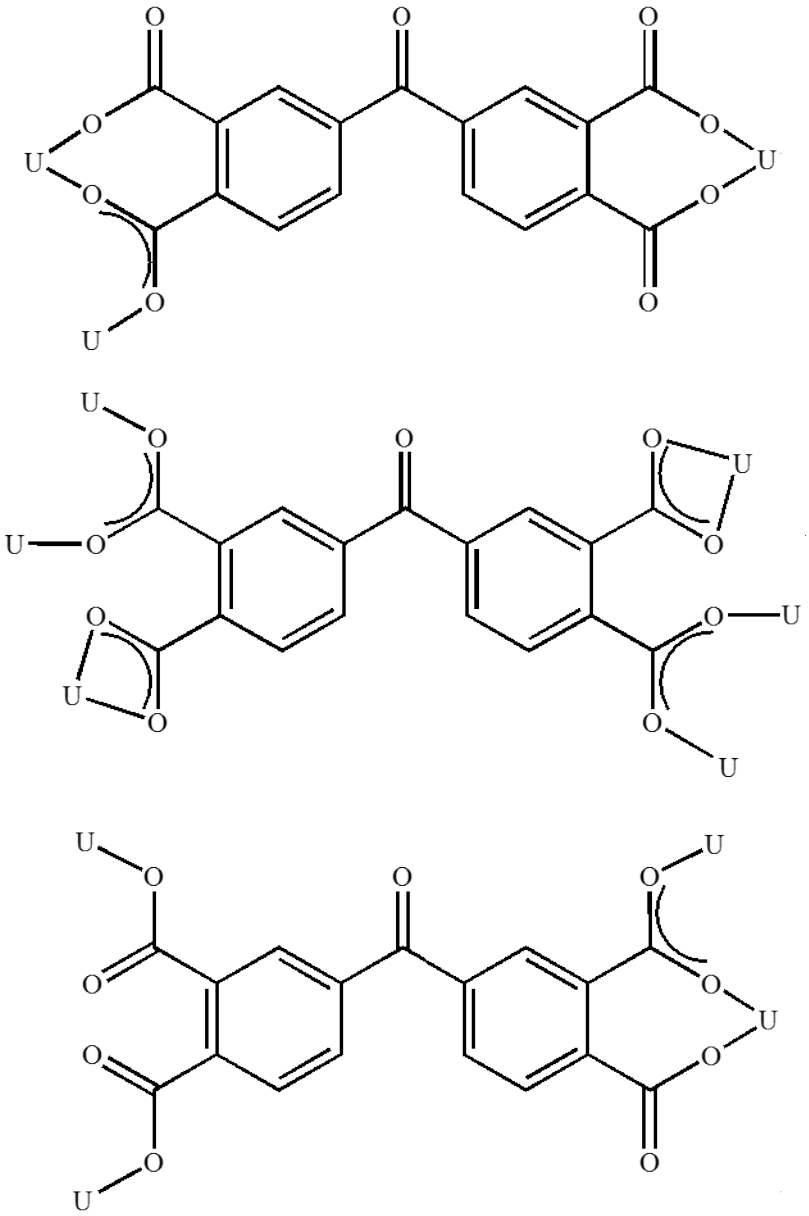
Two Novel Uranyl Complexes of Semi-rigid Aromatic Tetracarboxylic Acid Supported by Organic Base as Auxiliary Ligand or Templating Agent: an Experimental and Theoretical Exploration

Liu-Zheng Zhu,[a,b,†] Cong-Zhi Wang,[b,†] Lei Mei,[b] Lin Wang,[b] Yun-Hai Liu,*[a] Zhen-Tai Zhu,[d] Yu-Liang Zhao,[b] Zhi-Fang Chai,[b,c] and Wei-Qun Shi*[b]

Supporting Information

Table of contents



Scheme S1. The different coordination modes of $bptc^{4-}$ ligand in **1** and **2**

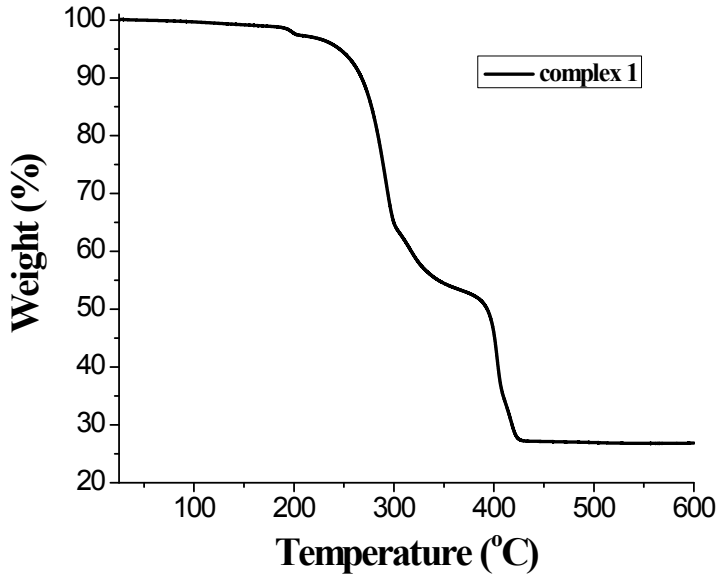


Fig. S1. The TGA diagrams of complex **1.**

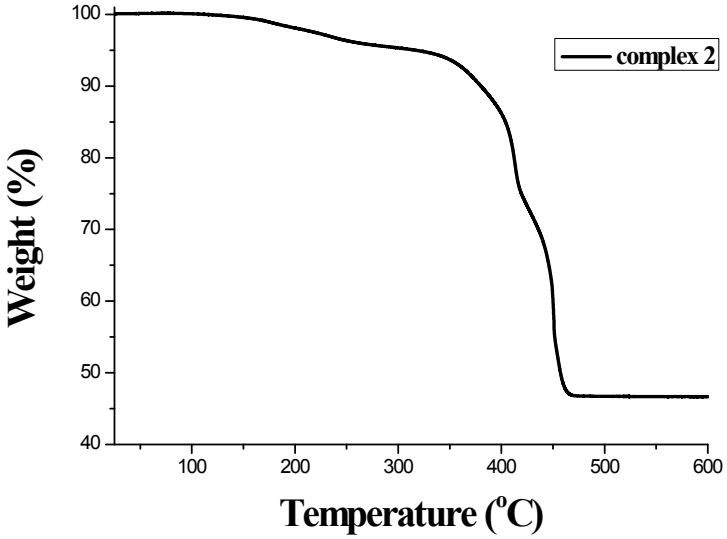


Fig. S2. The TGA diagrams of complex **2.**

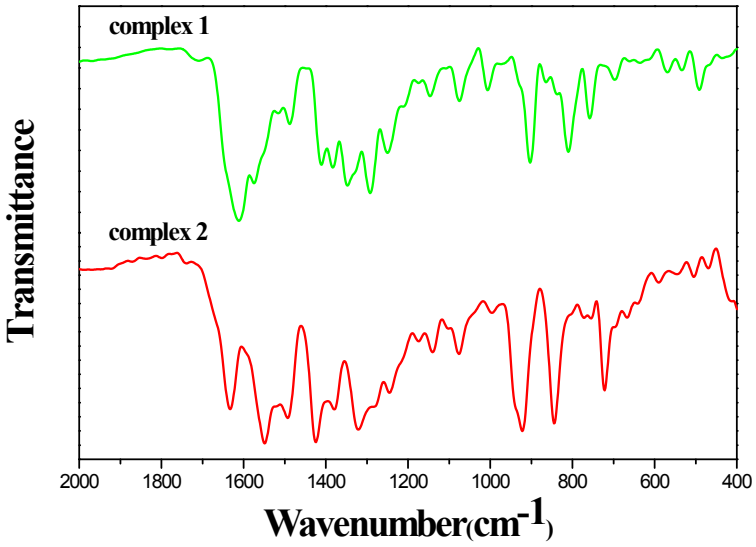


Fig. S3. The IR spectra of complex **1** and **2**.

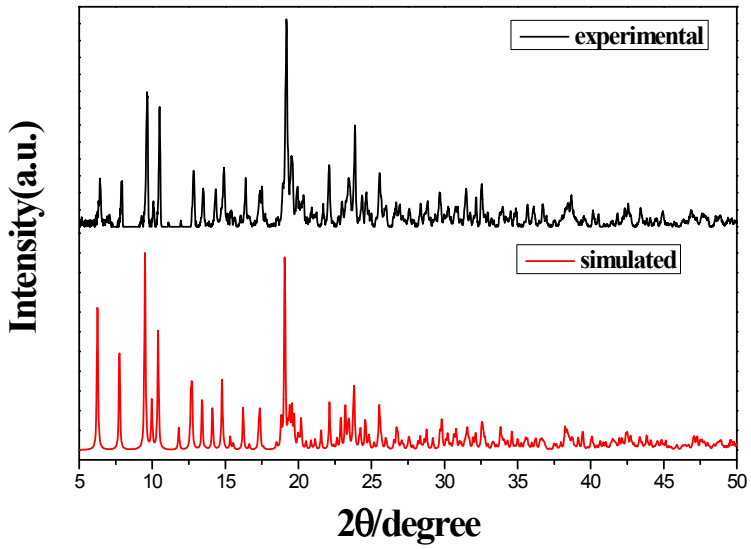


Fig. S4. Powder X-ray diffraction patterns of complex **1**.

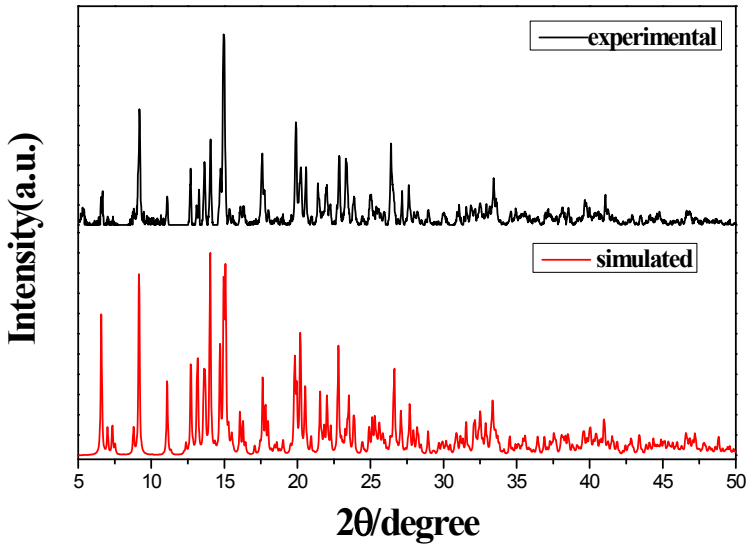


Fig. S5. Powder X-ray diffraction patterns of complex **2**.

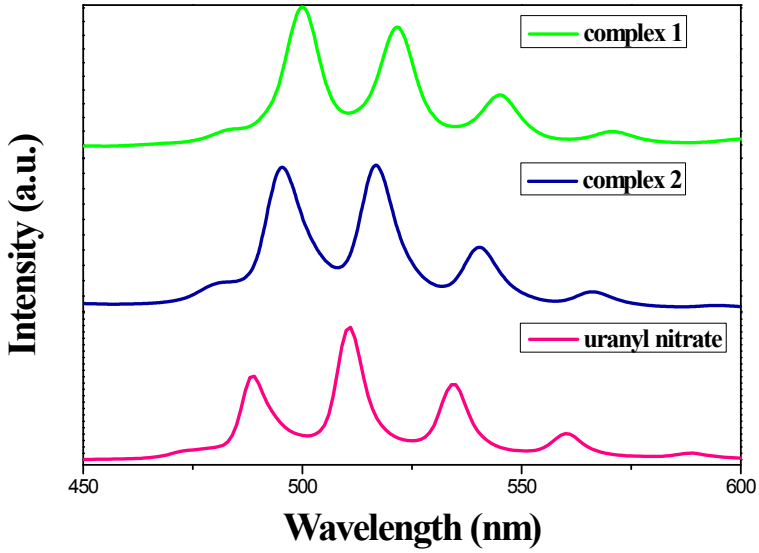


Fig. S6. Solid-state fluorescence spectra of complex **1**, **2** and uranyl nitrate (λ_{ex}=310nm).

Table S1. Selected Calculated and Experimental Bond Lengths (Å) of the U-O Bonds, Mayer Bond Order, and the Electron Density (ρ, a.u.) at U-O Bond Critical Points for the Model Fragments of Complex **1**.

Complex **1**		U1=O1	U1=O2	U1-O3	U1-O5	U1-O7	U1-O9	U1-O10
Bond Lengths	Calc.	1.788	1.788	2.376	2.385	2.345	2.412	2.417
	Exp.	1.784(4)	1.774(4)	2.328(4)	2.319(5)	2.364(4)	2.417(5)	2.383(4)
Mayer Bond Order		2.053	2.055	0.470	0.458	0.506	0.407	0.396
ρ		0.2894	0.2895	0.0652	0.0634	0.0698	0.0575	0.0589
		U1'=O1'	U1'=O2'	U1'-O3'	U1'-O5'	U1'-O7'	U1'-O9'	U1'-O10'
Bond Lengths	Calc.	1.787	1.787	2.399	2.388	2.342	2.415	2.400
	Exp.	1.784(4)	1.774(4)	2.328(4)	2.319(5)	2.364(4)	2.417(5)	2.383(4)
Mayer Bond Order		2.059	2.063	0.440	0.448	0.504	0.396	0.401
ρ		0.2901	0.2901	0.0616	0.0627	0.0695	0.0566	0.0600

Table S2. Selected Calculated and Experimental Bond Lengths (Å) of the U-O and U-N Bonds, Mayer Bond Order, and the Electron Density (ρ, a.u.) at U-O and U-N Bond Critical Points for the Model Fragments of Complex **2**.

Complex **2**-U1		U1=O13	U1=O14	U1-O7	U1-O11	U1-O12	U1-N3	U1-N4
Bond Lengths	Calc.	1.789	1.789	2.340	2.284	2.369	2.662	2.658
	Exp.	1.77(1)	1.77(1)	2.31(1)	2.279(9)	2.369(7)	2.640(9)	2.61(1)
Mayer Bond Order		2.049	2.068	0.463	0.565	0.424	0.305	0.310
ρ		0.2891	0.2887	0.0693	0.0779	0.0640	0.0511	0.0435
Complex **2**-U2		U2=O1	U2=O2	U2-O3	U2-O4	U2-O5	U2-N1	U2-N2
Bond Lengths	Calc.	1.785	1.785	2.455	2.481	2.255	2.591	2.619
	Exp.	1.77(1)	1.76(1)	2.410(9)	2.436(9)	2.26(1)	2.523(9)	2.56(1)
Mayer Bond Order		2.086	2.065	0.442	0.390	0.595	0.330	0.321
ρ		0.2920	0.2919	0.0598	0.0564	0.0808	0.0511	0.0482
Complex **2**-U3		U3=O18	U3=O19	U3-O16	U3-O17	U3-O20	U3-O21	U3-O22
Bond Lengths	Calc.	1.816	1.801	2.518	2.252	2.454	2.518	2.528
	Exp.	1.75(1)	1.74(1)	2.34(2)	2.38(2)	2.37(1)	2.41(1)	2.48(2)
Mayer Bond Order		1.863	2.055	0.352	0.628	0.372	0.361	0.272
ρ		0.2674	0.2790	0.0407	0.0787	0.0543	0.0480	0.0468

Table S3. Percent Contribution of the U-O and U-N Bonding in Complexes **1** and **2**.

Species	Orbitals	Element	Contributions of Each Atomic Orbital (%)			
			2p	5f	6d	7p
Complex **1**	a	U1		2	3	
		U1'		4		1
		O3'	2			
		O5'	2			
		O7'	3			
		O9	7			
		O9'	12			
		O10	5			
		O10'	16			
	b	U1		1		
		U1'		4		
		O3	4			
		O3'	5			
		O5	5			
		O5'	11			
		O7	3			
		O7'	7			
		O9	2			
		O9'	2			
		O10	3			
		O10'	5			
	c	U1		3	1	
		U1'		4	1	1
		O3	7			
		O3'	13			
		O7	2			
		O7'	1			
		O9	7			
		O10	4			
		O10'	2			
	d	U1		3		
		U1'		2		
		O3	5			
		O3'	2			
		O5	1			
		O5'	7			
		O7'	6			

		O9'	14			
		O10	20			
		O10'	2			
		U1		2		
		U1'		2		
		O3	1			
		O3'	7			
	e	O5	7			
		O7	8			
		O9	9			
		O10	2			
		O10'	14			
		U1		4		1
		U1'		3		
		O3	8			
		O3'	8			
		O5	6			
	f	O5'	5			
		O7'	1			
		O9	12			
		O9'	2			
		O10	2			
		O10'	12			
		U3		1		
		O16	2			
	a	O20	5			
		O21	20			
		O22	41			
		U3		9		2
		O16	2			
	b	O17	13			
Complex **2**		O20	3			
		O21	2			
		U3		5		1
		O16	2			
	c	O17	13			
		O20	3			
		U3		3		1
	d	O16	5			
		O17	7			

	O20	8			
	U1		24		5
	N1	5			
e	O3	5			
	O4	4			
	O5	4			
	U2		7		2
f	N1	2			
	O3	4			
	O4	1			
	U2		2		
	N1	3			
g	N2	6			
	O3	7			
	O4	11			
	O5	7			
	U2		2	1	2
	N1	6			
h	N2	2			
	O3	3			
	O4	17			
	O5	36			
	U1		19		4
	N4	1			
i	O7	2			
	O11	1			
	O12	3			
	U1		3		1
	N3	1			
j	N4	2			
	O11	3			
	O12	8			
	U1		1		3
	N3	6			
k	O7	14			
	O11	4			
	O12	10			
	U1		3		
l	O7	13			
	O11	7			
	O12	3			