

Supporting Information

Table S1. Detailed conditions of the U/PDA solutions for NMR analysis

Solution	$W(\text{HL})$ mg	$V(\text{HClO}_4)$ μL	$V(\text{NaOH})$ μL	$V(\text{U-stock})$ μL	$V(\text{D}_2\text{O})$ μL	$[\text{U}]$ mM	$[\text{L}]$ mM	$[\text{H}]$ mM	L/M
A	10.0	0.0	0.0	0.0	1000.0	0.00	80.6	80.6	-
B	10.0	50.4	0.0	50.0	899.6	12.95	80.6	137.0	6.2
C	10.0	55.2	0.0	10.0	934.8	2.59	80.6	137.0	31.1
D	10.0	17.1	0.0	19.3	963.6	5.00	80.6	100.0	16.1
E	10.0	0.0	38.0	19.3	942.7	5.00	80.6	120.9	16.1

Table S2. Speciation of the NMR solutions calculated by HySS 2009

Solution	pH(calc)	Speciation of PDA (%)						Speciation of U(VI) (%)			
		L	HL	H ₂ L	UL	UL ₂	UL ₃	U	UL	UL ₂	UL ₃
A	2.14	14.9	79.3	5.8	-	-	-	-	-	-	-
B	1.34	1.8	59.2	27.1	6.9	4.7	0.4	41.8	42.6	14.7	0.8
C	1.41	4.8	68.0	26.7	1.4	1.3	0.2	32.8	44.8	20.8	1.6
D	1.72	5.2	72.2	13.9	2.5	5.0	1.2	13.5	39.9	39.9	6.6
E	2.77	37.7	46.3	0.8	0.4	5.3	9.6	0.3	5.8	42.5	51.4

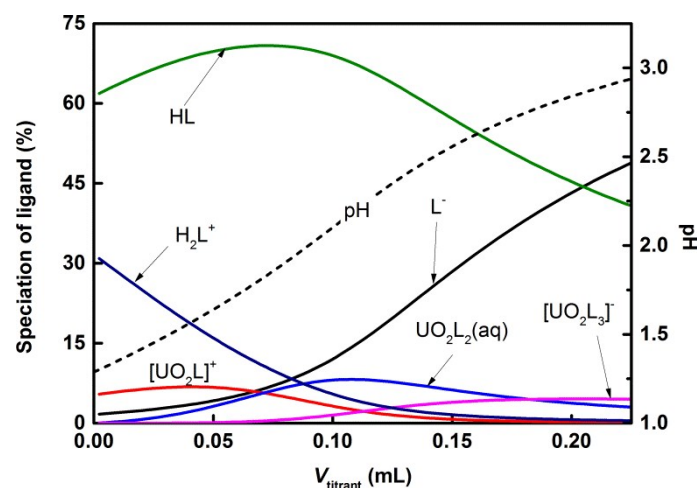


Fig. S1. Speciation of PDA in the calorimetric titration of U(VI)/PDA complexation by HySS. Experimental conditions: titrant: 0.400 M NaL, 0.005 mL $\times$ 45 additions; initial solution: $V^0 = 0.750$ mL, $C_U^0 = 5.280 \times 10^{-3}$ mol $\cdot$ dm⁻³, $C_H^0 = 5.187 \times 10^{-2}$ mol $\cdot$ dm⁻³.

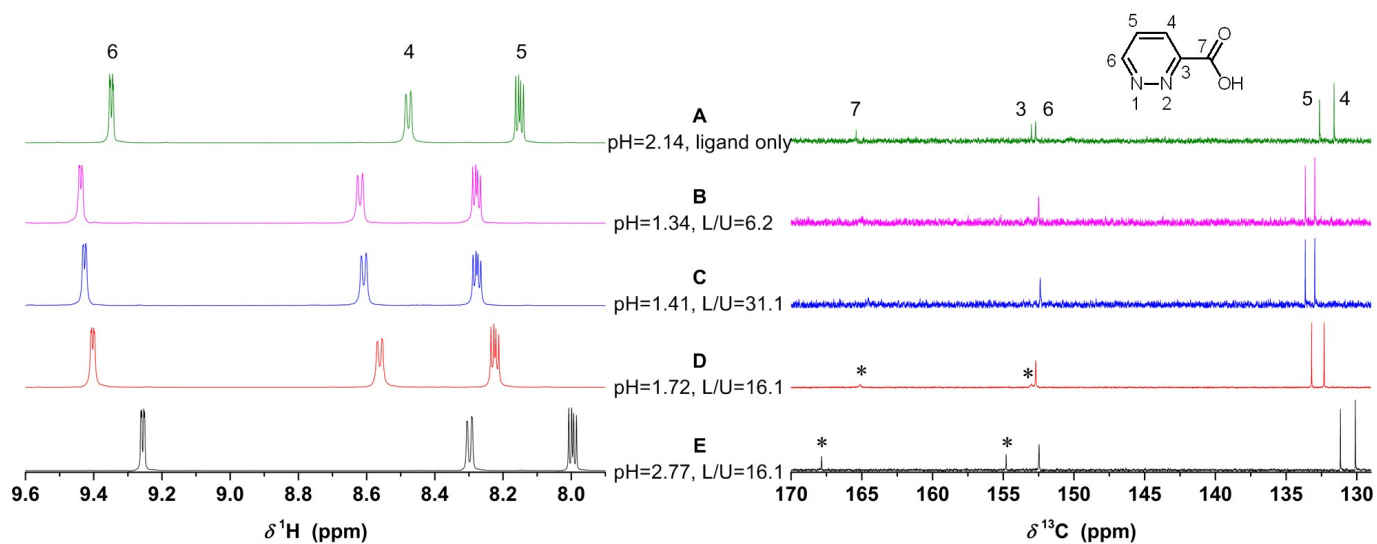


Fig. S2. ^1H (left) and ^{13}C NMR (right) spectra of PDA solutions at 298 K. Detailed conditions of the solutions are provided in ESI, Table S1 and S2.

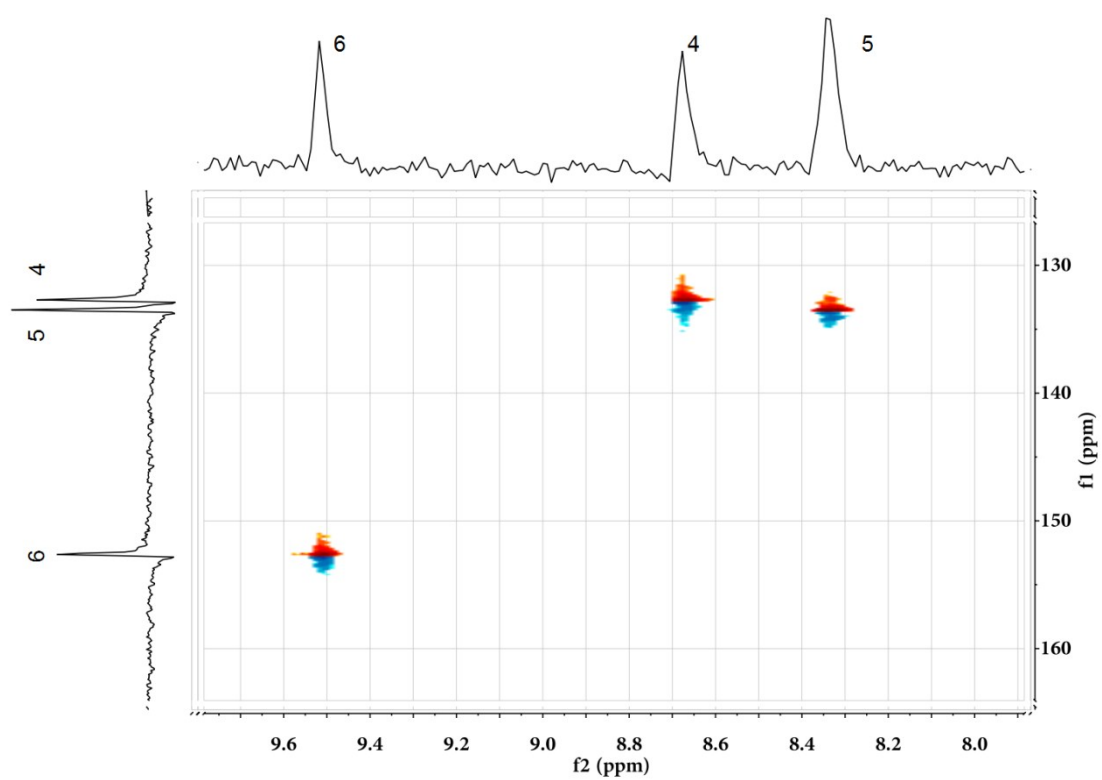


Fig. S3. ^1H - ^{13}C COSY spectrum of solution A