

Supporting Information

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1. Spectrophotometric titration of Eu/BQPhen

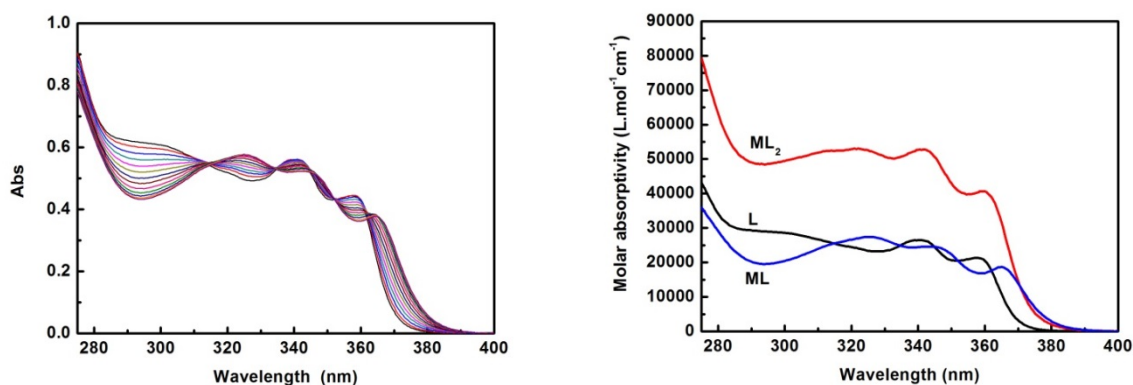


Figure S1. Representative spectrophotometric titrations of ligand BQPhen with europium(III) perchlorate in DMF ($I=0.1$ mol/L TMA) at 25°C. Left: absorption spectra of the titration. Initial solution in the cuvette: 2.0 mL, $c^0(\text{BQPhen})=2.11 \times 10^{-5}$ mol/L; Titrant: 2.13×10^{-4} mol/L $\text{Eu}(\text{ClO}_4)_3$. Right: Calculated molar absorptivity of free L (black), ML (green) and ML_2 (red)

2. Calorimetric titration of Nd/BQPhen

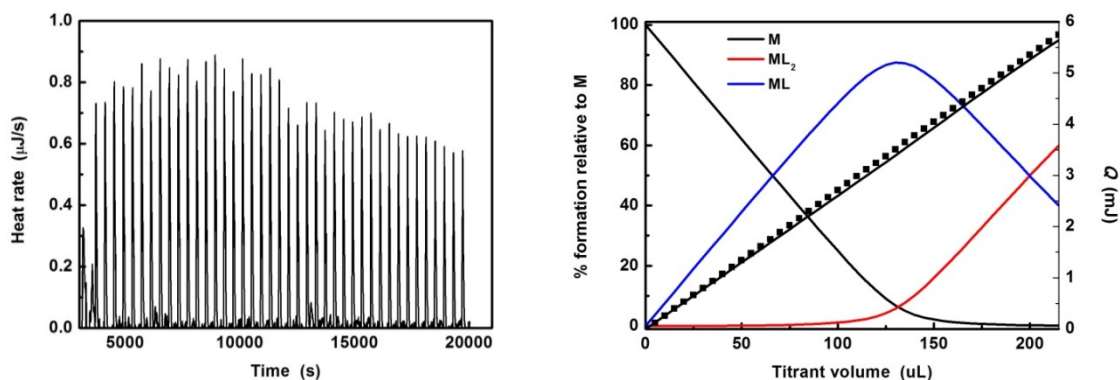


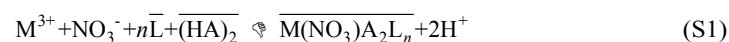
Figure S2. Representative microcalorimetric titration of Nd(III)/BQPhen complexation ($t=25.0$ °C, $I=0.1$ M TMA in DMF). Titrant: 0.0048 mol/L ligand BQPhen, about 42 additions of 0.005 mL each. Initial solution in ampoule: $V_0=0.9$ mL, $c_0(\text{Nd})=7.0 \times 10^{-4}$ mol/L. Left: thermogram, right: total heat (right y axis, closed symbol, experimental; line, calculated) and speciation of Nd(III) (left y axis, lines, black, Nd^{3+} , blue, NdBQPhen^+ ; red, NdL_2^{3+}) versus the volume of the titrant.

3 Solvent extraction of ^{241}Am and ^{152}Eu

Table S1. The distribution of ^{241}Am and ^{152}Eu between the organic phase and the aqueous phase as a function of the extractant (BQPhen) concentration. The organic phase: nitrobenzene as diluent, and 0.2 M 2-bromohexanoic acid as phase modifier; aqueous phase: 0.01 M nitric acid with trace metallic ions.

[L]	D_{Am}	D_{Eu}	$SF_{\text{Am/Eu}}$
4.84E-05	2.1	0.3	7.8
7.26E-05	4.3	0.4	10.9
9.68E-05	6.7	0.7	9.3
1.33E-04	18.2	1.8	10.1
1.99E-04	21.9	1.8	12.0
2.42E-04	47.2	4.1	11.6
6.05E-04	211.0	26.2	8.1

In the extraction system, the organic phase contains BQPhen (L) and 2-bromohexanoic acid (HA) as the synergistic extractants. HA is also responsible for the transport of the metal ions from the aqueous phase to the organic phase. Because HA exists in the dimeric form,^[1,2] the extraction equilibrium is expressed as reaction S1,



where the bar above a species denotes the species is in the organic phase. The extraction equilibrium constant K_{ex} can be described as

$$K_{\text{ex}} = \frac{[\text{H}^+]^2 [\overline{\text{M}(\text{NO}_3)_2\text{L}_n}]}{[\text{M}^{3+}] [\text{NO}_3^-] [\overline{(\text{HA})_2}] [\overline{\text{L}}]^n} = D \frac{[\text{H}^+]^2}{[\text{NO}_3^-] [\overline{(\text{HA})_2}] [\overline{\text{L}}]^n} \quad (\text{S2})$$

Then,

$$\log D = n \log [\overline{\text{L}}] + \log K_{\text{ex}} - \log \left(\frac{[\text{H}^+]^2}{[\text{NO}_3^-] [\overline{(\text{HA})_2}]} \right) \quad (\text{S3})$$

The plot of $\log D$ vs. $\log [\overline{\text{L}}]$ is linear, with the slope = n and the intercept = $\log K_{\text{ex}} - \log ([\text{H}^+]^2 / ([\text{NO}_3^-] [\overline{(\text{HA})_2}]))$. In the experiments, the aqueous concentrations of H^+ and NO_3^- and the organic phase concentration of HA ($[\overline{(\text{HA})_2}]$) are constant and identical for the extraction of Am(III) and Eu(III) (both in tracer quantities). Therefore, the difference in the intercepts between Am(III) and Eu(III) is equal to the difference in K_{ex} :

$$(\text{Intercept})_{\text{Am}} - (\text{Intercept})_{\text{Eu}} = \log K_{\text{ex}}(\text{Am}) - \log K_{\text{ex}}(\text{Eu})$$

References for extraction

1. T. Sekine, M. Isayama, S. Yamaguchi, H. Moriya, *Bull. Chem. Soc. Jap.*, 1967, **40**, 27.
2. S. Andersson, C. Ekberg, M. R. S. Foreman, M. J. Hudson, J.-O. Liljenzin, M. Nilsson, G. Skarnemark, K. Spahiu, *Solv. Extra. Ion Exch.*, 2003, 21, 621.

4 Isomers of BQPhen

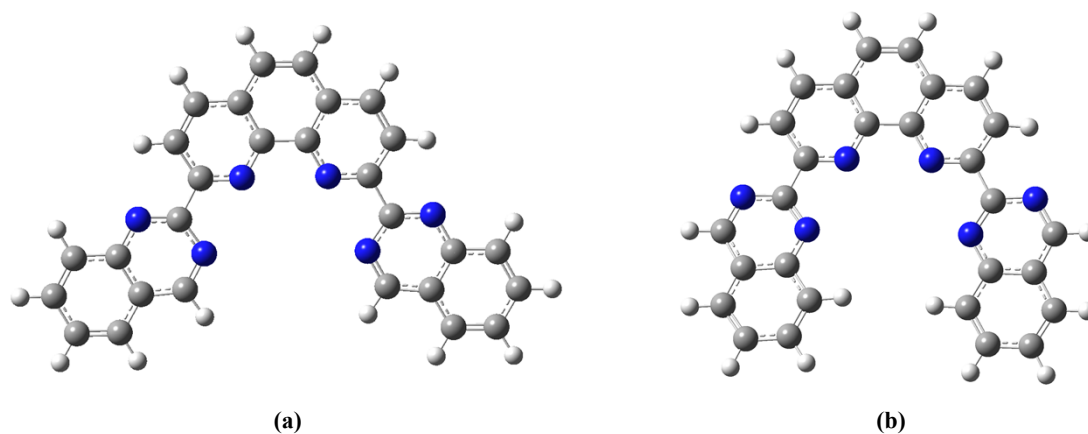


Figure S3. 3D structures of BQPhen isomers calculated by B3LYP method in the gas phase. Blue, grey and white colors denote N, C, and H atoms respectively.

5 Calculated free energy of species

Table S2. Calculated ΔG_g , $\Delta\Delta G_{\text{solv}}$ and ΔG_{solv} of the relative species of $[\text{ML}_2(\text{NO}_3)]^{2+}$ formation reactions

Species	ΔG_g	$\Delta\Delta G_{\text{solv}}$	ΔG_{solv}
	Hartree	kcal/mol	Hartree
BQPhen	-1405.163	6.13	-1405.153
$[\text{Am}(\text{BQPhen})_2(\text{NO}_3)]^{2+}$	-3685.886	-53.58	-3685.971
$[\text{Eu}(\text{BQPhen})_2(\text{NO}_3)]^{2+}$	-3800.778	-51.34	-3800.860
BTPhen	-1756.936	16.07	-1756.910
$[\text{Am}(\text{NO}_3)(\text{H}_2\text{O})_7]^{2+}$	-1410.504	-150.45	-1410.744
$[\text{Eu}(\text{NO}_3)(\text{H}_2\text{O})_7]^{2+}$	-1525.392	-151.11	-1525.633
$[\text{Am}(\text{BTPhen})_2(\text{NO}_3)]^{2+}$	-4389.474	-10.06	-4389.490
$[\text{Eu}(\text{BTPhen})_2(\text{NO}_3)]^{2+}$	-4504.368	-5.90	-4504.377
H_2O	-76.444	-1.94	-76.447
NO_3^-	-280.436	-59.12	-280.530

6. NMR data: Ligand characterization

^1H NMR spectrum was measured on a Bruker AM400 NMR spectrometer. HRMS spectral data were recorded on a Bruker Daltonics Bio TOF mass spectrometer.

Figure S4. ^1H NMR spectrum of BQPhen in DMSO

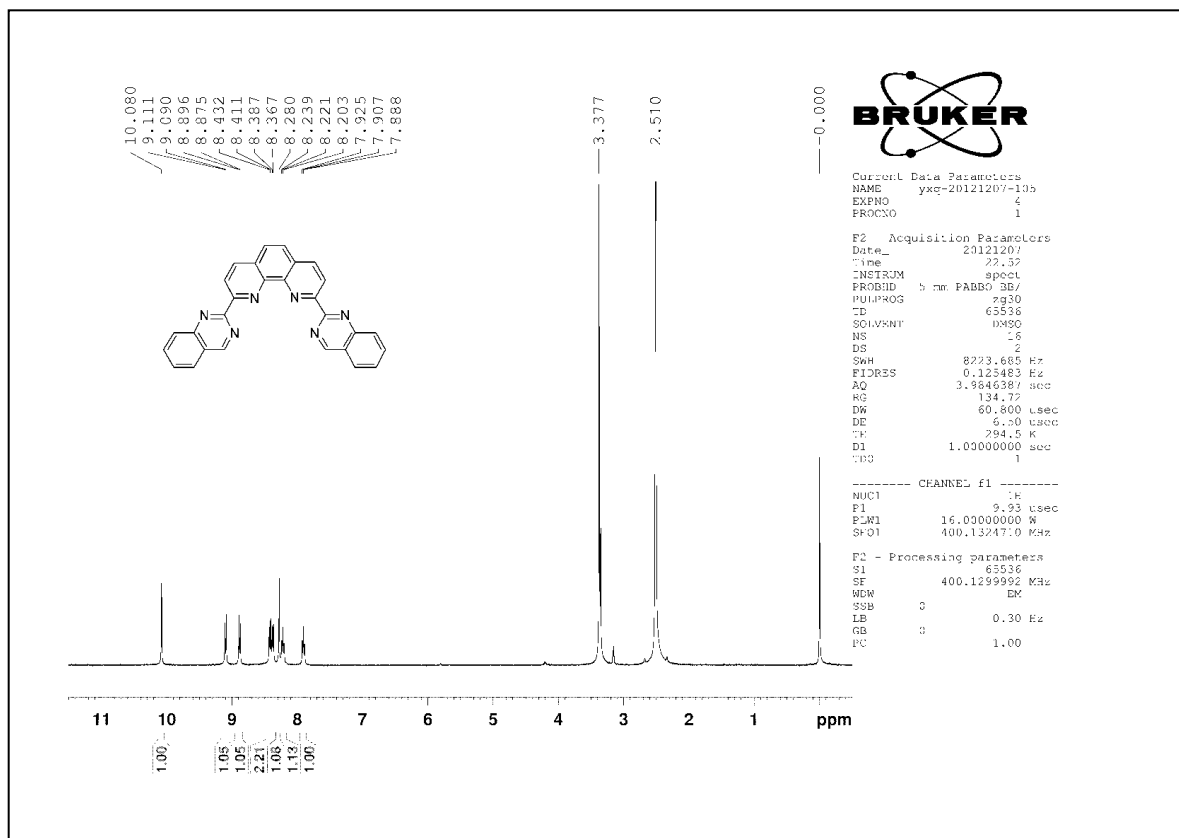


Figure S5. HRMS spectrum of BQPhen

