# Solvent Extraction of Americium(III) and Europium(III) with Tridentate N,N-dialkyl-1,10-Phenanthroline-2-Amides-Derived Ligands: Extraction, Complexation and Theoretical Study

Shiwei Cao,[†ac] Jieru Wang,[†a] Cunmin Tan,[†abc] Xin Zhang,[b], Guo Hangxu,[ac] Lei Wang,[d] Zhi Qin*[a]

*a. Institute of Modern Physics, Chinese Academy of Sciences, No. 509 Nanchang Rd., 730000, Lanzhou, China.*

*b. School of Nuclear Science and Technology, Lanzhou University, No. 222 Tianshuinan Rd., 730000, Lanzhou, China.*

*c. School of Physical Science and Technology, University of Chinese Academy of Sciences, No. 19A Yuquan Rd., 100049, Beijing. China.*

*d. College of Chemistry, Sichuan University, No. 24 South Section1, Yihuan Road, Chengdu, 610065, P.R. China.*

*† These authors contributed equally to this work.*

** Author for correspondence (E-mail: qinzhi@impcas.ac.cn).*

## Electronic supplement information

### 1. FT-IR

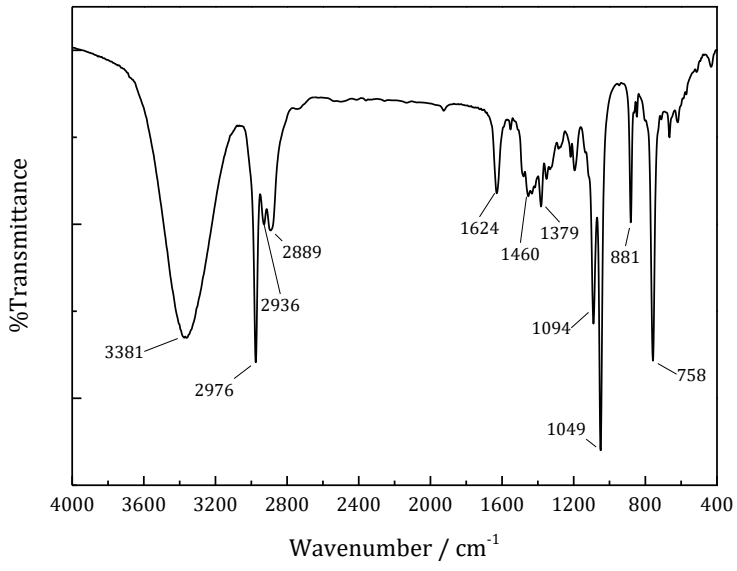


Fig. S1 FT-IR spectrum of C2-PTA

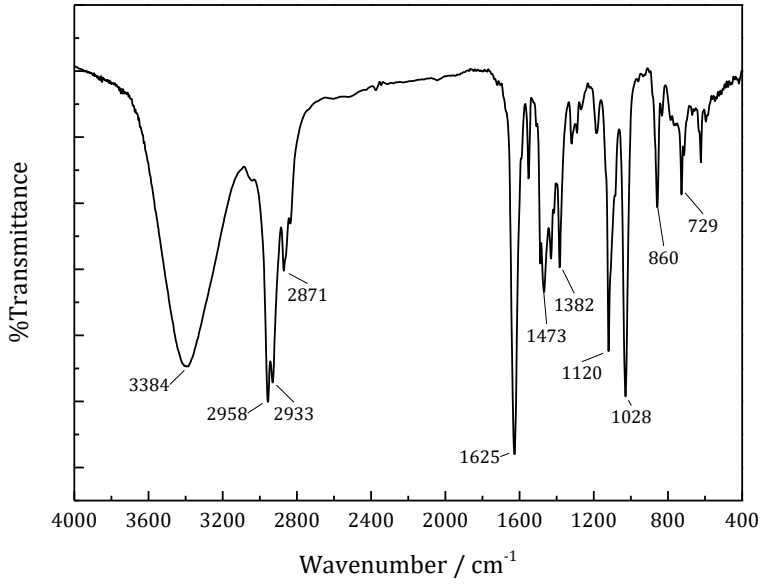


Fig. S2 FT-IR spectrum of C4-PTA

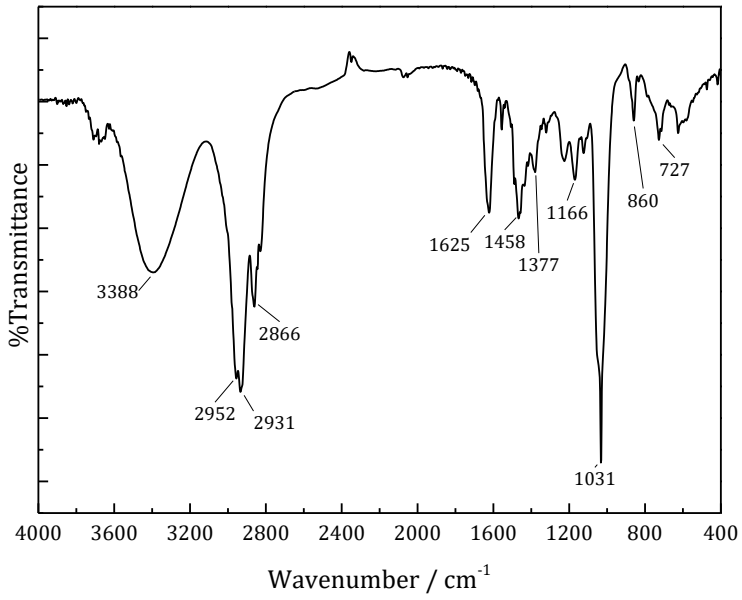


Fig. S3 FT-IR spectrum of C6-PTA

**2. $^{1}$H NMR**

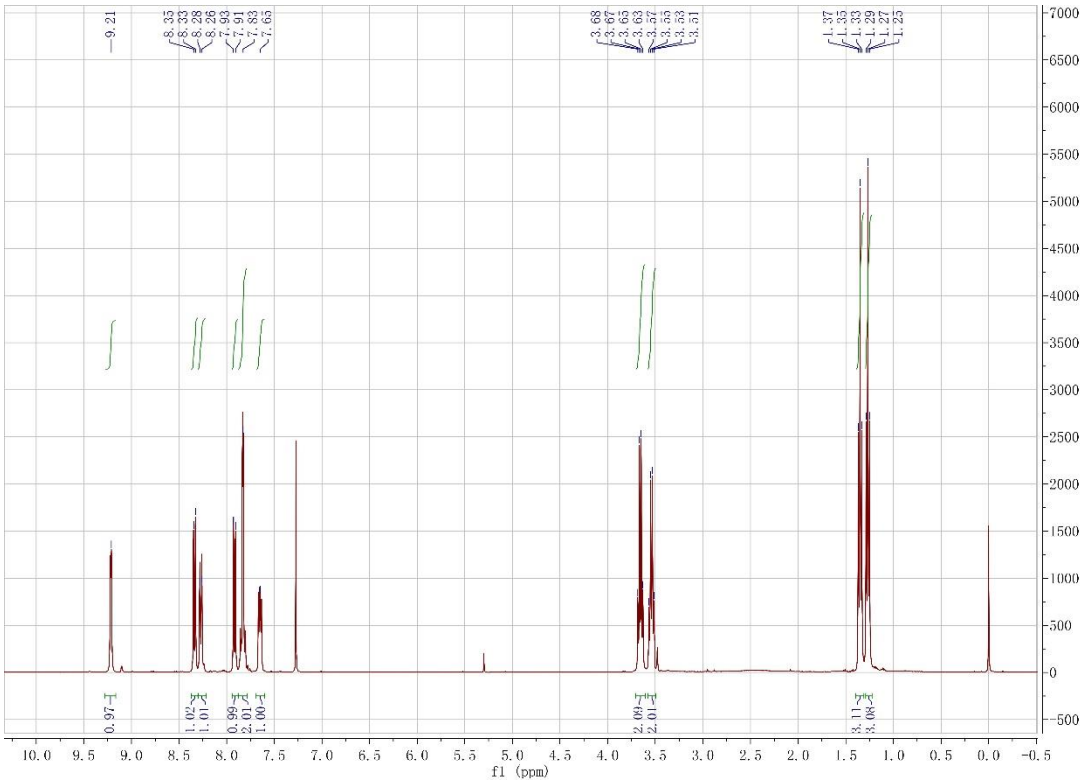


Fig. S4 $^{1}$H NMR spectrum of C2-PTA

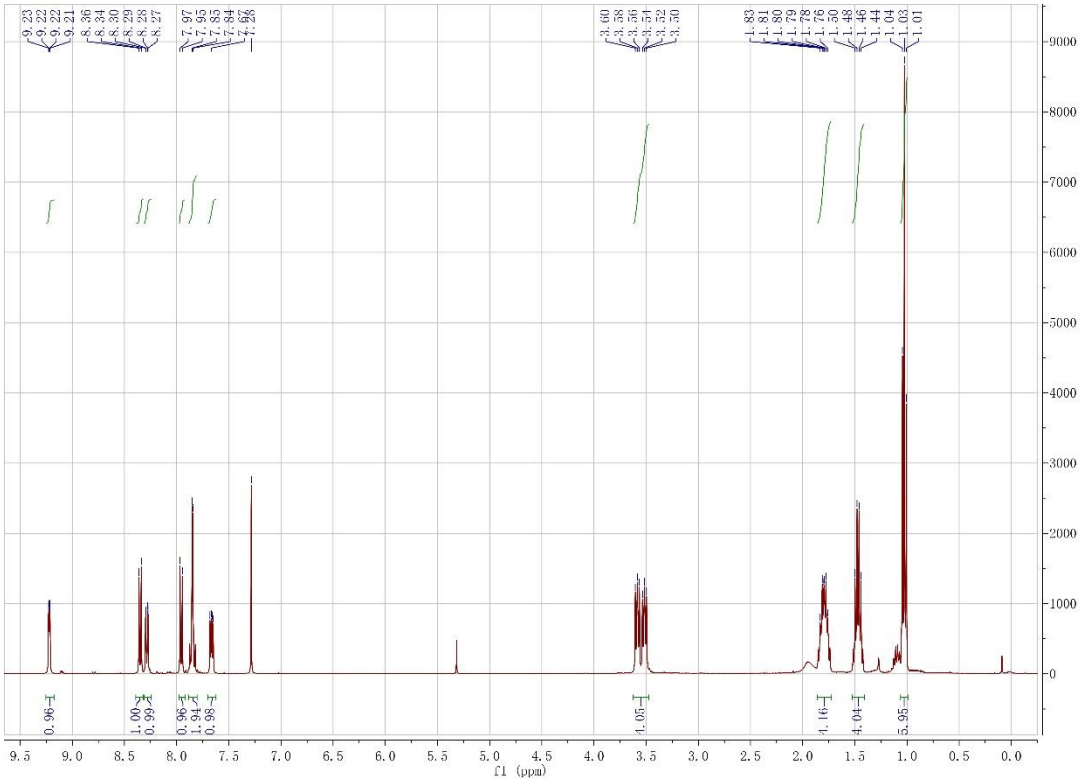


Fig. S5 $^{1}$H NMR spectrum of C4-PTA

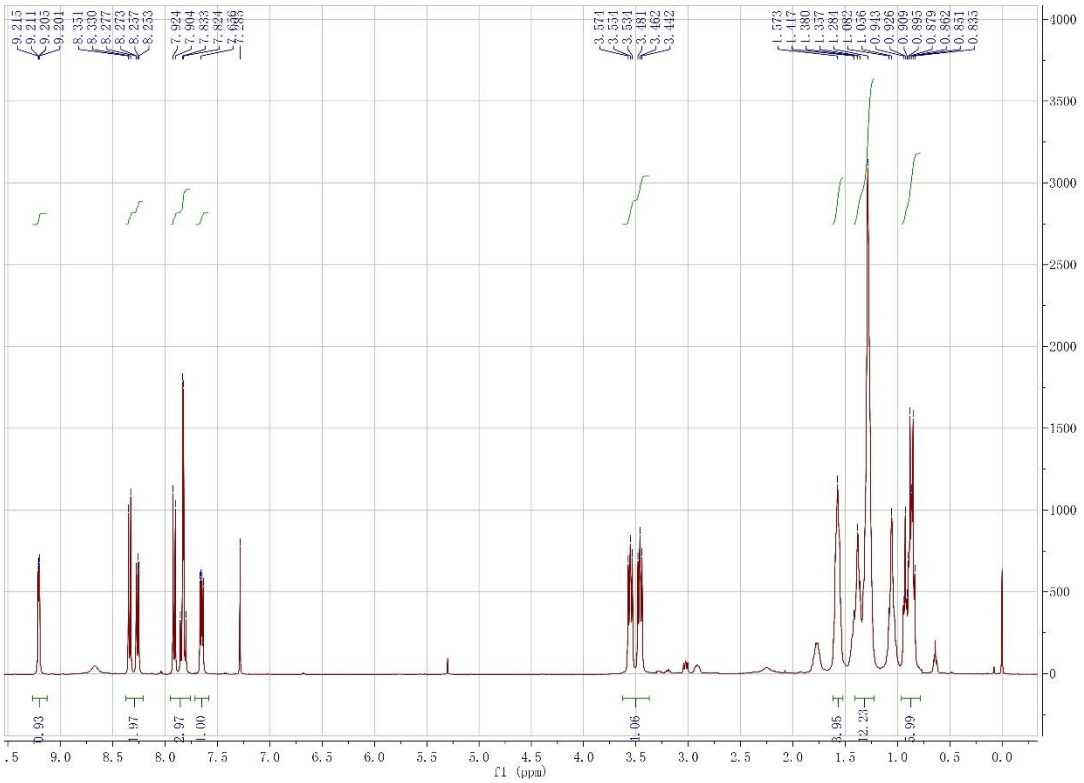


Fig. S6 $^{1}$H NMR spectrum of C6-PTA

## 3. $^{13}$C NMR

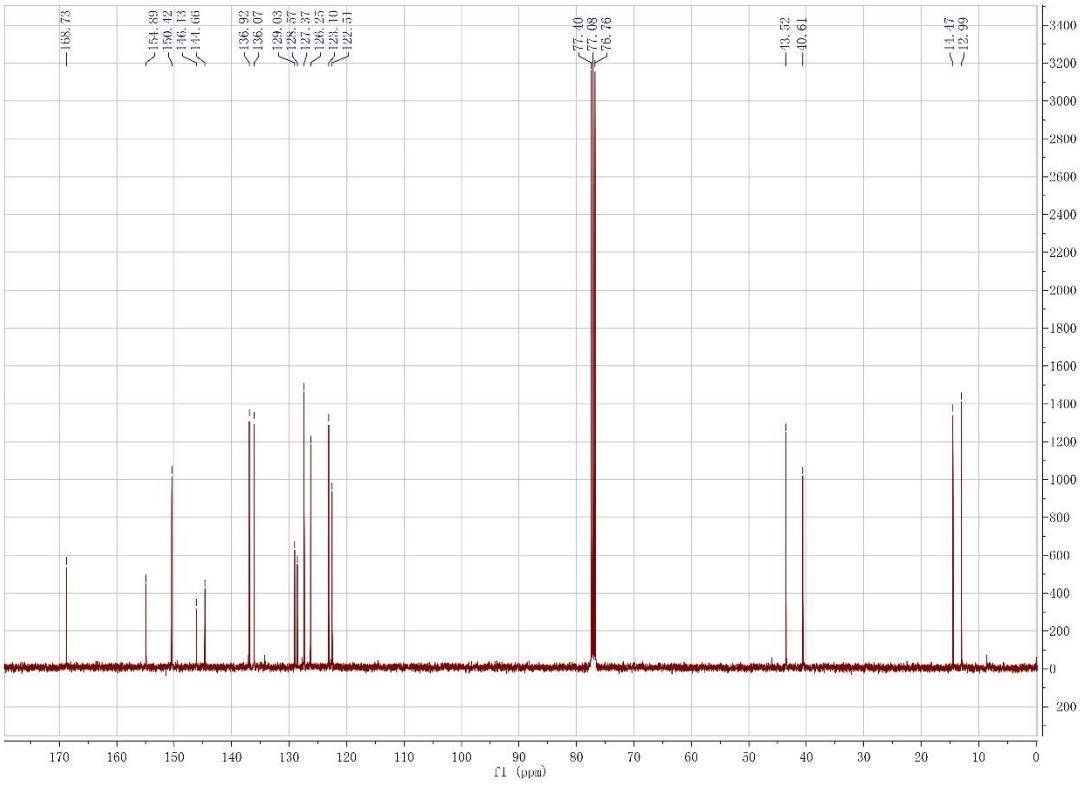


Fig. S7 $^{13}$C NMR spectrum of C2-PTA

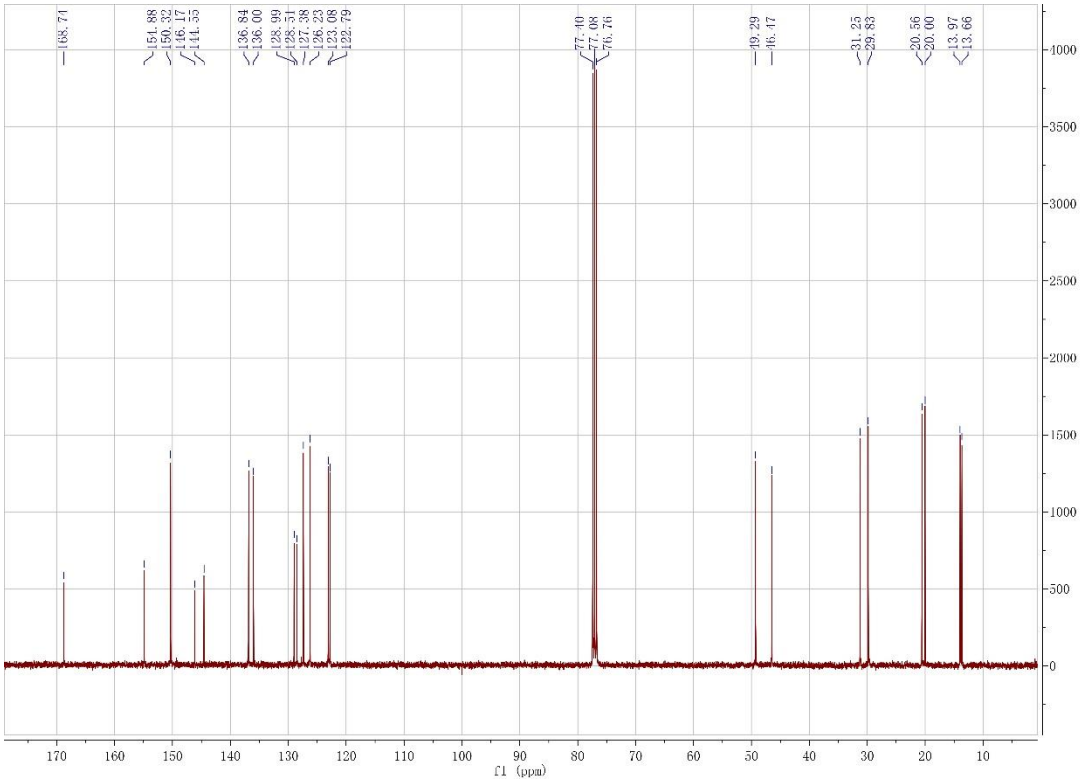


Fig. S8 $^{13}$C NMR spectrum of C4-PTA

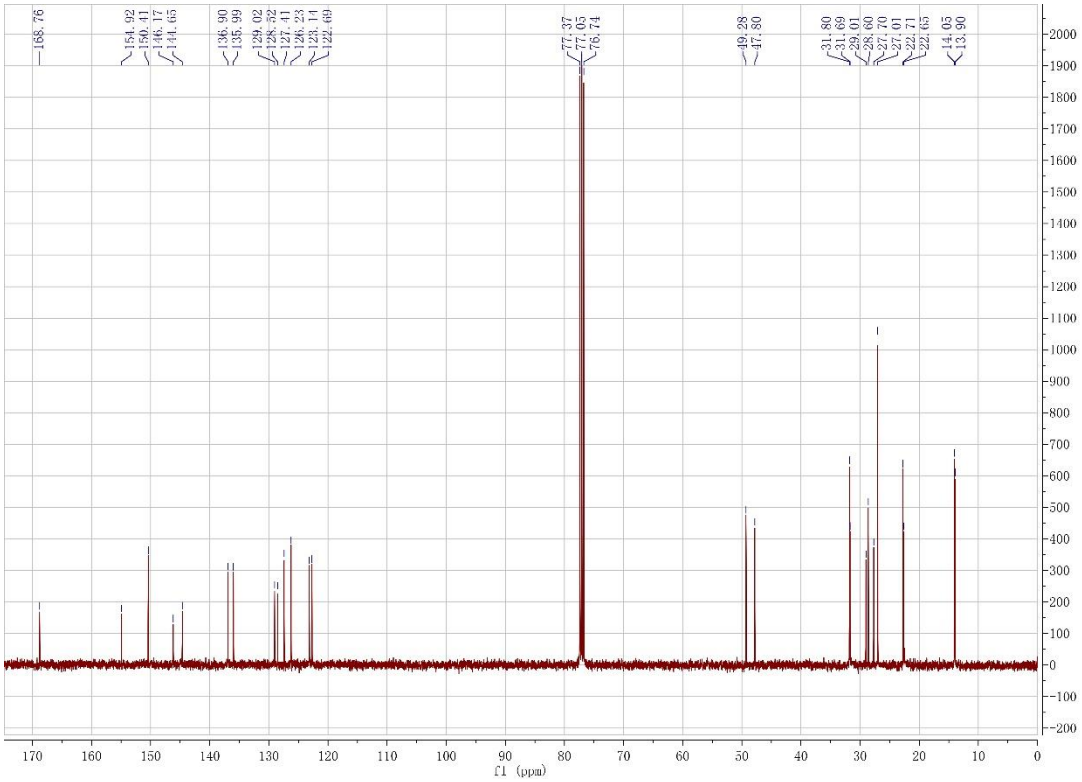


Fig. S9 $^{13}$C NMR spectrum of C6-PTA

**4. ESI-MS**

Acquisition Parameter

Source Type: ESI
Focus: Active
Scan Begin: 100 m/z
Scan End: 1000 m/z
Ion Polarity: Positive
Set Capillary: 4500 V
Set End Plate offset: -500 V
Set Collision Cell RF: 280.0 Vpp
Set Nebulizer: 0.4 Bar
Set Dry Heater: 180 °C
Set Dry Gas: 4.0 l/min
Set Divert Valve: Waste

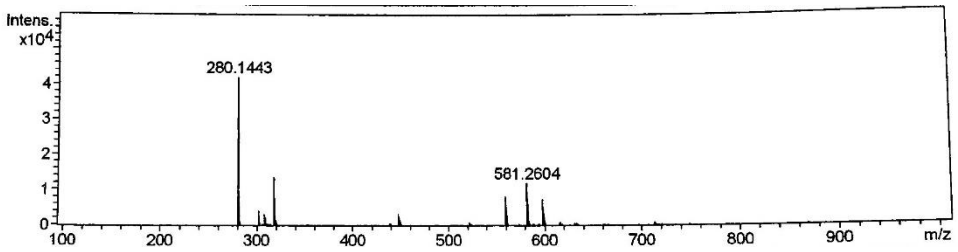

Fig. S10 ESI-MS spectrum of C2-PTA.
Formula: C17H18N3O. m/z: 280.1443. Err: 1.8 ppm.

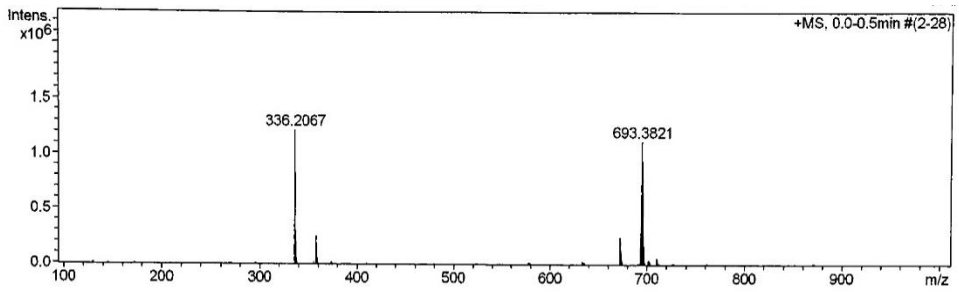

Fig. S11 ESI-MS spectrum of C4-PTA.
Formula: C21H26N3O. m/z: 336.2070. Err: 0.9 ppm.

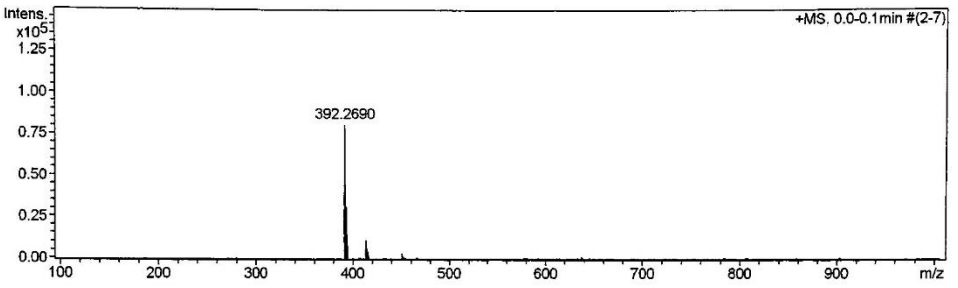

Fig. S12 ESI-MS spectrum of C6-PTA.
Formula: C25H34N3O. m/z: 392.2696. Err: 1.6 ppm.

**2. Solvent extraction data**

*Effect of diluents*

Solubilities test shows that C2-PTA is well soluble in cyclohexanone, 1,2-dichloroethane, 2-chrolomethane and chloroform, incompletely soluble in n-octanol and tert-butylbenzene (TBB), and almost insoluble n-hexane and kerosene. The extraction behaviors of Am(III) and Eu(III) with C2-PTA in such diluents were measured, and the results are shown in Table S1.

In spite of the good performance of tetradentate N,N'-diethyl-N,N'-ditolyl-2,9-diamide-1,10-phenanthroline (Et-Tol-DAPhen) in the solvent extraction in cyclohexanone [*Xiao, C.-L., et al. (2014). Inorganic chemistry **53**(3): 1712-1720.*], the solubilities of cyclohexanone (8.6 g/100 mL) is much higher than 1,2-dichloroethane (0.81 g/100 mL) and chloroform (0.82 g/100 mL) at 293 K in water, which may lead to a vulnerable organic phase as well as an unstable extraction process. And as is seen from Table S1, the distribution ratios of both Am(III) and Eu(III) with C2-PTA present much higher in chloroform than in cyclohexanone and 1,2-dichloroethane. Such results showed that chloroform is favorable for the extraction of Am(III) and Eu(III) with C2-PTA.

Table S1 Solubilities of C2-PTA, the distribution ratios and the extraction efficient of Am(III) and Eu(III). Organic phase: 0.2 mol/L C2-PTA. Aqueous phase: $10^{-3.63}$ mol/L $HNO_3$ + $^{241}Am/^{152}Eu$ radiotracers. *T* = 293 K. The statistical error values were less than 5%.

| Diluent | Cyclohexanone | 1,2-dichloroethane | Chloroform |
|---|---|---|---|
| *D*(Am) | 0.23 | 2.2 | 25.2 |
| *D*(Eu) | 0.33 | 1.4 | 3.3 |
| *E*(Am) | 19% | 69% | 96% |
| *E*(Eu) | 25% | 58% | 76% |

*Effect of extractant concentration*

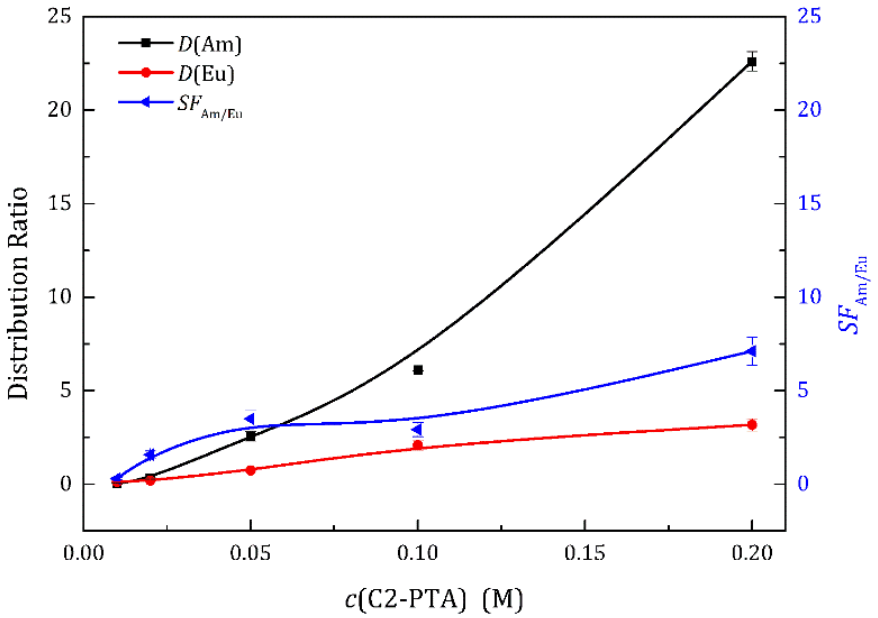


Fig. S13 Effect of extractant concentration. Organic phase: C2-PTA in chloroform. Aqueous phase: $10^{-3.63}$ mol/L $HNO_3$ + $^{241}Am/^{152}Eu$ tracers. *T* = 293 K.

## 3. Solution spectroscopy

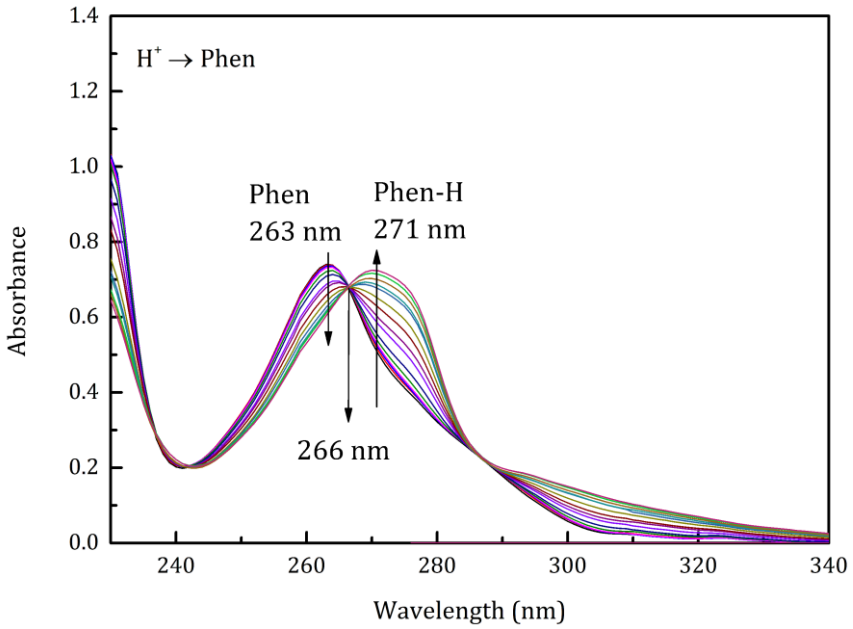


Fig. S14 UV-vis titration of Phen by $H^+$ in $HNO_3$/methanol media. $c_{Phen}$ = 2.5×10$^{-5}$ mol/L, $c_{H+}$ = 0–4.0×10$^{-5}$ mol/L, $T$ = 293 K.

## 4. Optimized structures

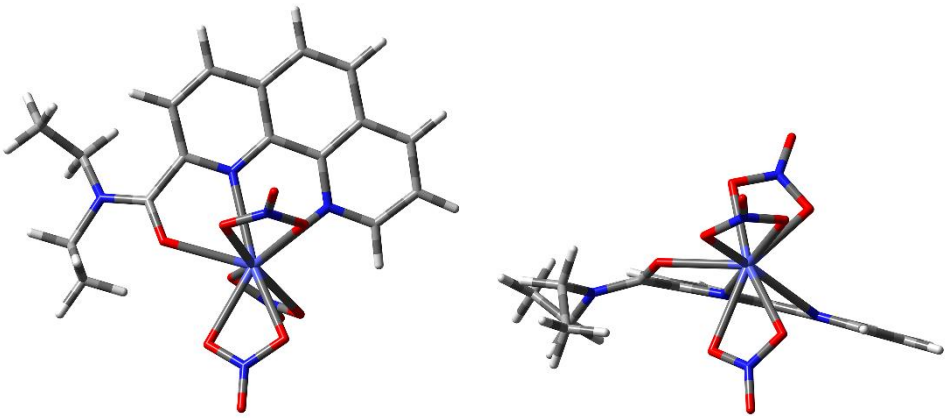

Fig. S15 Optimized structures of Am(C2-PTA)$(NO_3)_3$ in front view (left) and lateral view (right).

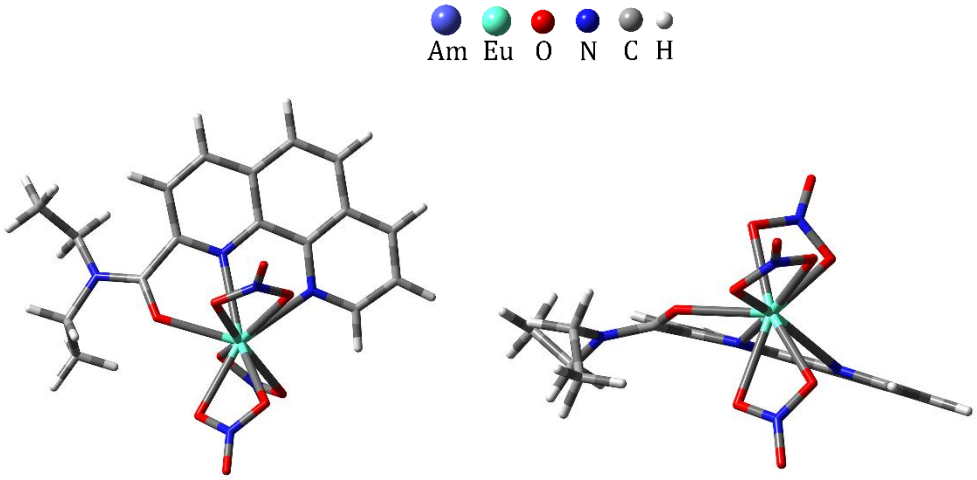

Fig. S16 Optimized structures of Eu (C2-PTA)$(NO_3)_3$ in front view (left) and lateral view (right).

## 5. Cartesian coordinates in the optimized structures

Table S2 Cartesian coordinates in the optimized structure of Am(C2-PTA)$(NO_3)_3$

| Standard orientation | | | | | |
|---|---|---|---|---|---|
| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
| 1 | 6 | 0 | -0.571877 | 4.192021 | 0.634449 |
| 2 | 6 | 0 | -1.646207 | 3.320528 | 0.630439 |
| 3 | 6 | 0 | -1.439161 | 1.984736 | 0.227706 |
| 4 | 7 | 0 | -0.226233 | 1.535516 | -0.086798 |
| 5 | 6 | 0 | 0.824312 | 2.378282 | -0.122889 |
| 6 | 6 | 0 | 0.702791 | 3.751576 | 0.221240 |
| 7 | 6 | 0 | 2.104493 | 1.851447 | -0.548551 |
| 8 | 6 | 0 | 3.211060 | 2.730901 | -0.641333 |
| 9 | 6 | 0 | 3.053941 | 4.111920 | -0.277189 |
| 10 | 6 | 0 | 1.853951 | 4.603220 | 0.143953 |
| 11 | 7 | 0 | 2.186113 | 0.534329 | -0.861511 |
| 12 | 6 | 0 | 3.344689 | 0.056743 | -1.300572 |
| 13 | 6 | 0 | 4.499490 | 0.852974 | -1.437101 |
| 14 | 6 | 0 | 4.434271 | 2.188458 | -1.097654 |
| 15 | 6 | 0 | -2.477064 | 0.879104 | 0.168616 |
| 16 | 8 | 0 | -2.079243 | -0.280003 | 0.399987 |
| 17 | 7 | 0 | -3.770557 | 1.109424 | -0.138807 |
| 18 | 6 | 0 | -4.660540 | -0.074518 | -0.189516 |
| 19 | 6 | 0 | -4.579996 | -0.818599 | -1.525315 |
| 20 | 1 | 0 | -0.705240 | 5.222694 | 0.952103 |
| 21 | 1 | 0 | -2.620414 | 3.657136 | 0.960801 |
| 22 | 1 | 0 | 3.920897 | 4.763704 | -0.343217 |
| 23 | 1 | 0 | 1.749683 | 5.648596 | 0.420298 |
| 24 | 1 | 0 | 5.419440 | 0.405731 | -1.798211 |
| 25 | 1 | 0 | 5.307940 | 2.829794 | -1.179224 |
| 26 | 1 | 0 | -5.676764 | 0.284950 | -0.001540 |
| 27 | 1 | 0 | -4.377419 | -0.734453 | 0.631170 |
| 28 | 1 | 0 | -5.253950 | -1.681711 | -1.502626 |
| 29 | 1 | 0 | -3.564793 | -1.179381 | -1.709507 |
| 30 | 1 | 0 | -4.882005 | -0.180256 | -2.363732 |
| 31 | 7 | 0 | 0.010681 | -3.883485 | 0.872012 |
| 32 | 8 | 0 | -0.085481 | -5.061541 | 1.129349 |
| 33 | 8 | 0 | 1.131664 | -3.248836 | 0.938326 |
| 34 | 8 | 0 | -1.002287 | -3.166836 | 0.514680 |
| 35 | 7 | 0 | 1.130816 | -0.169650 | 2.825018 |
| 36 | 8 | 0 | -0.110028 | -0.357190 | 2.546298 |

| | | | | | |
|---|---|---|---|---|---|
| 37 | 8 | 0 | 1.509208 | 0.188686 | 3.920046 |
| 38 | 8 | 0 | 1.948492 | -0.371241 | 1.847448 |
| 39 | 7 | 0 | 0.228089 | -1.622440 | -2.714469 |
| 40 | 8 | 0 | -0.700470 | -0.936836 | -2.148223 |
| 41 | 8 | 0 | 0.266426 | -1.805508 | -3.912615 |
| 42 | 8 | 0 | 1.123741 | -2.100882 | -1.917717 |
| 43 | 6 | 0 | -4.319552 | 2.352001 | -0.701869 |
| 44 | 1 | 0 | -4.861363 | 2.076006 | -1.613966 |
| 45 | 1 | 0 | -3.497497 | 2.994126 | -1.021397 |
| 46 | 6 | 0 | -5.260952 | 3.095599 | 0.250296 |
| 47 | 1 | 0 | -4.753446 | 3.399795 | 1.172035 |
| 48 | 1 | 0 | -5.651385 | 3.993488 | -0.241039 |
| 49 | 1 | 0 | -6.115179 | 2.473715 | 0.536115 |
| 50 | 1 | 0 | 3.356840 | -0.998090 | -1.560386 |
| 51 | 95 | 0 | 0.261413 | -1.085459 | 0.171003 |

Table S3 Cartesian coordinates in the optimized structure of Eu(C2-PTA)($NO_3$)$_3$

| Standard orientation | | | | | |
|---|---|---|---|---|---|
| Center | Atomic | Atomic | Coordinates (Angstroms) | | |
| Number | Number | Type | X | Y | Z |
| 1 | 6 | 0 | 0.035418 | 4.107204 | 0.590091 |
| 2 | 6 | 0 | -1.151501 | 3.396046 | 0.572214 |
| 3 | 6 | 0 | -1.126155 | 2.038713 | 0.189499 |
| 4 | 7 | 0 | 0.018689 | 1.418947 | -0.087988 |
| 5 | 6 | 0 | 1.176807 | 2.104508 | -0.114800 |
| 6 | 6 | 0 | 1.243140 | 3.486691 | 0.208777 |
| 7 | 6 | 0 | 2.376167 | 1.396297 | -0.512283 |
| 8 | 6 | 0 | 3.597008 | 2.109778 | -0.592707 |
| 9 | 6 | 0 | 3.630001 | 3.504084 | -0.246391 |
| 10 | 6 | 0 | 2.504212 | 4.166493 | 0.144344 |
| 11 | 7 | 0 | 2.273273 | 0.078683 | -0.812848 |
| 12 | 6 | 0 | 3.360342 | -0.563113 | -1.222863 |
| 13 | 6 | 0 | 4.619762 | 0.058870 | -1.343587 |
| 14 | 6 | 0 | 4.739111 | 1.394390 | -1.019770 |
| 15 | 6 | 0 | -2.303145 | 1.085173 | 0.096056 |
| 16 | 8 | 0 | -2.067434 | -0.122327 | 0.304421 |
| 17 | 7 | 0 | -3.549499 | 1.485623 | -0.228393 |
| 18 | 6 | 0 | -4.579790 | 0.424525 | -0.329054 |
| 19 | 6 | 0 | -4.554153 | -0.294574 | -1.680750 |
| 20 | 1 | 0 | 0.041986 | 5.150603 | 0.893943 |
| 21 | 1 | 0 | -2.073531 | 3.872091 | 0.879149 |
| 22 | 1 | 0 | 4.581319 | 4.026381 | -0.302464 |
| 23 | 1 | 0 | 2.543788 | 5.220231 | 0.405398 |

| | | | | | |
|---|---|---|---|---|---|
| 24 | 1 | 0 | 5.473273 | -0.519047 | -1.681846 |
| 25 | 1 | 0 | 5.696219 | 1.904462 | -1.090962 |
| 26 | 1 | 0 | -5.547601 | 0.905706 | -0.158654 |
| 27 | 1 | 0 | -4.405460 | -0.283316 | 0.481948 |
| 28 | 1 | 0 | -5.331238 | -1.066201 | -1.697788 |
| 29 | 1 | 0 | -3.587214 | -0.776578 | -1.846667 |
| 30 | 1 | 0 | -4.748922 | 0.395390 | -2.510071 |
| 31 | 7 | 0 | -0.575624 | -3.870380 | 0.953803 |
| 32 | 8 | 0 | -0.847224 | -5.014395 | 1.239526 |
| 33 | 8 | 0 | 0.553147 | -3.329888 | 1.261128 |
| 34 | 8 | 0 | -1.397862 | -3.101850 | 0.324195 |
| 35 | 7 | 0 | 0.938788 | -0.367844 | 2.841987 |
| 36 | 8 | 0 | -0.298497 | -0.528039 | 2.537668 |
| 37 | 8 | 0 | 1.301247 | -0.057478 | 3.957886 |
| 38 | 8 | 0 | 1.770097 | -0.537499 | 1.872559 |
| 39 | 7 | 0 | 0.188541 | -1.848198 | -2.610178 |
| 40 | 8 | 0 | -0.622262 | -0.966169 | -2.150714 |
| 41 | 8 | 0 | 0.276218 | -2.100310 | -3.794254 |
| 42 | 8 | 0 | 0.914243 | -2.449168 | -1.728279 |
| 43 | 63 | 0 | 0.091122 | -1.213860 | 0.209394 |
| 44 | 6 | 0 | -3.932807 | 2.804102 | -0.754622 |
| 45 | 1 | 0 | -4.507313 | 2.624008 | -1.670543 |
| 46 | 1 | 0 | -3.035531 | 3.343523 | -1.060700 |
| 47 | 6 | 0 | -4.769888 | 3.633984 | 0.223387 |
| 48 | 1 | 0 | -4.223112 | 3.850046 | 1.147539 |
| 49 | 1 | 0 | -5.050678 | 4.584888 | -0.242366 |
| 50 | 1 | 0 | -5.691340 | 3.112953 | 0.501664 |
| 51 | 1 | 0 | 3.224917 | -1.611850 | -1.472410 |