

Electronic Supplementary Information (ESI)

Epimeric Effects on Complexation Behaviours of Phenanthroline-based Phosphine-oxide Ligands with Uranyl Ion

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1. Experimental section

1.1 General

The chemicals and reagents used in this work, such as 3-nitrobenzotrifluoride, uranyl nitrates, and tetraethylammonium nitrate with analytical purity (AR), are commercially obtained, which were directly used without any purification. The CH₃CN with HPLC purity (Merck. Co. Ltd.) was used as the solvent in spectroscopic titration and ITC studies.

1.2 Organic synthesis

The Et-Ph-BPPhen(R,R) and Et-Ph-BPPhen(R,S) were prepared using the synthetic method as reported previously in the literature (*Inorg. Chem. Front.*, **2022**, 9, 4671). The obtained brown oily crude product was loaded on a silica gel column and separated from the epimers by elution (eluent: dichloromethane: methanol = 50:1). Then the final products Et-Ph-BPPhen(R,R) and Et-Ph-BPPhen(R,S) were obtained as white powders with yields of 25% and 28%, respectively.

1.3 Single-crystal X-ray diffraction

The single crystals of Et-Ph-BPPhen(R,R) and Et-Ph-BPPhen(R,S) ligands suitable for X-ray diffraction analysis were prepared by cooling crystallization. The solutions of Et-Ph-BPPhen(R,R) and Et-Ph-BPPhen(R,S) (10 mM) in HPLC-grade CH₃CN were heated and dissolved to obtain a supersaturated solution. Then the transparent crystal particles were obtained by standing the solution at room temperature (293 K) for 48 h. Further, the single crystals of uranyl complexes with Et-Ph-BPPhen(R,R) and Et-Ph-BPPhen(R,S) were prepared by solvent diffusion. Et-Ph-BPPhen(R,R) and Et-Ph-BPPhen(R,S) ligands and uranyl nitrate with 0.01 mM were dissolved by CH₃CN or acetone in a small glass bottle. Ethyl ether was added into the outer glass bottle as an undesirable solvent in diffusion. After three days, the yellow single crystals suitable for X-ray diffraction analysis were obtained from the inner wall of the glass bottles. The single-crystal X-ray diffraction data for the ligands and uranyl complexes were collected with Mo-K α ($\lambda = 0.71073 \text{ \AA}$) or Ga-K α ($\lambda = 1.34139 \text{ \AA}$) radiation on a Bruker D8 Venture Ims3.0 model diffractometer. The crystals were kept at 170 K during

data collection. The X-ray diffraction data was analyzed and refined with the SHELXT program on the Olex2 software platform.

1.4 Solubility test

The mother liquors of Et-Ph-BPPhen(R,R/R,S) ligands crystallization samples are the saturated solution of the two ligands at 293 K. The CH₃CN solutions with ligand concentrations of 0.002, 0.005, 0.01, 0.02, and 0.05 mM were prepared by using the weighing-dissolving method and placed in a quartz cuvette (optical path = 1 cm) with a volume of 2.0 mL. The absorbance of Et-Ph-BPPhen(R,R) and Et-Ph-BPPhen(R,S) ligands in the wavelength of 240-400 nm were collected on a UH-5300 (Hitachi, Japan) model UV-Vis spectrophotometer. The absorbance at maximum absorption wavelength ($\lambda = 278.2$ nm) was selected to establish the linear relationship between ligand concentration and its absorbance based on the Lambert-Beer law. The saturated solutions of ligands were diluted in 100, 200, 500, and 1000 times, respectively before being measured. Then the solubility of the ligands in CH₃CN solution (T = 293 K) were obtained by the linear relationship established between the concentration of ligands and their absorbance tested.

1.5 Circular dichroism

The Uranyl nitrate and Et-Ph-BPPhen(R,R)/(R,S) ligands with a concentration of 0.1 mM were dissolved in CH₃CN and thoroughly mixed by a magnetic stirrer (600 r/min, 3 min) to prepare the complex solution for circular dichroism test. Then 2.0 mL of ligand and complex solutions respectively were placed in a quartz cuvette with an optical path of 1 cm and the corresponding circular dichroism spectra in the wavelength range of 240-400 nm were collected on a J-1700 (JASCO, Japan) model circular dichroism spectrophotometer. The data pitch and scanning speed were set to 1 nm and 100 nm/min during the measurement, respectively.

1.6 Circularly polarized luminescence

The Uranyl nitrate and Et-Ph-BPPhen(R,R)/(R,S) ligands with a concentration of 4.0 mM were dissolved in CH₃CN and thoroughly mixed by a magnetic stirrer (600 r/min, 3 min) to produce the complex solutions. Then 2.0 mL of the complex solutions were placed in a quartz

cuvette with an optical path of 1 cm and the corresponding circularly polarized luminescence spectra in the range of 500-700 nm were collected by a CPL-300 (JASCO, Japan) model spectrophotometer with an excitation light at $\lambda_{ex} = 420$ nm.

1.7 Solvent extraction

The Et-Ph-BPPhen(R,R) and Et-Ph-BPPhen(R,S) extractants dissolving in 3-nitrobenzotrifluoride with different concentrations (1-10 mM) were used as the organic phases for solvent extraction. The uranyl nitrates (0.1 mM) dissolving in aqueous solutions with nitric acid concentrations ranging from 0.1-4.0 M were used as aqueous phases. The aqueous phase and organic phase with an equal volume of 1.0 mL were mixed in a centrifugal tube with a vortex oscillator (10 min). After phase separation by centrifugation (3000 r/min, 1 min), the concentrations of metal ions in aqueous phases before and after extraction were measured by a 730-ES (Varian, America) ICP-OES instrument. The difference subtraction method as presented in **Equation S1** was used to calculate the distribution ratio (D) of metal ions. The slope analysis method was used to identify the chemical composition of extracted complexes and the corresponding calculation equations were shown in **Equations S2** to **S6**.

The distribution ratio (D) was calculated as equation S1:

$$D = \frac{C_{org.}}{C_{aq.}} \quad \text{S1}$$

The general extraction equilibriums can be described by equation S2. (The subscript (org.) or (aq.) indicates the substance exists in organic phase or aqueous phase, respectively.



Where n is the coordination number of ligands to metal ion, the corresponding extraction equilibrium constant K_{ex} can be defined as:

$$K_{ex} = \frac{[M(NO_3)_m(L)_n]_{(org.)}}{[M^{m+}]_{(aq.)}[NO_3^-]_{(aq.)}^m[L]_{(org.)}^n} \quad \text{S3}$$

The distribution ratio of metal ion D_M can be represented as:

$$D_M = \frac{[M(NO_3)_m(L)_n]_{(org.)}}{[M^{m+}]_{(aq.)}} \quad \text{S4}$$

By substituting equation S4 into equation S3, and transforming S4 into the log form to obtain equations S5 and S6 as follows:

$$\text{Log}D_M = \text{log}K_{ex} + n\text{log}[L]_{(org.)} + m\text{log}[NO_3]_{(aq.)} \quad \text{S5}$$

$$\text{Log}D_M = n\text{log}[L]_{(org.)} + C_1 \quad (C_1 = \text{log}K_{ex} + m\text{log}[NO_3]_{(aq.)}) \quad \text{S6}$$

Where C_1 and C_2 are the conditional constants. Based on above analysis, the slope of $\text{log } D$ vs. $\text{log}[L]$ which presents the number of extractant molecules coordinated to metal ion in organic phase, was obtained by keeping the concentration of nitric acid as constant.

1.8 NMR titration

The stock solutions for NMR titration were prepared by dissolving Et-Ph-BPPhen(R,R), Et-Ph-BPPhen(R,S), and uranyl nitrate in CD_3OD , respectively. The concentration of ligands and metal ions in the stock solution is 10 mM and 50 mM, respectively. For a representative titration, the initial 0.5 mL of stock solutions of Et-Ph-BPPhen(R,R) and Et-Ph-BPPhen(R,S) were placed into one NMR tube respectively, and then the 10 μL of metal ions stock solution was added into the tube in one drop. Before the test, the NMR tube was rotated and oscillated for 3 min to ensure the coordination reaction between ligands and metal ions reached the equilibrium state. The resulting ^1H and ^{31}P NMR spectra of the Uranyl complexation with ligands for each titration were obtained on an AVANCE NEO 500 (Bruker, Germany) model NMR spectrometer. The titration was stopped until no changes were found in the ^1H and ^{31}P NMR spectra ($M/L = 2.0$).

1.9 UV-Vis titration

The Et-Ph-BPPhen(R,R) and Et-Ph-BPPhen(R,S) dissolving in CH_3CN with a concentration of 1.0 mM were used as the initial stock solutions for UV-Vis titration studies. Uranyl nitrates with a concentration of 1.0 mM dissolving in CH_3CN were used as the titrant. The concentration of ligand in the sample was diluted to 0.03 mM ($V_0 = 2.0$ mL), and then 0.1-molar equivalent of metal ion was added in one drop. Tetraethylammonium nitrate was added to the samples to control the ionic strength at around 10.0 mM. After each addition, it needed to be mixed for 3 min under magnetic stirring (600 r/min) to reach the complexation equilibrium. All the UV-Vis titration spectra were collected on a UH-5300 (Hitachi, Japan)

model UV-vis spectrophotometer. The titration data were fitted with the HyperSpec software to obtain the stability constants ($\log \beta$), molar absorbance, and species distribution curves for the ligands and Uranyl complexes formed during titration.

1.10 Fluorescence titration

The stock solutions of 2.0 mM ligand and 0.2 mM uranyl nitrate in CH_3CN were used in fluorescence titration experiments. The tetraethylammonium nitrate (10 mM) was added into the solutions to keep the ionic strength constant. The uranyl nitrate solution with an initial volume of 2.0 mL was put in a quartz cuvette with an optical path of 1 cm. The fluorescence emission spectra with a wavelength ranging from 440 to 700 nm were obtained by an FLSP 920 model fluorometer (Edinburgh, United Kingdom) with an excitation wavelength set at $\lambda_{\text{ex}} = 420$ nm. The titration was stopped until on significant changes were found in the fluorescence emission spectra. After each addition, it needed to be mixed for at least 3 min under magnetic stirring (600 r/min) to reach the complexation equilibrium.

1.11 Isothermal micro-thermometric titration

The calorimetric titration experiments were carried out on Nano-ITC (TA instruments, America) at 298 ± 1 K. In a typical titration, the sample cell was initially injected with 400 μL of ligand solution (5 mM) with a microinjector. The tetraethylammonium nitrate (50 mM) was added into the solutions to keep the ionic strength constant. The buret syringe was filled with the solution of 50 mM uranyl nitrate in CH_3CN . The injection was performed 46 times with a volume of 1 μL for each drop. The injection interval was set to 600 seconds with a stirring rate of 300 r/min. The recorded heat released in each titration ($\Delta Q_{\text{ex},j}$, $j = 1-46$) was corrected by dilution heat ($\Delta Q_{\text{dil},j}$) of titrant, which was measured with CH_3CN as the initial solution in a separate run. The net reaction heat ($\Delta Q_{\text{r},j}$) was calculated from the difference: $\Delta Q_{\text{r},j} = \Delta Q_{\text{ex},j} - \Delta Q_{\text{dil},j}$. The data was fitted using the *NanoAnalyze* program to calculate the thermodynamics parameters including n , enthalpy (ΔH), and entropy (ΔS).

2. Result and discussion

2.1 Organic synthesis

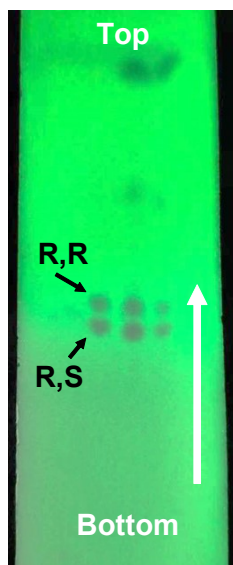


Figure S1. The positions of two Et-Ph-BPPhenisomers shown on TLC. (Silica gel GF254, CH₂Cl₂: MeOH= 10:1, v:v)

Table S1. Predicted value, measured value and difference value of organic element analysis for two epimers of Et-Ph-BPPhenligand.

Ligand		C (%)	H (%)	N (%)
Et-Ph-BPPhen(R,R)	predicted value	69.42	5.41	5.78
	measured value	69.44	5.39	5.75
	difference value	0.02	-0.02	-0.03
Et-Ph-BPPhen(R,S)	predicted value	69.42	5.41	5.78
	measured value	69.25	5.37	5.53
	difference value	-0.17	-0.04	-0.25

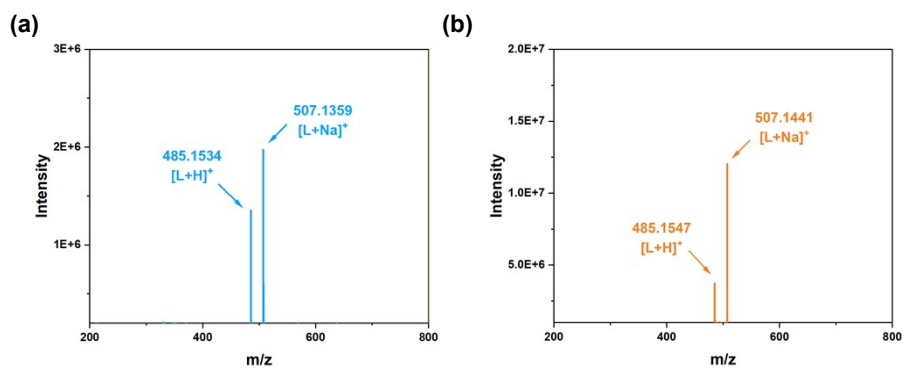


Figure S2. The ESI-HRMS result of (a) Et-Ph-BPPhen(R,R) and (b) Et-Ph-BPPhen(R,S).

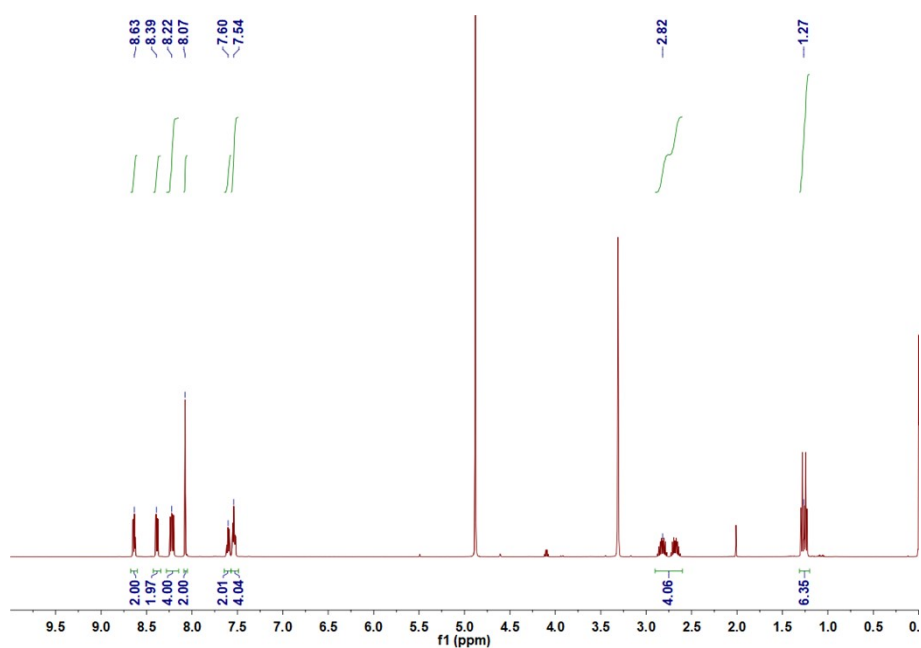


Figure S3. ¹H NMR result of Et-Ph-BPPhen(R,R) in CD₃OD.

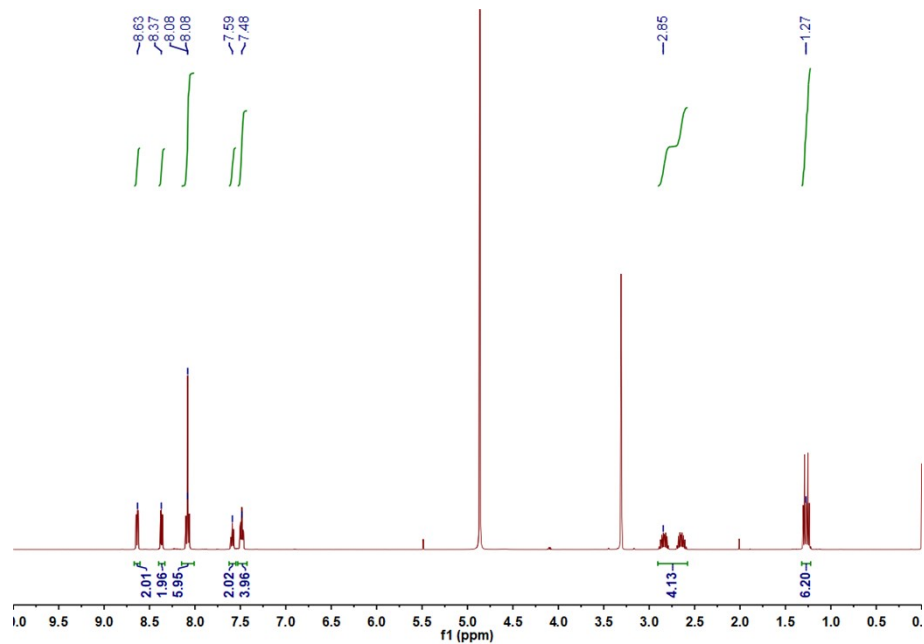


Figure S4. ^1H NMR result of Et-Ph-BPPhen(R,S) in CD_3OD .

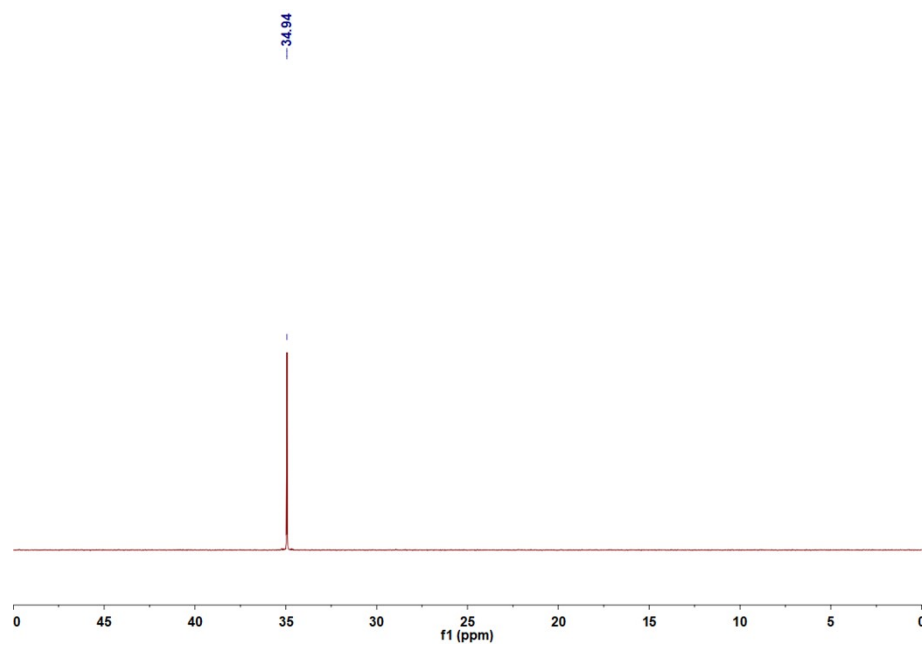


Figure S5. ^{31}P NMR result of Et-Ph-BPPhen(R,R) in CD_3OD .

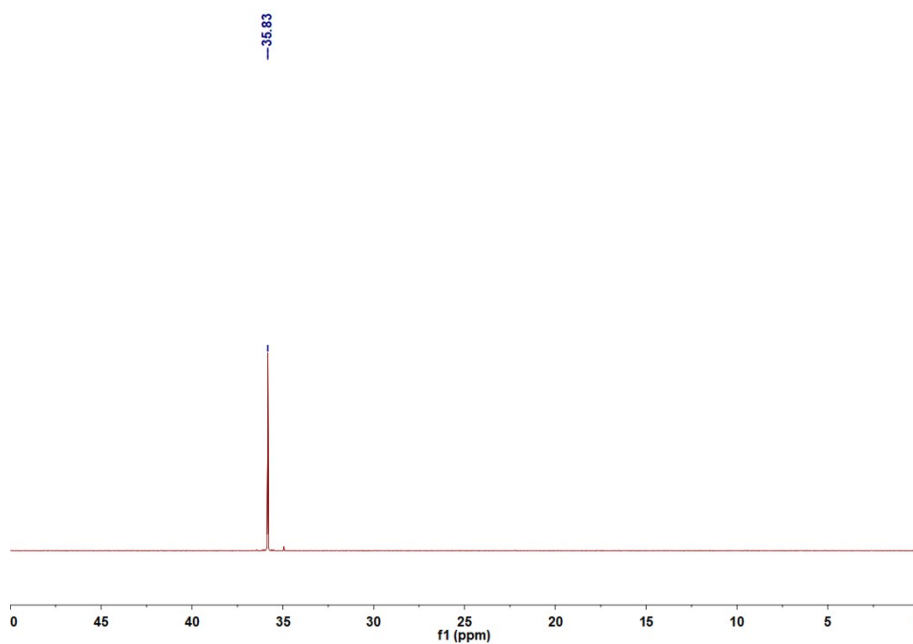


Figure S6. ^{31}P NMR result of Et-Ph-BPPhen(R,S) in CD_3OD .

2.2 Solubility

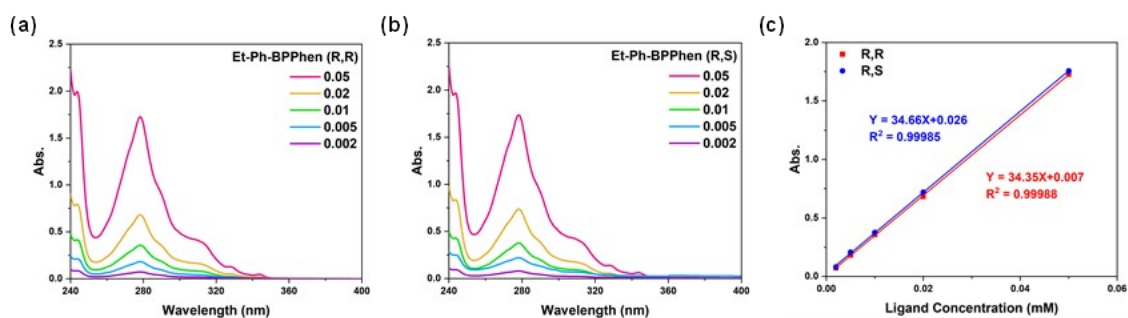


Figure S7. Absorbance curves of (a) Et-Ph-BPPhen(R,R) and (b) Et-Ph-BPPhen(R,S) with different concentrations in CH_3CN , $[\text{L}] = 0.002\text{--}0.05$ mM; (c) Linear relationship between absorbance and concentration of two for two epimers of Et-Ph-BPPhen ligand.

Table S2. Saturation solubility of two for two epimers of Et-Ph-BPPhen ligand in CH_3CN , $T = 293$ K.

Ligand	Solubility	Diluent	Temperature
Et-Ph-BPPhen(R,R)	5.31 mM	CH_3CN	293 K
Et-Ph-BPPhen(R,S)	4.91 mM		

2.3 Solvent extraction

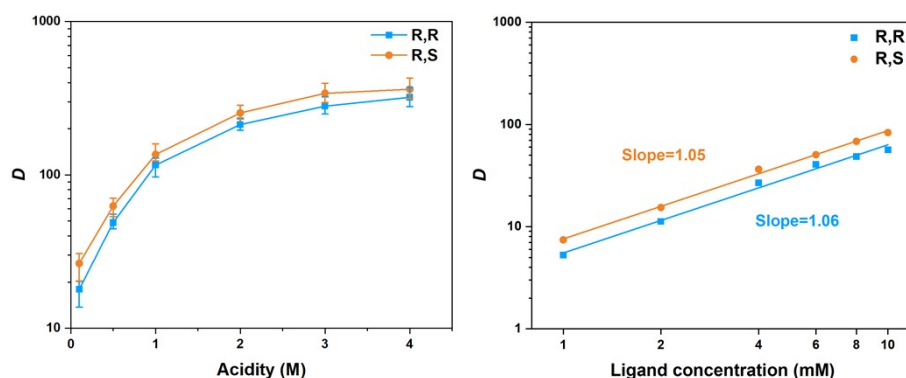


Figure S8. The influence of (a) HNO_3 concentration ($[\text{L}] = 10 \text{ mM}$, $[\text{HNO}_3] = 0.1 - 4.0 \text{ M}$) and (b) ligand concentration ($[\text{L}] = 1-10 \text{ mM}$, $[\text{HNO}_3] = 1.0 \text{ M}$) on the extraction of uranyl by Et-Ph-BPPhen(R,R) and Et-Ph-BPPhen(R,S), $[\text{M}] = 0.01 \text{ mM}$, $V_O/V_A = 1 \text{ mL}/1 \text{ mL}$, $T = 298 \text{ K}$.

2.4 UV-vis titration

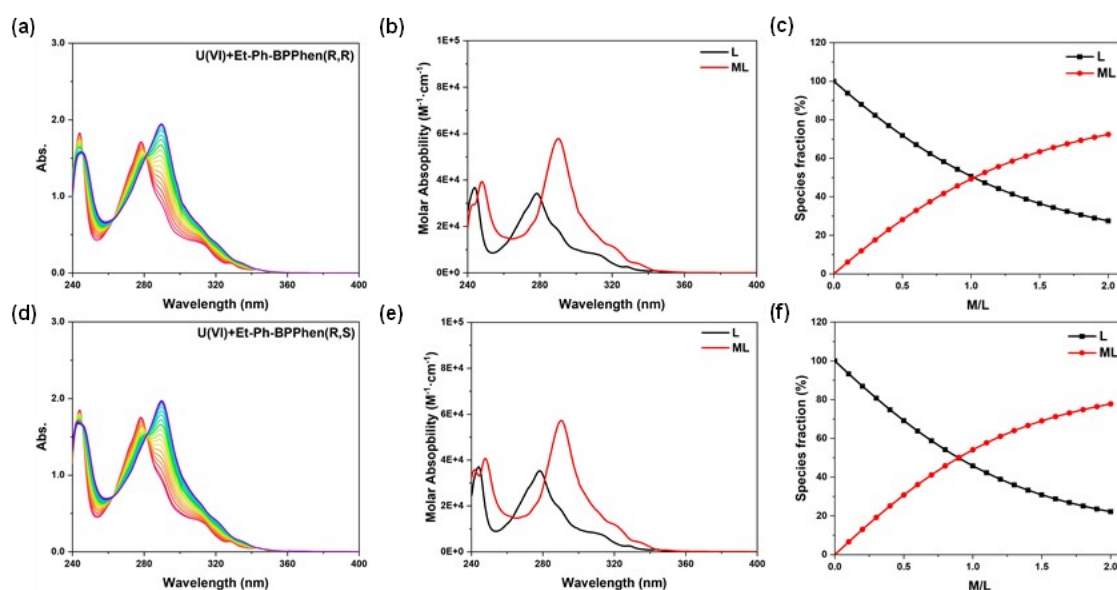


Figure S9. UV-Vis titration spectra of uranyl with (a) Et-Ph-BPPhen(R,R) and (d) Et-Ph-BPPhen(R,S). Molar absorptivity of the ligand and uranyl complexes with (b) Et-Ph-BPPhen(R,R) and (e) Et-Ph-BPPhen(R,S). Species fractions of ligand and uranyl complexes with (c) Et-Ph-BPPhen(R,R) and (f) Et-Ph-BPPhen(R,S) during titration. $[\text{L}] = 0.05 \text{ mM}$, $[\text{M}] = 1 \text{ mM}$, $V_0 = 2 \text{ mL}$, $V_{\text{inj}} = 10 \text{ }\mu\text{L}$, $T = 298 \text{ K}$.

Table S3. The fitted stability constants ($\log \beta$) for formation of uranyl complexes with Et-Ph-BPPhen(R,R) and Et-Ph-BPPhen(R,S) during UV-Vis titration.

Ligand	Reaction	$\log \beta$	Standard deviation	Anion concentration
R,R	$\text{UO}_2^{2+} + \text{L} \rightarrow \text{UO}_2\text{L}^{2+}$	4.98	0.03	10 mM $\text{Et}_4\text{N} \cdot \text{NO}_3$
R,S		5.14	0.02	

2.5 Fluorescence titration

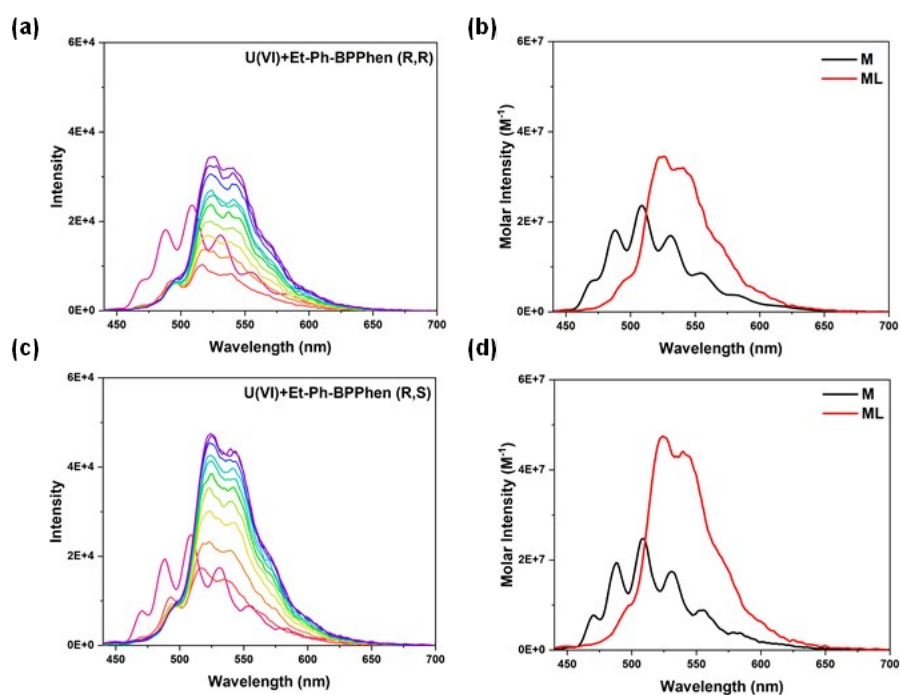


Figure S10. Fluorescence spectra of uranyl with (a) Et-Ph-BPPhen(R,R) and (c) Et-Ph-BPPhen(R,S). Molar intensity of the ligand and uranyl complexes with (b) Et-Ph-BPPhen(R,R) and (d) Et-Ph-BPPhen(R,S). $[\text{M}] = 1 \text{ mM}$, $[\text{L}] = 5 \text{ mM}$, $V_0 = 2 \text{ mL}$, $V_{\text{inj}} = 40 \text{ }\mu\text{L}$, $T = 298 \text{ K}$, $\lambda_{\text{EX}} = 420 \text{ nm}$.

2.6 Isothermal micro-thermometric titration

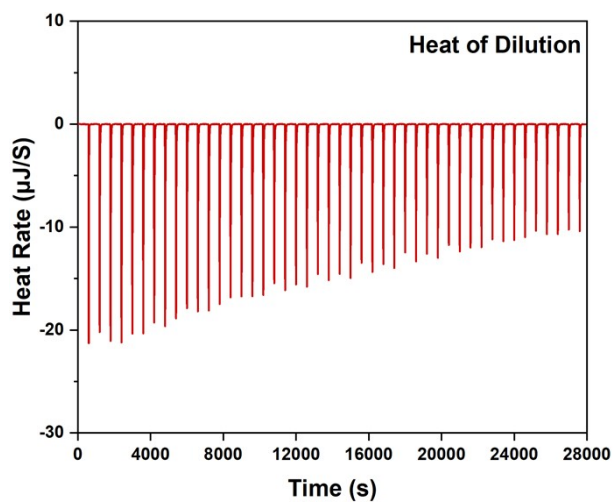


Figure S11. Heat of dilution in ITC experiment. $V_0 = 0.4$ mL, $V_{inj} = 1$ μ L, $[L] = 5 \times 10^{-3}$ mol/L, $T = 298$ K.

2.7 Single-crystal X-ray diffraction

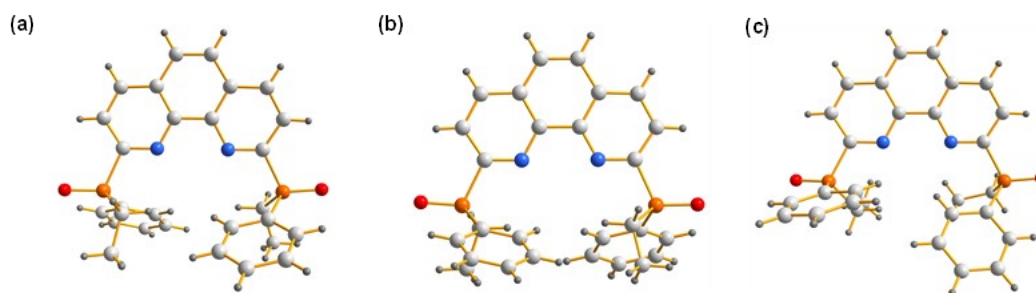


Figure S12. Crystal structure of (a) Et-Ph-BPPhen(R,R), (b) Et-Ph-BPPhen(S,S), and (c) Et-Ph-BPPhen(R,S).

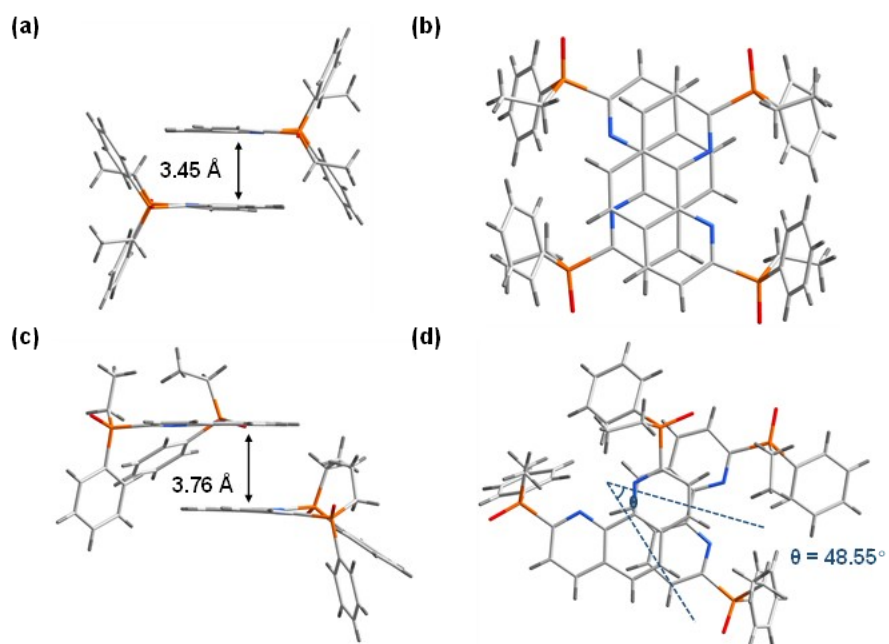


Figure S14. Stacking model of Et-Ph-BPPhen(R,R/S,S): (a) side view, (b) top view; Stacking model of Et-Ph-BPPhen(R,S): (c) side view, (d) top view.

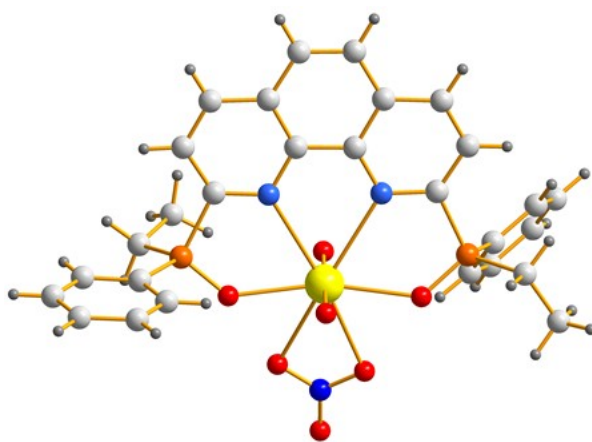


Figure S15. Crystal structure of $[\text{UO}_2(\text{S,S})\text{NO}_3]^+$.

Table S4. Crystal data and structure refinement for Et-Ph-BPPhen(R,R/S,S) and Et-Ph-BPPhen(R,S).

Name	Et-Ph-BPPhen(R,R/S,S)	Et-Ph-BPPhen(R,S)
CCDC number	2293651	2293650
Empirical formula	C ₂₈ H ₂₆ N ₂ O ₂ P ₂	C ₂₈ H ₂₆ N ₂ O ₂ P ₂
Formula weight	484.45	484.45
Temperature/K	170.00	170.00
Crystal system	triclinic	monoclinic
Space group	P-1	P21/c
<i>a</i> /Å	8.2310(3)	10.1143(4)
<i>b</i> /Å	11.7984(5)	28.2649(12)
<i>c</i> /Å	13.6524(5)	8.4249(4)
α /°	73.8290(10)	90
β /°	85.3630(10)	98.202(2)
γ /°	76.8650(10)	90
Volume/Å ³	1239.83(8)	2383.87(18)
<i>Z</i>	2	4
$\rho_{\text{calc}}/\text{cm}^3$	1.298	1.350
μ/mm^{-1}	0.204	1.232
F(000)	508.0	1016.0
Crystal size/mm ³	0.42 × 0.35 × 0.28	0.18 × 0.09 × 0.07
Radiation	MoK α (λ = 0.71073)	GaK α (λ = 1.34139)
2 Θ range for data collection/°	4.13 to 55.122	7.684 to 121.782
Index ranges	-10 ≤ <i>h</i> ≤ 10, -15 ≤ <i>k</i> ≤ 15, -17 ≤ <i>l</i> ≤ 13, -35 ≤ <i>k</i> ≤ 36, -10 ≤ <i>l</i> ≤ 17	-13 ≤ <i>h</i> ≤ 13, -35 ≤ <i>k</i> ≤ 36, -10 ≤ <i>l</i> ≤ 10
Reflections collected	62474	59219
Independent reflections	5697 [R _{int} = 0.0295, R _{sigma} = 0.0165]	5466 [R _{int} = 0.0625, R _{sigma} = 0.0310]
Data/restraints/parameters	5697/0/309	5466/0/309
Goodness-of-fit on F ²	1.085	1.059
Final R indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	R ₁ = 0.0332, wR ₂ = 0.0887	R ₁ = 0.0387, wR ₂ = 0.0983
Final R indexes [all data]	R ₁ = 0.0351, wR ₂ = 0.0903	R ₁ = 0.0434, wR ₂ = 0.1009
Largest diff. peak/hole / e Å ⁻³	0.34/-0.33	0.31/-0.37

Table S5. Crystal data and structure refinement for $[\text{UO}_2(\text{R,R})\text{NO}_3]_2 \cdot [\text{UO}_2(\text{S,S})\text{NO}_3]_2 \cdot [\text{UO}_2(\text{NO}_3)_4]$ and $[\text{UO}_2(\text{R,S})\text{NO}_3] \cdot \text{H}_2\text{O} \cdot \text{C}_3\text{H}_6\text{O}$.

Name	$[\text{UO}_2(\text{R,R})\text{NO}_3] \cdot [\text{UO}_2(\text{S,S})\text{NO}_3] \cdot [\text{UO}_2(\text{NO}_3)_4]$	$[\text{UO}_2(\text{R,S})\text{NO}_3] \cdot 0.5\text{H}_2\text{O} \cdot \text{C}_3\text{H}_6\text{O}$
CCDC number	2293649	2271317
Empirical formula	$\text{C}_{56}\text{H}_{52}\text{N}_{10}\text{O}_{28}\text{P}_4\text{U}_3$	$\text{C}_{62}\text{H}_{66}\text{N}_6\text{O}_{17}\text{P}_4\text{U}_2$
Formula weight	2151.04	1767.14
Temperature/K	170.00	170
Crystal system	monoclinic	monoclinic
Space group	$\text{P}2_1/\text{c}$	$\text{C}2/\text{c}$
$a/\text{\AA}$	19.1125(8)	31.0258(11)
$b/\text{\AA}$	10.6852(4)	12.8733(5)
$c/\text{\AA}$	17.9947(7)	16.8307(6)
$\alpha/^\circ$	90	90
$\beta/^\circ$	107.7160(10)	114.1570(10)
$\gamma/^\circ$	90	90
Volume/ \AA^3	3500.6(2)	6133.6(4)
Z	2	4
$\rho_{\text{calc}}/\text{cm}^3$	2.041	1.914
μ/mm^{-1}	15.608	12.167
F(000)	2036.0	3440
Crystal size/ mm^3	$0.07 \times 0.05 \times 0.03$	$0.114 \times 0.11 \times 0.052$
Radiation	$\text{GaK}\alpha$ ($\lambda = 1.34139$)	$\text{GaK}\alpha$ ($\lambda = 1.34139$)
2Θ range for data collection/ $^\circ$	4.222 to 121.67	5.432 to 107.804
Index ranges	$-24 \leq h \leq 24, -13 \leq k \leq 13, -23 \leq l \leq 23$	$-37 \leq h \leq 34, 0 \leq k \leq 15, 0 \leq l \leq 20$
Reflections collected	43861	5502
Independent reflections	7954 [$R_{\text{int}} = 0.0665, R_{\text{sigma}} = 0.0501$]	5502 [$R_{\text{int}} = ?, R_{\text{sigma}} = 0.0626$]
Data/restraints/parameters	7954/0/459	5502/96/450
Goodness-of-fit on F^2	1.082	1.114
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0375, wR_2 = 0.0793$	$R_1 = 0.0470, wR_2 = 0.1111$
Final R indexes [all data]	$R_1 = 0.0487, wR_2 = 0.0827$	$R_1 = 0.0483, wR_2 = 0.1121$
Largest diff. peak/hole / $e \text{\AA}^{-3}$	1.23/-1.18	3.31/-2.14