Electronic Supplementary Information (ESI)

Table S1 Potentiometric titration conditions for the p*K*a determination of picolinate (denoted as HL)

Titr. No.	*T*, K	C_L^0, mM	C_H^0, mM	V^0, mL	$C_{tiratant}$(NaOH), mM	$V_{tiatrant}$, mL
1	283	8.395	9.056	18.13	101.0	2.00
2	298	8.400	9.073	18.12	101.0	2.00
3	313	8.405	9.056	18.12	101.5	2.00
4	328	8.355	9.045	18.12	101.5	2.00
5	343	12.69	13.65	24.14	101.5	3.50

Table S2 Calorimetric titration conditions for the enthalpy determination of picolinate (denoted as HL) protonation

Titr. No.	*T*, K	C_L^0, mM	C_H^0, mM	V^0, mL	$C_{tiratant}$($HClO_4$), mM	$V_{tiatrant}$, mL
1	298	13.49	1.300	0.900	91.5	0.230
2	298	61.50	5.911	0.900	91.5	0.220

Table S3 Selected speciation data points of Fig. 4. Speciation simulation conditions: C_{Np} = 0.10 M (constant), C_L = 0.30 M (constant), pH varied from 0.5 to 5.0, I = 1.0 M $NaClO_4$

pH	Molar Fraction (%, relevant to total concentration of Np)					
	NpO_2^+		NpO_2L(aq)		$NpO_2L_2^-$	
	298 K	343 K	298 K	343 K	298 K	343 K
0.500	97.23	97.93	2.76	2.07	0.01	0.00
0.725	95.46	96.58	4.52	3.40	0.02	0.01
0.950	92.65	94.42	7.30	5.55	0.05	0.03
1.175	88.36	91.04	11.51	8.87	0.13	0.09
1.400	82.11	85.96	17.55	13.81	0.33	0.23
1.625	73.63	78.76	25.58	20.68	0.79	0.57
1.850	63.04	69.28	35.21	29.41	1.75	1.31
2.075	51.07	57.93	45.34	39.29	3.59	2.79
2.300	38.88	45.64	54.35	48.88	6.77	5.48
2.525	27.73	33.70	60.51	56.41	11.77	9.89
2.750	18.50	23.27	62.61	60.34	18.88	16.38
2.975	11.57	15.04	60.37	59.94	28.06	25.02
3.200	6.80	9.12	54.41	55.50	38.79	35.38
3.425	3.76	5.21	46.04	48.15	50.19	46.64
3.650	1.97	2.81	36.76	39.40	61.27	57.79
3.875	0.97	1.45	27.85	30.65	71.18	67.90
4.100	0.46	0.72	20.16	22.90	79.39	76.38
4.325	0.21	0.35	14.08	16.67	85.71	82.98
4.550	0.09	0.17	9.62	12.04	90.29	87.79
4.775	0.04	0.09	6.54	8.82	93.42	91.09
5.000	0.02	0.05	4.52	6.69	95.47	93.26

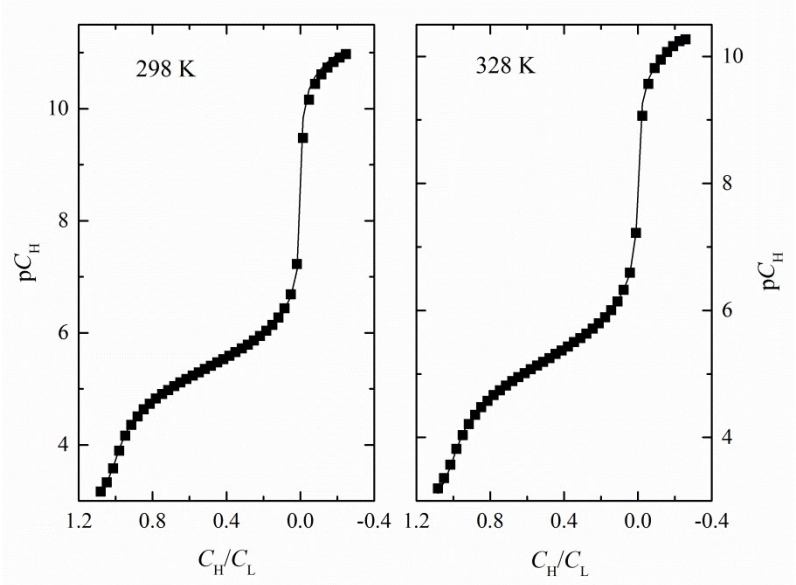

Fig. S1 Fitting of potentiometric titration data for the p*K*a determination at 298 and 328 K. Experimental conditions can be found in Table S1. Symbol (■): measured; solid line: calculated

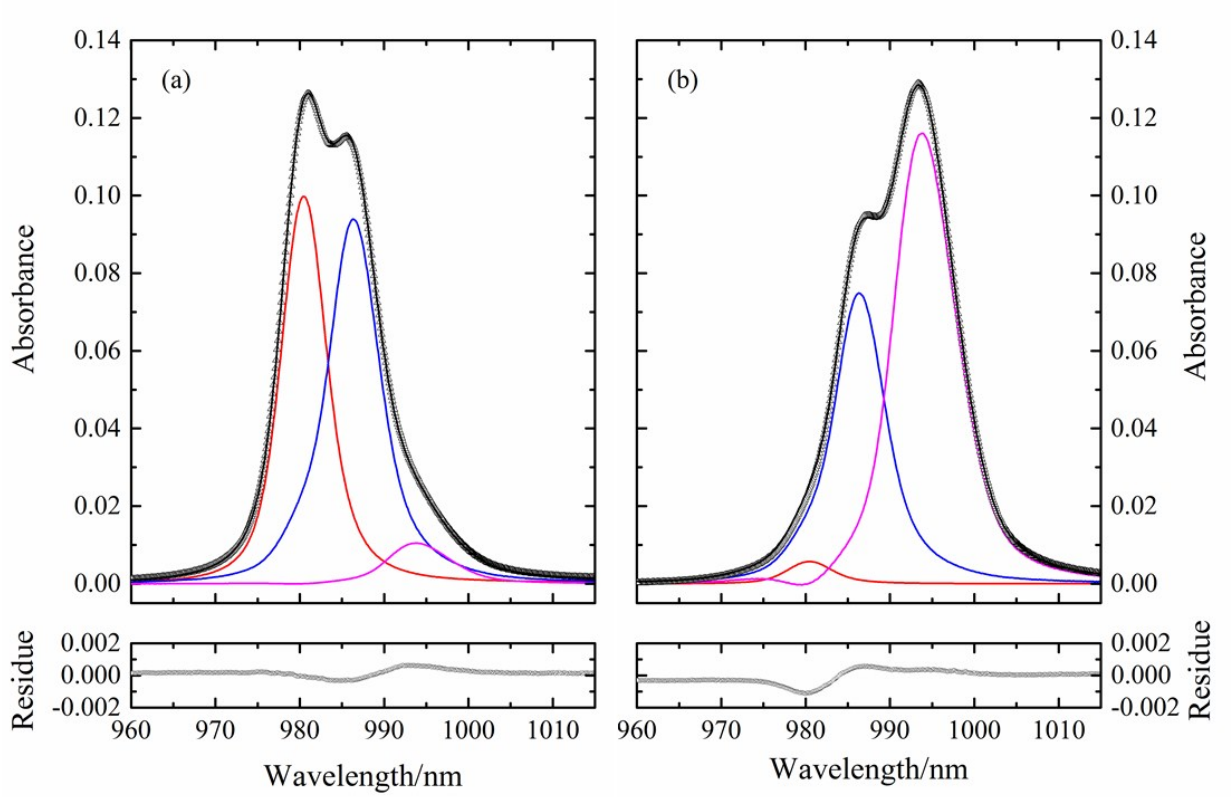

Fig. S2 Spectrum deconvolued results from the 298 K spectrophotometric titration. (a) $V_{titrant}$ = 0.030 mL; (b) $V_{titrant}$ = 0.110 mL. The detailed titration conditions could be found in Table S1. Symbol (Δ): observed absorbance; Solid lines: Calculated absorbance (black), deconvoluted absorbance of NpO_2^+ (red), NpO_2L(aq) (blue) and $NpO_2L_2^-$ (magenta).

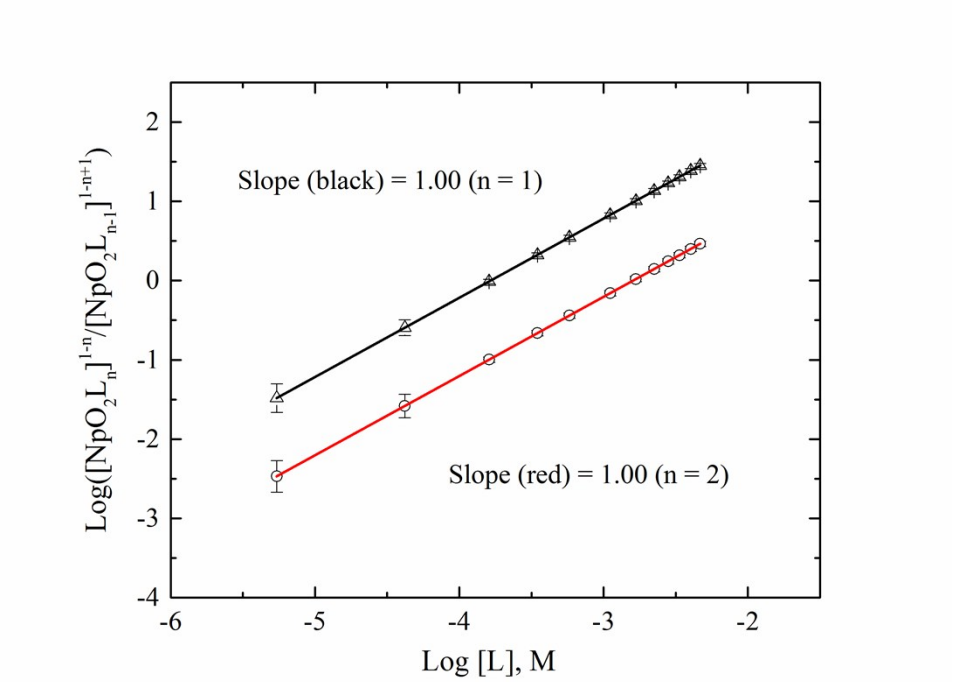

Fig. S3 Slope analysis for the stepwise formation of $NpO_2(L)_n^{1-n}$ (n=1,2) in the spectrophotometric titration at 298 K. (L = picolinate)

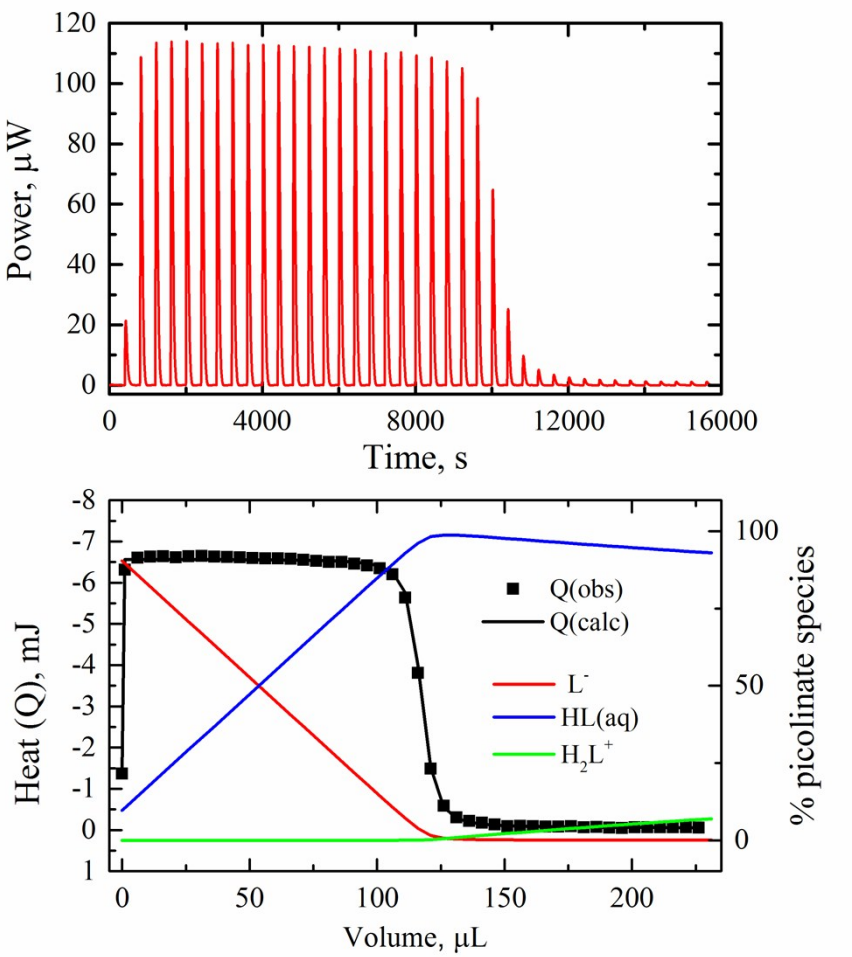

Fig. S4 Calorimetric titration of picolinate protonation (titration NO. 2 in Table S2). Upper graph: thermogram (dilution heat not corrected); lower graph: fitting and speciation. Note: the second protonation of picolinate was included in the fitting using its literature protonation constant log K_{H2} = 0.95.[16] The resulting enthalpy value is –(1.65 ± 1.2) kJ.mol^{-1}, which quite well agrees with the literature value (-2.1 kJ.mol^{-1} from the Martel database[16]).