-0.64754500	-6.82803500	6.93884800
C	-1.89279000	-7.70554300	7.12119700
C	-2.83186600	-7.21501000	8.23106800
C	-4.07941900	-8.09004400	8.41116700
C	-5.01228900	-7.59291000	9.52071000
C	4.73301500	-6.12275500	5.36929600
C	4.67047900	-4.94422400	6.36050300
C	5.88769600	-4.87912200	7.29706200
C	6.00428400	-6.04482100	8.29132900
C	7.17822100	-5.89009500	9.26776000

C	7.30375100	-7.04791100	10.26659700
C	8.47610400	-6.89106500	11.24419100
C	8.59408500	-8.05128300	12.23834000
H	1.17971100	-2.28023900	-3.49415800
H	1.15921600	-3.98055100	-3.91083200
H	3.42265900	-3.79460400	-4.95035500
H	3.52877700	-2.11360700	-4.46275500
H	2.94398000	-2.17078900	-6.80559500
H	1.55043000	-1.56137400	-5.93098200
H	0.43979500	-3.80662300	-6.10607900
H	1.87226400	-4.46185600	-6.88753700
H	1.56010900	-2.85178800	-8.79361200
H	0.13868900	-2.18645900	-8.00285200
H	-0.98895400	-4.43126100	-8.13228000
H	0.43283600	-5.10219800	-8.91915300
H	0.13325900	-3.48935600	-10.82785700
H	-1.28885900	-2.82359300	-10.04059100
H	-1.00599800	-5.74202600	-10.99479400
H	-1.95303400	-4.48027200	-11.79833100
H	-2.43856000	-5.07086800	-10.20143200
H	-2.41039400	-5.81400800	-0.33186000
H	-0.84169700	-5.00314700	-0.41248200
H	-2.02351700	-2.78440200	-0.52726700
H	-3.57918600	-3.61211100	-0.47207500
H	-3.00428000	-4.81112200	-2.62092500
H	-1.45959600	-3.97250800	-2.66734000
H	-2.66931400	-1.76514100	-2.79509900
H	-4.20843600	-2.61015100	-2.76349400
H	-3.60311200	-3.79405800	-4.90333700
H	-2.06537500	-2.94391400	-4.93660200
H	-3.28822600	-0.74417000	-5.06931600
H	-4.82265800	-1.59853200	-5.04377500
H	-4.20483900	-2.77228800	-7.18208200
H	-2.67166000	-1.91501700	-7.20906300
H	-4.33039100	-0.79425900	-8.71562300
H	-3.90130400	0.28982700	-7.38270700
H	-5.44454300	-0.57477000	-7.35724400
H	-3.74146800	-5.69427600	1.71794000
H	-2.77828800	-5.40046400	3.16452300
H	-1.15481400	-7.13539900	2.53020300
H	-2.01385300	-7.46149300	1.03015000
H	-4.05705900	-8.13679400	2.32840600
H	-3.20672700	-7.82239000	3.83445800
H	-1.51232000	-9.58428300	3.24975500
H	-2.35849000	-9.90111600	1.74180700
H	-4.41088600	-10.57390100	3.03905700
H	-3.55930700	-10.26002700	4.54433800
H	-1.86761300	-12.02870000	3.95655600
H	-2.71806500	-12.34284300	2.45108900
H	-4.76567500	-13.01495400	3.74899000
H	-3.91539500	-12.70099400	5.25327900
H	-3.88189300	-15.14887700	4.72000300
H	-2.23341100	-14.50369200	4.68664600
H	-3.08994100	-14.82007200	3.17085900
H	2.85144600	-7.96536700	4.84533200
H	1.95403400	-7.03032800	3.63823500
H	1.25197300	-5.41627900	5.43316600
H	2.07509900	-6.40597900	6.63900900
H	0.59790700	-8.35885100	6.04805700
H	-0.24731500	-7.35317900	4.87769800
H	-0.95553200	-5.79648100	6.71646000
H	-0.09607000	-6.78301900	7.88963800
H	-1.58272300	-8.73894600	7.33812500
H	-2.44859900	-7.74923100	6.17189600

H	-3.14112200	-6.18167900	8.01472200
H	-2.27929100	-7.17258300	9.18151000
H	-3.76917800	-9.12217300	8.62887000
H	-4.63148400	-8.13333800	7.46106200
H	-5.36705100	-6.57558600	9.31397800
H	-4.49882100	-7.57208400	10.48993400
H	-5.89241800	-8.23808600	9.62398100
H	5.71487600	-6.10599500	4.88096600
H	4.66037600	-7.08133800	5.89251500
H	3.75024300	-5.00334600	6.95400200
H	4.60369300	-4.01161600	5.78880000
H	5.83422700	-3.93806800	7.86059800
H	6.80688500	-4.81829500	6.69519500
H	6.11611100	-6.99587200	7.75035500
H	5.06674300	-6.12729300	8.86166400
H	7.06677000	-4.94468300	9.81885300
H	8.11480500	-5.79927900	8.69744000
H	7.41645100	-7.99407600	9.71572800
H	6.36708400	-7.13940000	10.83681300
H	8.36319700	-5.94666800	11.79531300
H	9.41220600	-6.79991200	10.67486600
H	7.68612000	-8.14546400	12.84696300
H	9.43937700	-7.90943600	12.92159500
H	8.74284500	-9.00579300	11.71806700
C	2.98297000	-4.87467300	-2.23924500
C	4.50378300	-4.93399400	-2.04774000
C	5.00660000	-6.37514700	-1.88945100
C	6.51746900	-6.45937200	-1.63294400
C	7.03122800	-7.89761900	-1.48465400
C	8.54075000	-7.98495600	-1.22383700
C	9.05581500	-9.42277300	-1.07547400
C	10.56399800	-9.50099400	-0.81543900
H	2.69482100	-5.41076600	-3.14913200
H	2.48564700	-5.35416700	-1.39021900
H	4.76743800	-4.35414400	-1.15699500
H	4.99902100	-4.45690400	-2.90454100
H	4.75638300	-6.95718700	-2.78962800
H	4.47241500	-6.85432800	-1.05609400
H	6.75913500	-5.88958100	-0.72399400
H	7.05495700	-5.96458400	-2.45548900
H	6.78687800	-8.46696700	-2.39404900
H	6.49169900	-8.39262800	-0.66335000
H	8.78607400	-7.41646700	-0.31429400
H	9.08100800	-7.48979400	-2.04459200
H	8.81113700	-9.99029700	-1.98476300
H	8.51650200	-9.91751500	-0.25499500
H	10.83534800	-8.97212900	0.10667700
H	11.13183000	-9.04521200	-1.63604900
H	10.90001500	-10.53940800	-0.71468800

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