

The solution chemistry and reactivity of lacunary Keggin silicotungstates monitored in real-time by a combination of mass spectrometry and electrochemistry

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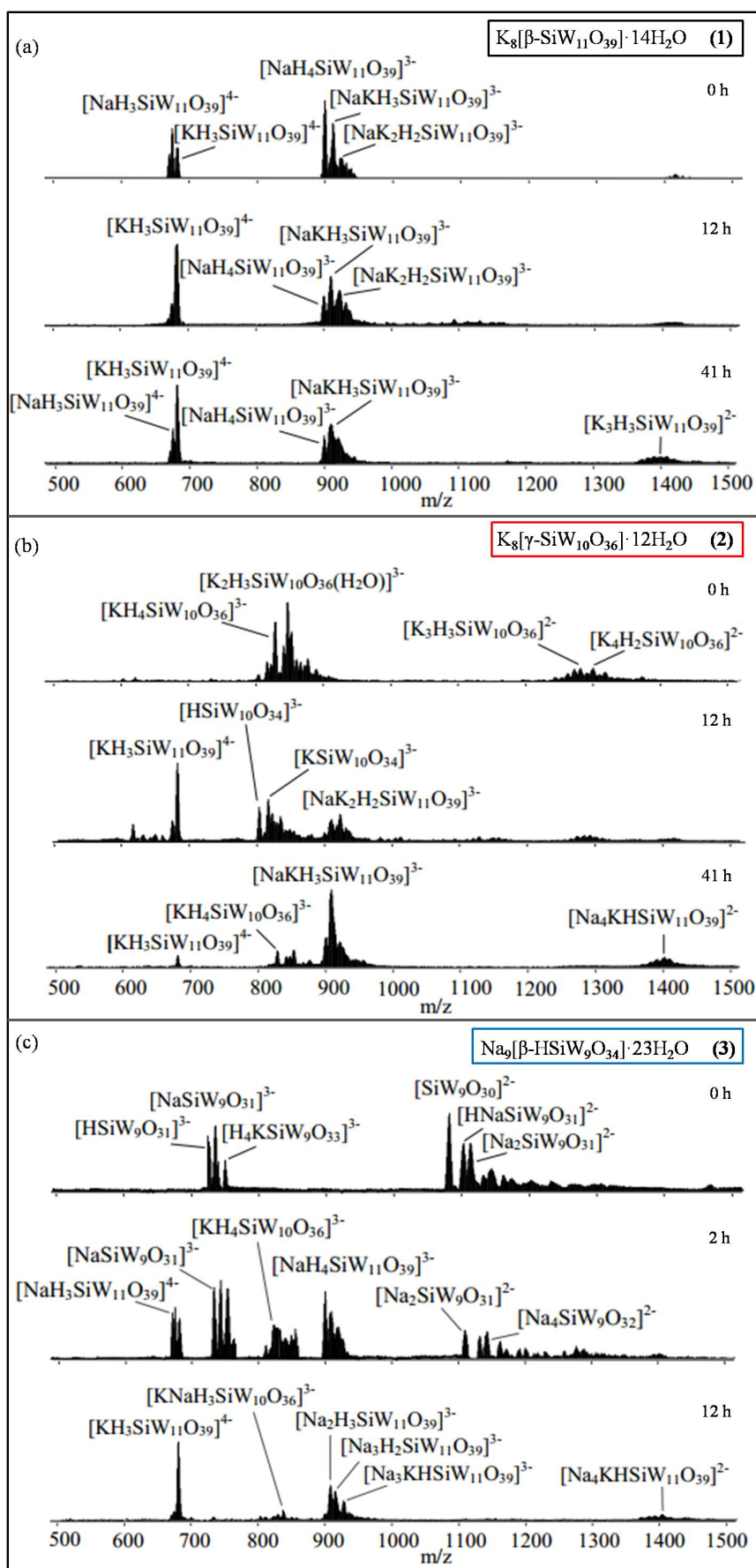


Figure S1. Real-time ESI-MS monitoring of the aqueous solutions containing (a) 1, (b) 2 and (c) 3, respectively, upon different standing time at constant pH at room temperature.

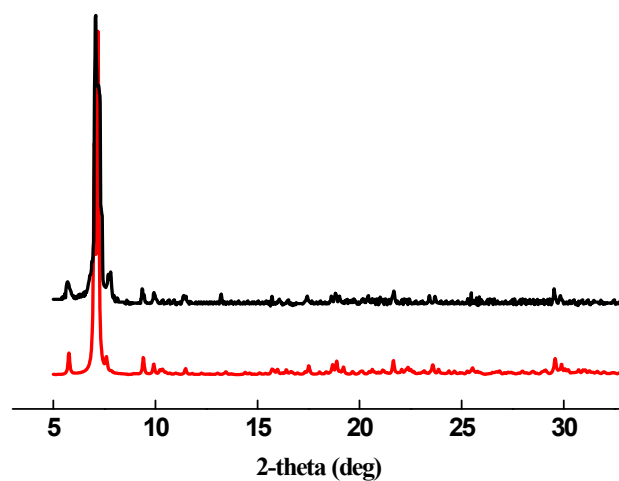


Figure S2. The simulated (red) and experimental (black) powder XRD pattern of compound 4. Simulation based on the single crystal X-ray diffraction data.

Table 1. The main species and the relative abundances for the aqueous solutions **1**, **2** and **3** at different standing time identified by ESI-MS.

SiW ₁₁ 1			SiW ₁₀ 2			SiW ₉ 3		
	Identification	Ions <i>m/z</i> (%)		Identification	Ions <i>m/z</i> (%)		Identification	Ions <i>m/z</i> (%)
0 h	[NaH ₄ SiW ₁₁ O ₃₉] ³⁻	900 (100)	0 h	[K ₂ H ₃ SiW ₁₀ O ₃₆ (H ₂ O)] ³⁻	847 (100)	0 h	[SiW ₉ O ₃₀] ²⁻	1082 (100)
	[NaKH ₃ SiW ₁₁ O ₃₉] ³⁻	913 (80)		[K ₂ H ₃ SiW ₁₀ O ₃₆ (H ₂ O) ₂] ³⁻	853 (70)		[NaSiW ₉ O ₃₁] ³⁻	734 (80)
	[NaH ₃ SiW ₁₁ O ₃₉] ⁴⁻	675 (80)		[K ₂ H ₃ SiW ₁₀ O ₃₆] ³⁻	841 (60)		[HSiW ₉ O ₃₁] ³⁻	727 (70)
	[KH ₃ SiW ₁₁ O ₃₉] ⁴⁻	679 (50)		[KH ₄ SiW ₁₀ O ₃₆] ³⁻	829 (80)		[Na ₂ SiW ₉ O ₃₁] ²⁻	1113 (60)
	[NaK ₂ H ₂ SiW ₁₁ O ₃₉] ³⁻	926 (25)		[K ₃ H ₃ SiW ₁₀ O ₃₆] ²⁻	1282 (10)		[NaHSiW ₉ O ₃₁] ²⁻	1102 (60)
12 h			12 h	[K ₄ H ₂ SiW ₁₀ O ₃₆] ²⁻	1301 (10)	2 h	[KH ₄ SiW ₉ O ₃₁] ³⁻	751 (40)
	[KH ₃ SiW ₁₁ O ₃₉] ⁴⁻	679 (100)					[NaH ₄ SiW ₉ O ₃₃] ³⁻	746 (100)
	[NaKH ₃ SiW ₁₁ O ₃₉] ³⁻	913 (60)		[KSiW ₁₀ O ₃₄] ³⁻	817 (50)		[NaSiW ₉ O ₃₁] ³⁻	734 (90)
	[NaK ₂ H ₂ SiW ₁₁ O ₃₉] ³⁻	926 (50)		[HSiW ₁₀ O ₃₄] ³⁻	804 (45)		[KH ₄ SiW ₉ O ₃₃] ³⁻	751 (90)
	[NaH ₄ SiW ₁₁ O ₃₉] ³⁻	900 (45)		[K ₂ H ₃ SiW ₁₀ O ₃₆] ³⁻	841 (40)		[NaH ₄ SiW ₁₁ O ₃₉] ³⁻	900 (90)
41 h			41 h	[NaK ₂ H ₂ SiW ₁₁ O ₃₉] ³⁻	926 (40)	12 h	[NaKH ₃ SiW ₁₁ O ₃₉] ³⁻	913 (70)
	[KH ₃ SiW ₁₁ O ₃₉] ⁴⁻	679 (100)		[NaKH ₃ SiW ₁₁ O ₃₉] ³⁻	913 (35)		[NaK ₂ H ₂ SiW ₁₁ O ₃₉] ³⁻	926 (50)
	[NaH ₄ SiW ₁₁ O ₃₉] ⁴⁻	675 (50)		[SiW ₁₀ O ₃₄] ⁴⁻	603 (20)		[NaH ₃ SiW ₉ O ₃₉] ⁴⁻	675 (70)
	[NaKH ₃ SiW ₁₁ O ₃₉] ³⁻	913 (60)					[KH ₃ SiW ₁₁ O ₃₉] ⁴⁻	679 (60)
	[NaH ₃ SiW ₁₁ O ₃₉] ³⁻	900 (50)					[KH ₄ SiW ₁₀ O ₃₆] ³⁻	829 (40)
	[NaK ₂ H ₂ SiW ₁₁ O ₃₉] ³⁻	926 (45)					[K ₂ H ₃ SiW ₁₀ O ₃₆ (H ₂ O) ₂] ³⁻	853 (40)
	[K ₃ H ₃ SiW ₁₁ O ₃₉] ²⁻	1397 (10)					[Na ₂ SiW ₉ O ₃₁] ²⁻	1113 (30)
							[Na ₄ SiW ₉ O ₃₂] ²⁻	1144 (30)

Table 2. The main species and the relative abundances for the reaction mixtures **1**, **2** and **3** at different reaction time identified by ESI-MS.

Reaction time	SiW ₁₁ + 1 eq V reaction mixture 1		SiW ₁₀ + 2 eq V reaction mixture 2		SiW ₉ + 3 eq V reaction mixture 3	
	Identification	Ions <i>m/z</i> (%)	Identification	Ions <i>m/z</i> (%)	Identification	Ions <i>m/z</i> (%)
before	[NaH ₄ SiW ₁₁ O ₃₉] ³⁻	900 (100)	[K ₂ H ₃ SiW ₁₀ O ₃₆ (H ₂ O)] ³⁻	847 (100)	[SiW ₉ O ₃₀] ²⁻	1082 (100)
	[NaKH ₃ SiW ₁₁ O ₃₉] ³⁻	913 (80)	[K ₂ H ₃ SiW ₁₀ O ₃₆ (H ₂ O) ₂] ³⁻	853 (70)	[NaSiW ₉ O ₃₁] ³⁻	734 (80)
	[NaH ₃ SiW ₁₁ O ₃₉] ⁴⁻	675 (80)	[K ₂ H ₃ SiW ₁₀ O ₃₆] ³⁻	841 (60)	[HSiW ₉ O ₃₁] ³⁻	727 (70)
	[KH ₃ SiW ₁₁ O ₃₉] ⁴⁻	679 (50)	[KH ₄ SiW ₁₀ O ₃₆] ³⁻	829 (80)	[Na ₂ SiW ₉ O ₃₁] ²⁻	1113 (60)
	[NaK ₂ H ₂ SiW ₁₁ O ₃₉] ³⁻	926 (25)	[K ₃ H ₃ SiW ₁₀ O ₃₆] ²⁻	1282 (10)	[NaHSiW ₉ O ₃₁] ²⁻	1102 (60)
0 h			[K ₄ H ₂ SiW ₁₀ O ₃₆] ²⁻	1301 (10)	[H ₄ KSiW ₉ O ₃₃] ³⁻	751 (40)
	[HSiVW ₁₁ O ₄₀] ⁴⁻	685 (100)	[H ₂ SiV ₂ W ₁₀ O ₄₀] ⁴⁻	652 (100)	[HSiV ₃ W ₉ O ₃₉] ⁴⁻	615 (100)
	[SiVW ₁₁ O ₃₉] ³⁻	908 (10)	[SiV ₂ W ₁₀ O ₃₉] ⁴⁻	648 (95)	[SiV ₃ W ₉ O ₃₈] ³⁻	815 (80)
			[NaSiV ₂ W ₁₀ O ₃₉] ³⁻	872 (40)	[NaH ₃ SiV ₃ W ₉ O ₄₀] ³⁻	834 (40)
			[KSiV ₂ W ₁₀ O ₃₉] ³⁻	877 (38)	[Na ₃ HSiV ₃ W ₉ O ₄₀] ³⁻	849 (40)
2 h					[Na ₄ HSiV ₃ W ₉ O ₄₀] ³⁻	1285 (12)
	[SiV ₂ W ₁₀ O ₃₉] ⁴⁻	648 (100)	[SiV ₂ W ₁₀ O ₃₉] ⁴⁻	648 (100)	[HSiV ₃ W ₉ O ₃₉] ⁴⁻	615 (100)
	[HSiVW ₁₁ O ₄₀] ⁴⁻	685 (50)	[KSiV ₂ W ₁₀ O ₃₉] ³⁻	877 (10)	[SiV ₃ W ₉ O ₃₈] ³⁻	815 (80)
	[H ₄ NaSiW ₁₁ O ₃₉] ³⁻	900 (50)			[NaH ₃ SiV ₃ W ₉ O ₄₀] ³⁻	834 (40)
	[SiVW ₁₁ O ₃₉] ³⁻	908 (30)			[Na ₃ HSiV ₃ W ₉ O ₄₀] ³⁻	849 (40)
24 h					[Na ₄ HSiV ₃ W ₉ O ₄₀] ³⁻	1285 (12)
	[SiV ₂ W ₁₀ O ₃₉] ⁴⁻	648 (100)	[SiV ₂ W ₁₀ O ₃₉] ⁴⁻	648 (100)	[HSiV ₃ W ₉ O ₃₉] ⁴⁻	615 (100)
	[HSiVW ₁₁ O ₄₀] ⁴⁻	685 (15)	[HSiV ₃ W ₉ O ₃₉] ⁴⁻	615 (20)	[SiV ₃ W ₉ O ₃₈] ³⁻	815 (90)
	[HSiV ₃ W ₉ O ₃₉] ⁴⁻	615 (10)	[HSiVW ₁₁ O ₄₀] ⁴⁻	685 (15)	[NaH ₃ SiV ₃ W ₉ O ₄₀] ³⁻	834 (50)
	[HSiV ₂ W ₁₀ O ₃₉] ³⁻	865 (10)	[HSiV ₂ W ₁₀ O ₃₉] ³⁻	865 (40)	[Na ₃ HSiV ₃ W ₉ O ₄₀] ³⁻	849 (40)
	[SiVW ₁₁ O ₃₉] ³⁻	908 (8)	[SiV ₃ W ₉ O ₃₈] ³⁻	815 (20)	[Na ₄ HSiV ₃ W ₉ O ₄₀] ³⁻	1285 (12)
	[SiV ₃ W ₉ O ₃₈] ³⁻	815 (5)				