Electronic Supplementary Information (ESI)

Identification of Complexes of Nd(III) with Dithiophosphinic Acids Verifying Difference in Complexation between Ln(III) and An(III)

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Detailed Experimental Information

Chemicals and Reagents

Cyanex 301 which contains about 70% Bis(2,4,4-trimethylpentyl) dithiophosphinic acid (denoted as HA), provided by the Institute of Nuclear and New Energy Technology of Tsinghua University, was purified by the reported procedure[1] and stored as the form of ammonium salt. The purity of the purified product was examined by ^{31}P-NMR. The content of HA was determined to be higher than 99% (w/w) by acid-base titration. The 50% aqueous solution of (iso-C_4H_9)$_2PS_2Na$ was purchased from Gelest Inc. (America). All other reagents are of analytical grade, purchased from the China National Pharmaceutical Group Corporation. The HA-toluene solution was prepared by the extraction of HA to the diluent after acidification with 3.0 M HCl. Milli-Q water was used in preparing all aqueous solutions. No attempts were made to control the ionic strength in the experiments.

Extraction

Add 2 mL HA-toluene solution and 1 mL $Nd(NO_3)_3$ stock solutions into one flat-bottom vial, then add certain amounts of NaOH solution according to the desired percentage of neutralization (5%, 10%, 20%, 40%, 60%, 80%, 90%, 95%), and finally add Milli-Q water to make sure the phase volume ratio, V_o/V_a, as 1.

Stir vigorously using magnetic stirrer under 10, 25 or 45℃ water bath for 2 hours to ensure the complete extraction. After the extraction, leave the bottle still for 1 hour under water bath to allow the separation of the two phases. Transfer 1.0 mL of the organic phase into a 10×4 mm quartz cuvette for absorption spectra measurement.

The Nd(III)-loaded organic phase was stripped (V_o/V_a = 1) by 1.0 M HNO_3 solution for 30 minutes under magnetic stirring. After separation, transfer 1.0 mL of the aqueous phase into a 10×4 mm quartz cuvette for absorption spectra measurement. The concentration of Nd(III) in the initial Nd(III)-loaded organic phases can be calculated by the absorption spectra of the aqueous phase of stripping.

Spectrophotometry

The absorption spectra of the organic phases were collected on an Agilent Cary 7000 UV-Vis-NIR Spectrophotometer, in the range of 490-630 nm, with an interval of 0.1 nm and a bandwidth of 0.5 nm. A semiconductor temperature control accessories was used to control the temperature of the samples.

The molar absorption spectra were obtained by normalizing the absorption spectra with the concentration of Nd(III) in organic phases.

The deconvoluted absorption spectra of species I, II and III were calculated by Multivariate Curve Resolution-Alternating Least Squares(MCR-ALS) method[2]. The distribution of the three species under different conditions can be calculated by absorption spectrophotometry, based on the deconvoluted absorption spectra of species I, II and III.

Water Content

The water contents of the organic phases were determined by Karl Fischer coulometry on a Metrohm 852 water analyzer.

The water content of the extracted complex(W_e) was calculated as following equation:

$$W_e = W_o - W_b \quad (1)$$

W_o is the water content of the samples after extraction, and W_b is the blank water content of the organic sample when the percent neutralization(α) is 0.

The accuracy of this method to determine the water content in this system has been examined by the standard addition experiments: (1) Mix the HA-toluene solutions or organic phases at different Nd(III) loadings with certain amount of methanol containing water at different volume ratios (3:1, 2:1, 1:1, 1:2, 1:3); (2) Determine the water content of each sample (organic phase before mixing, mixed samples, methanol) by Karl Fischer coulometry analysis method.

The results showed a good linear relationship of the water concentration to the response signal, which indicated that the presence of HA did not affect the measurement of water content by Karl Fischer coulometry analysis method.

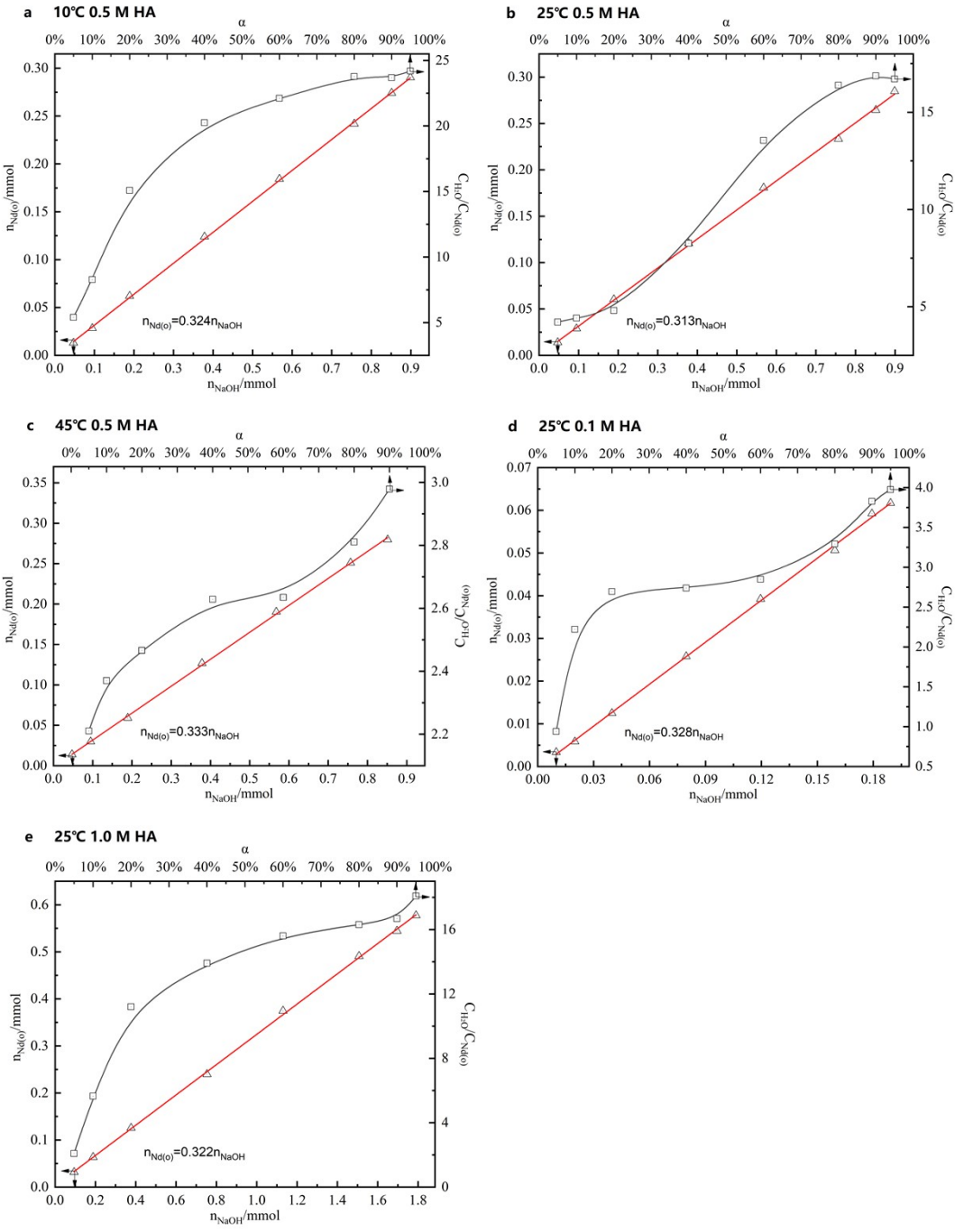

Fig. S1 The relationships between loaded Nd(III) to NaOH added for neutralization (red line, lower x-axis and left y-axis) and to the water content of the extracted complex (black curve, upper x-axis and right y-axis) prepared under different conditions. α refers to the percent neutralization.

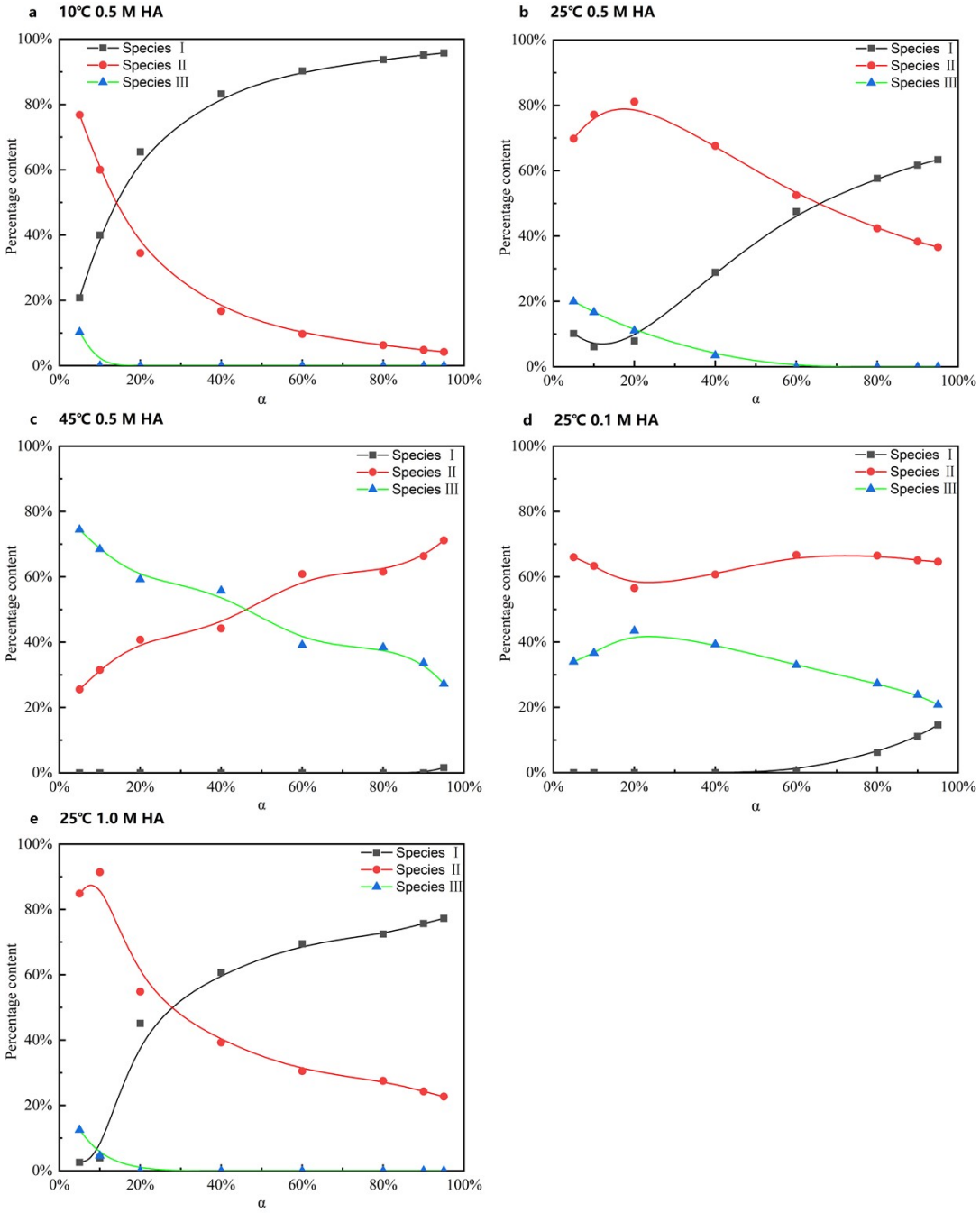

Fig. S2 The distribution of the three species under different conditions. α refers to the percent neutralization.

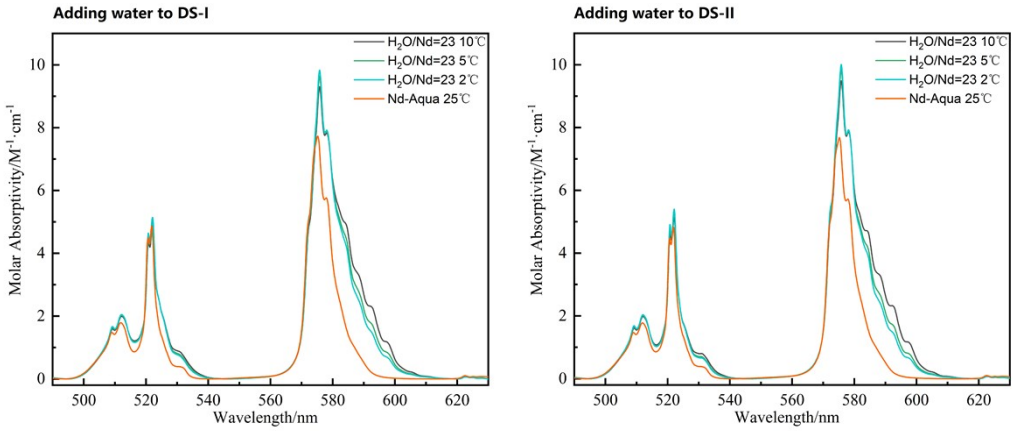

Fig. S3 Spectra of DS-I and DS-II samples with water added at low temperature.

Table S1. Crystal Data and Structure Refinement for $Nd(H_2O)_9 \cdot H_2O \cdot 3B$ (HB = bis(iso-butyl)dithiophosphinic acid)

Complex	$Nd(H_2O)_9 \cdot H_2O \cdot 3\mathbf{B}$
Empirical formula	$C_{24}H_{74}NdO_{10}P_3S_6$
Formula weight	952.34
Temperature	100.02(10) K
Radiation	MoKα (λ =0.71073)
Crystal system, space group	Monoclinic, $P2_1/c$
Unit cell parameters	a =16.9097(4) Å, α =90°
	b =25.6255(5) Å, β =98.040(2)°
	c =10.9443(3) Å, γ =90°
Cell volume	4695.76(19) $Å^3$
Z	4
Calculated density	1.347 g/cm^3
Absorption coefficient	1.514 mm^{-1}
F(000)	1996.0
Crystal size	0.2 × 0.2 × 0.15 mm^3
Range for data collection	6.544 to 62.358°
Index ranges	-21 ≤ h ≤ 21, -32 ≤ k ≤ 36, -14 ≤ l ≤ 15
Reflections collected	44211
Independent reflections	11970 [R_{int} = 0.0589, R_{sigma} = 0.0519]
Data/restraints/parameters	11970/24/420
Goodness-of-fit on F^2	1.041
Final R indexes [I>=2σ (I)]	R_1 = 0.0578, wR_2 = 0.1495
Final R indexes [all data]	R_1 = 0.0694, wR_2 = 0.1587
Largest diff. peak and hole	6.65 and -1.51 e/$Å^{-3}$

References

1. Y. Zhu, J. Chen and R. Jiao, *Solvent Extraction and Ion Exchange*, 1996, **14**, 61-68.
2. J. Jaumot, A. D. Juan and R. Tauler, *Chemometrics & Intelligent Laboratory Systems*, 2015, **140**, 1-12.