ELECTRONIC SUPPLEMENTARY INFORMATION

Tin(II)-functionalization of the archetypal $\{P_8W_{48}\}$ Polyoxotungstate

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Table S1. Bond lengths and angles in **1** as determined from the crystal structure of **KLi-1**.

Bond type	**Bond length, Å**	**Angle type**	**Angle, °**
P–O	1.526(10) – 1.575(13)	O–Sn–O	91.5(4)
W=O_{term}	1.716(11) – 1.731(11)	O–Sn–Cl	85.8(3) – 86.2(3)
W–μ_2-O (W–O–W)	1.879(10) – 1.992(10)	O–P–O	106.5(7) – 112.0(5)
W–μ_2-O (W–O–Sn)	1.826(10) – 1.836(11)	W–O_P–P	125.4(4) – 131.6(6)
W–μ_3-O (P, W, K)	2.189(9) – 2.199(10)	W–O_P–W	94.2(5) – 94.8(5)
W–μ_3-O (P, 2W)	2.266(9) – 2.278(9)	W–μ_2-O–Sn	121.0(5) – 122.4(5)
Sn–O	2.143(10) – 2.153(10)	W–μ_2-O–W	95.9(4) – 121.2(8)
Sn–Cl	2.518(6)		145.9(6) – 162.9(6)
K–Cl	3.152(5) – 3.302(8)	O–W–O	72.0(4) – 103.6(5)
K–O *	2.815(11) – 2.828(11)		155.8(5) – 176.8(4)

* Within polyanion **1**

Bond valence sum calculations

Bond valence sum calculations[1,2] for **KLi-1** (Table S2) are consistent with the +VI oxidation state for all W centers and +V for all P centers in **1**. The BVS values for the oxygen atoms suggest that there is no protonation of any oxygen positions in **1**.

Table S2. Bond valence sum values for different atoms in **KLi-1**

W, P, Sn and Cl centers		**μ_2-O (W–O–W)**		**Terminal oxygens**	
W1	6.18	O11	–1.99	O1T	–1.86
W2	6.21	O12	–2.04	O2T	–1.83
W3	6.31	O13	–2.10	O3T	–1.88
W4	6.32	O16	–2.08	O4T	–1.78
W5	6.14	O22	–1.91	O5T	–1.85
W6	6.35	O23	–2.05	O6T	–1.73
P1	4.80	O24	–2.10	**Oxygens of {PO_4} groups**	
P2	4.70	O35	–2.13	O1P1	–1.89
Sn1	1.33	O44	–2.03	O2P1	–1.92
Cl1	–1.07	O45	–2.08	O3P1	–1.90
μ_2-O (Sn–O–W)		O46	–1.94		O1P2
O3S1	–1.85	O56	–2.06	O2P2	–1.90
O5S1	–1.89	O66	–2.00	O3P2	–1.90

Figure S1. Crystal packing of polyanions **1** and K^+ countercations in **KLi-1**; view along the crystallographical *c* axis. The WO_6 octahedra of polyanions **1** in neighboring layers are shown alternatingly in yellow and orange for clarity. Phosphate groups are shown as pink tetrahedra, Sn, K, Cl and O atoms as blue, cyan blue, lime green and red spheres, respectively. Crystal water molecules are omitted.

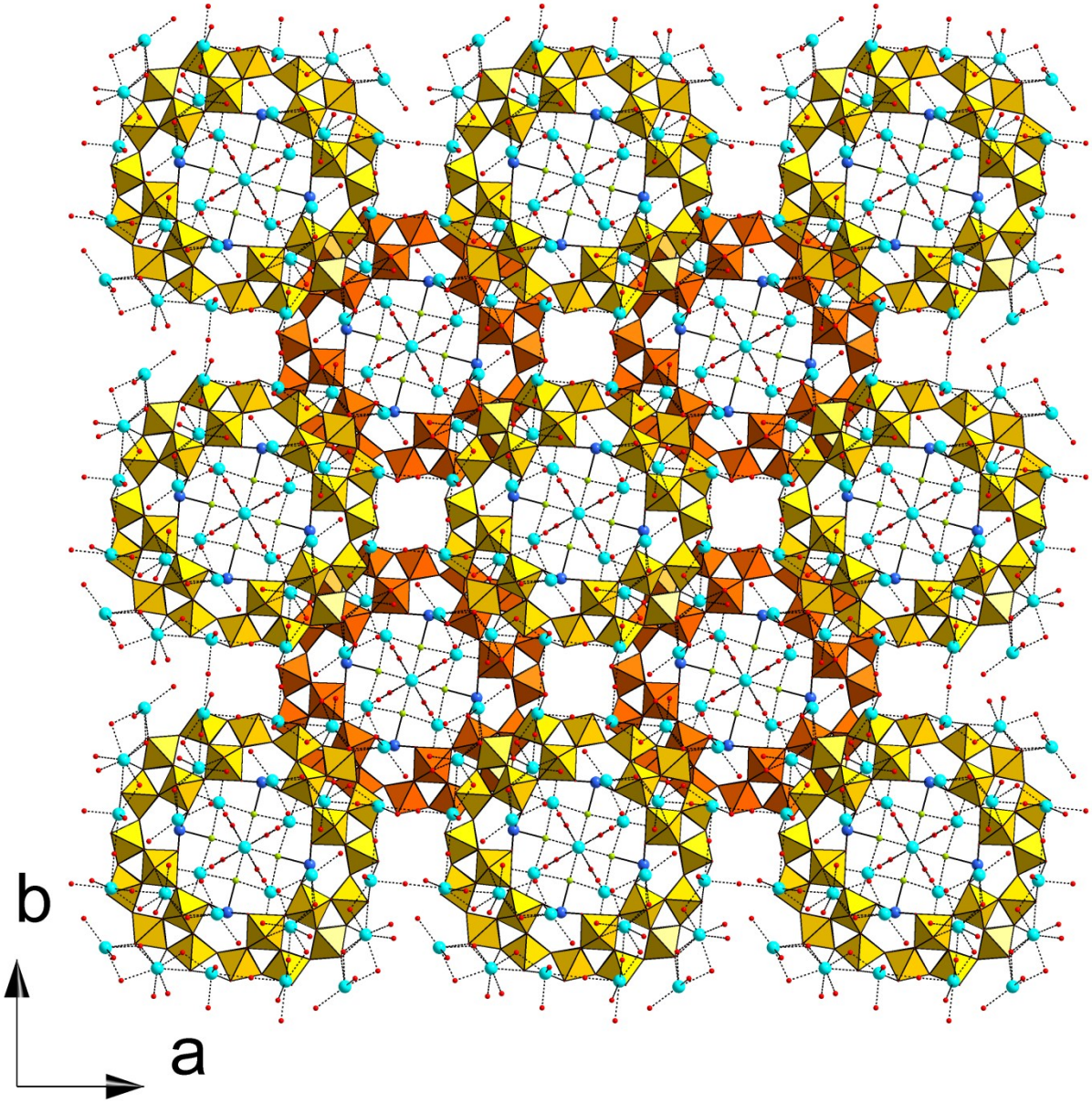


Figure S2. Crystal packing of polyanions **1** and K^+ countercations in **KLi-1**; view along the crystallographical *b* axis. Color legend as in Fig. S1.

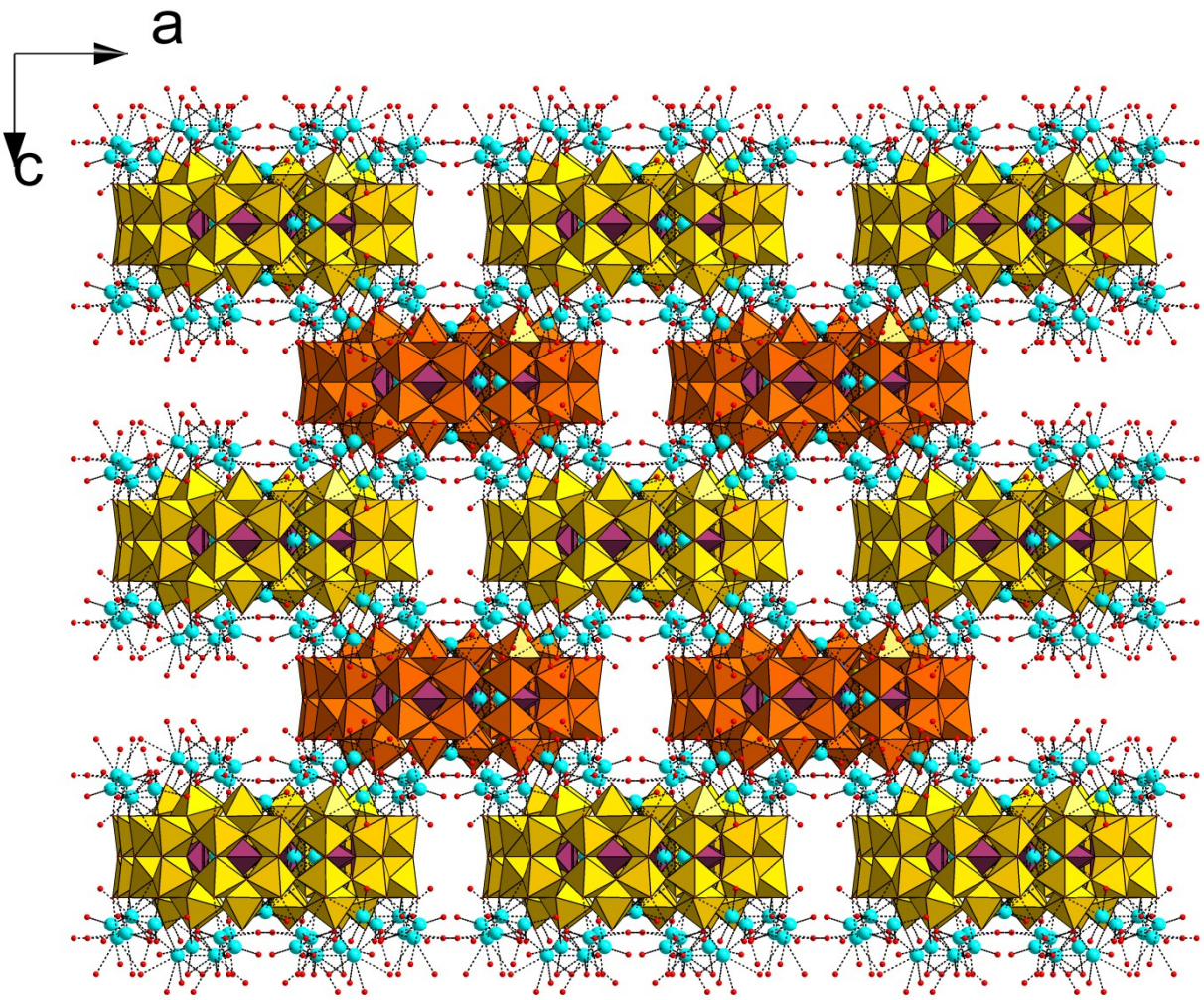


Figure S3. FT-IR spectrum of **KLi-1** (black) in comparison with that of **KLi-P_8W_{48}** (blue).

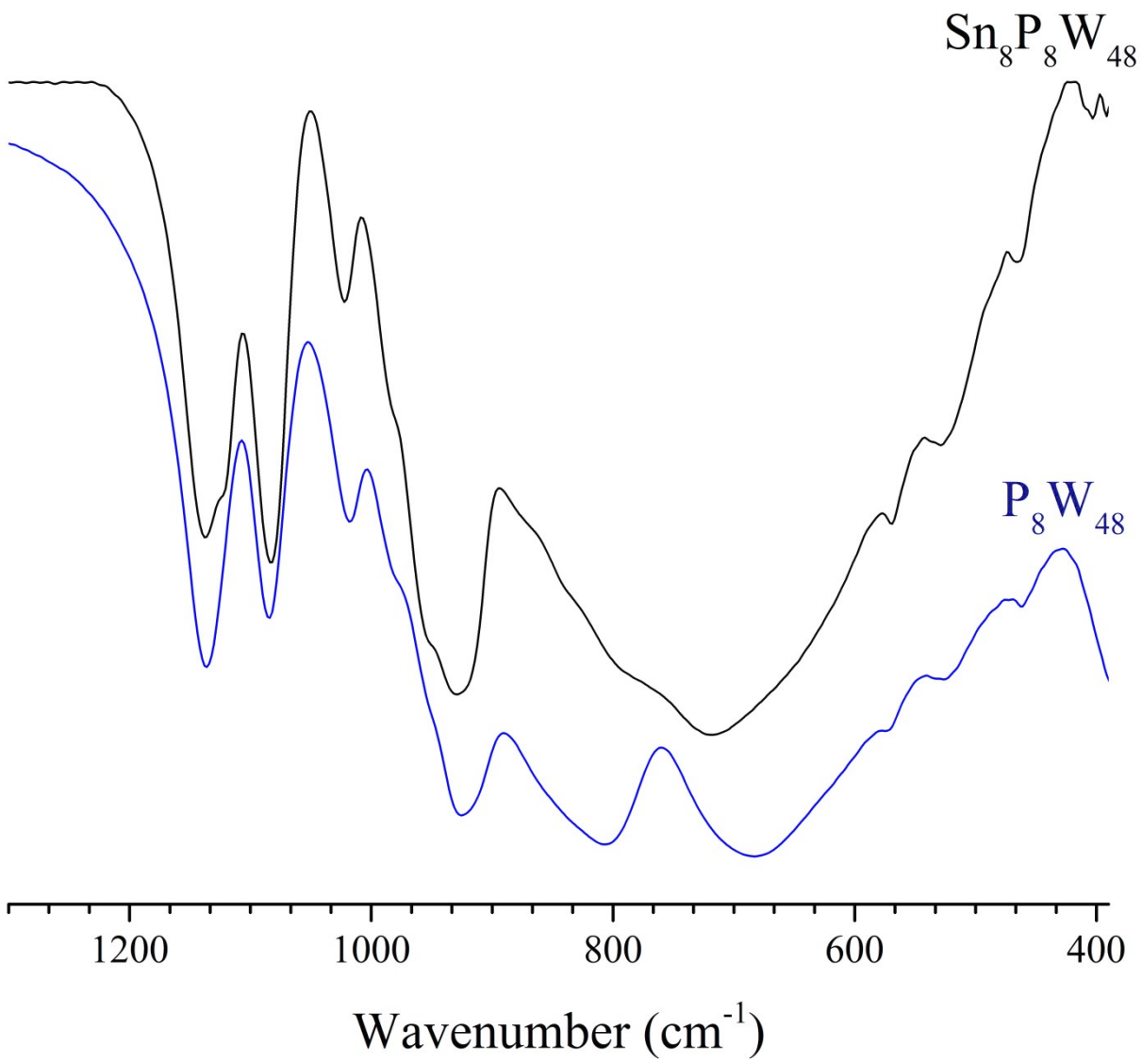
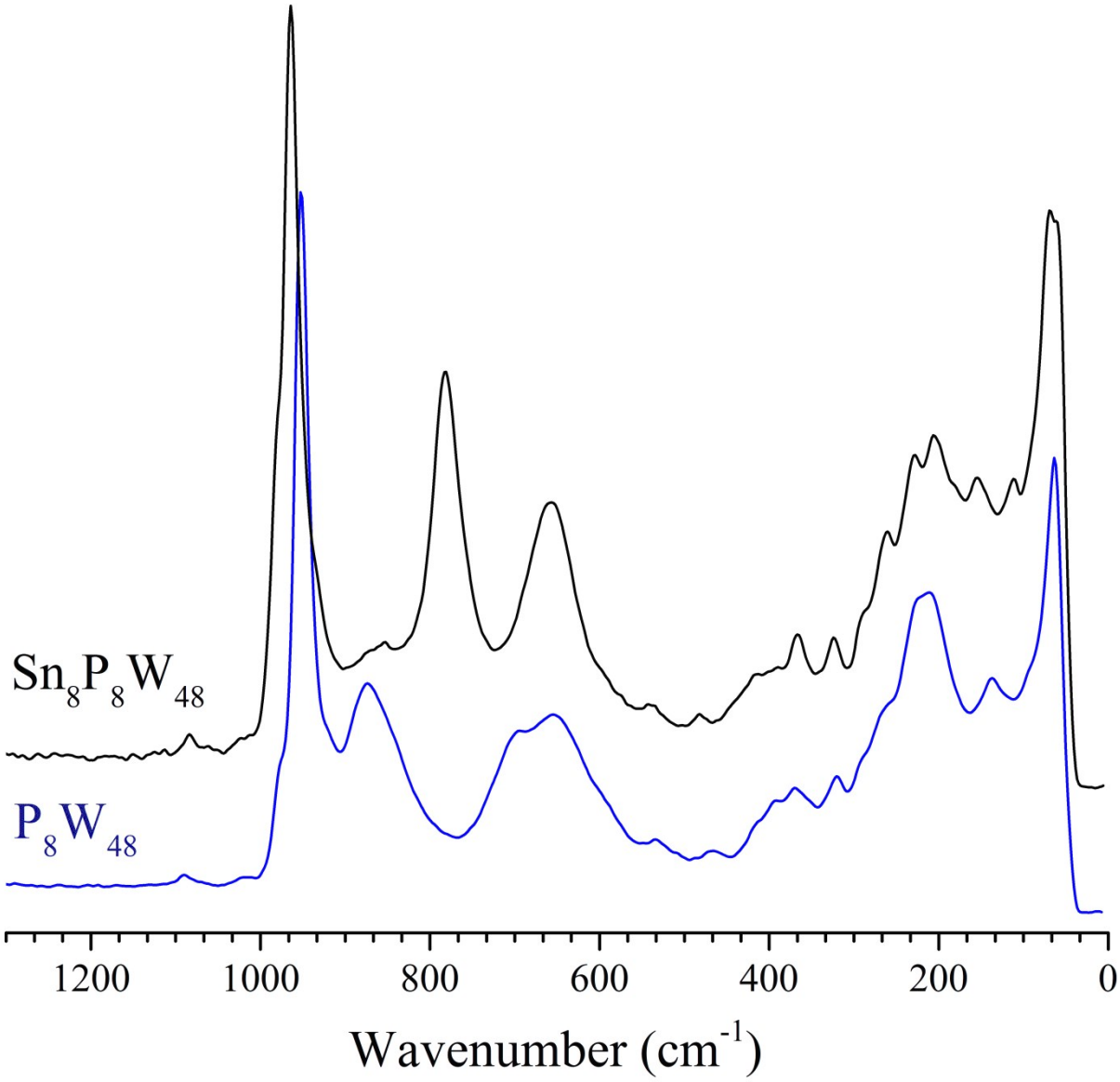


Figure S4. Solid-state Raman spectrum of **KLi-1** (black) in comparison with that of **KLi-P_8W_{48}** (blue).



Thermogravimetrical analysis

The TGA curve of **KLi-1** exhibits two successive mass-loss steps (Fig. S5). The first one starts at 25 °C and is complete at 290 °C and corresponds to the loss of 102 crystal water molecules per formula unit (11.60% obs. vs. 11.65% calculated). The second step occurs in the temperature range 290 – 480 °C and most likely is attributed to the release of Cl_2 (2.20% obs. vs. 1.80% calculated). The total weight loss at 800 °C is 13.81%.

Figure S5. TGA (blue) and SDTA (green) curves for **KLi-1**.

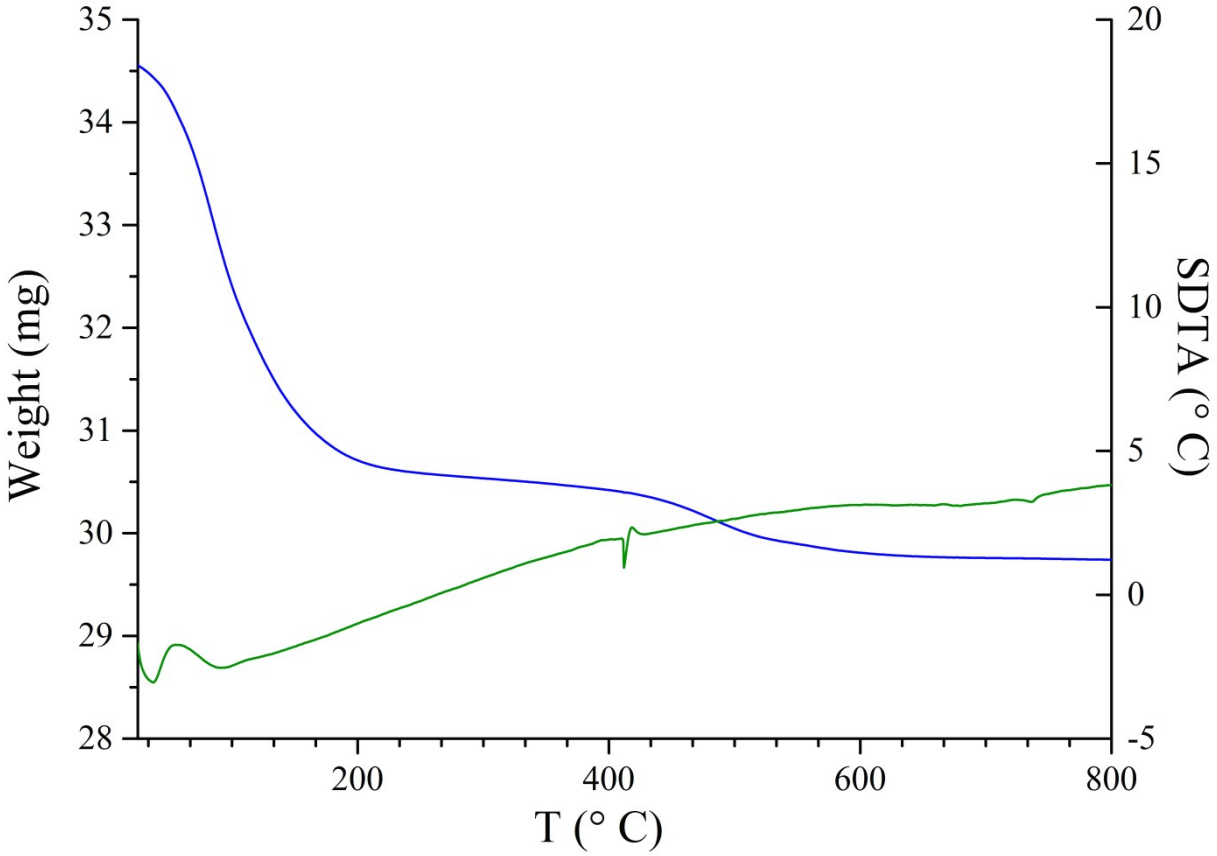


Figure S6. ^{31}P MAS NMR spectrum of **KLi-1** under 9.4 T at ν = 67 kHz (black) and without sample spinning (grey).

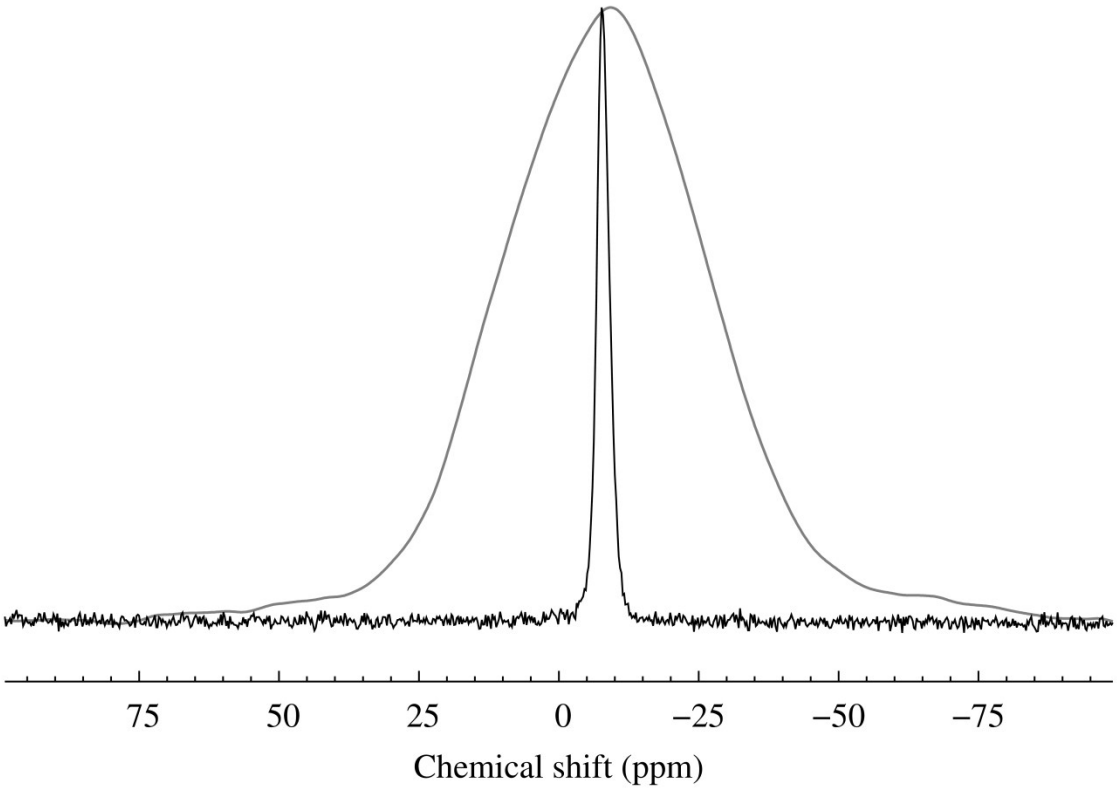


Figure S7. Comparison of room temperature ^{31}P NMR spectra of **KLi-1** (black) and **KLi-P_8W_{48}** (blue) redissolved in 2 M Li_2SO_4 buffer (pH 3.0).

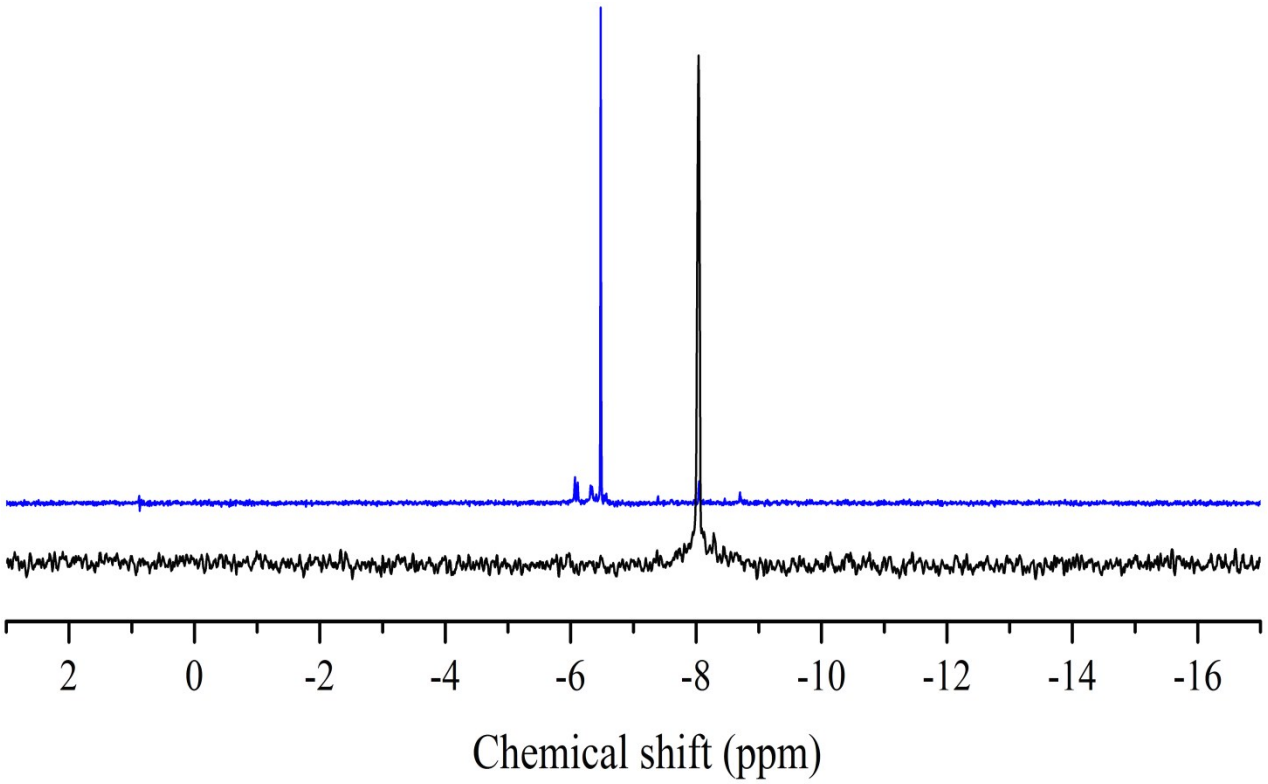


Figure S8. Room temperature ^{31}P NMR spectrum of **KLi-1** redissolved in 2 M Li_2SO_4 buffer (pH 3.0) after 1 day.

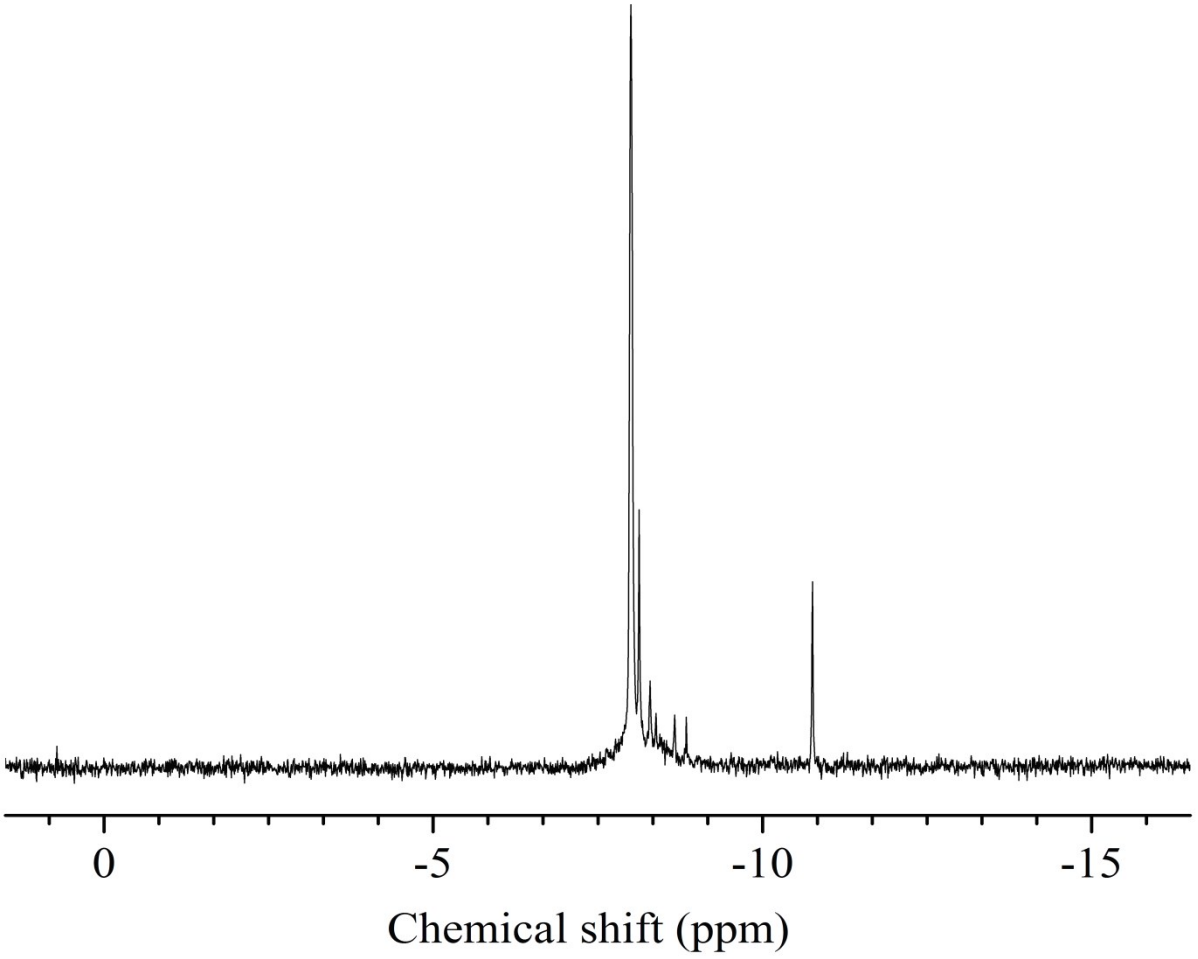


Figure S9. Room temperature ^{31}P NMR spectrum of **KLi-1** redissolved in 4 M LiCl after 1 day.

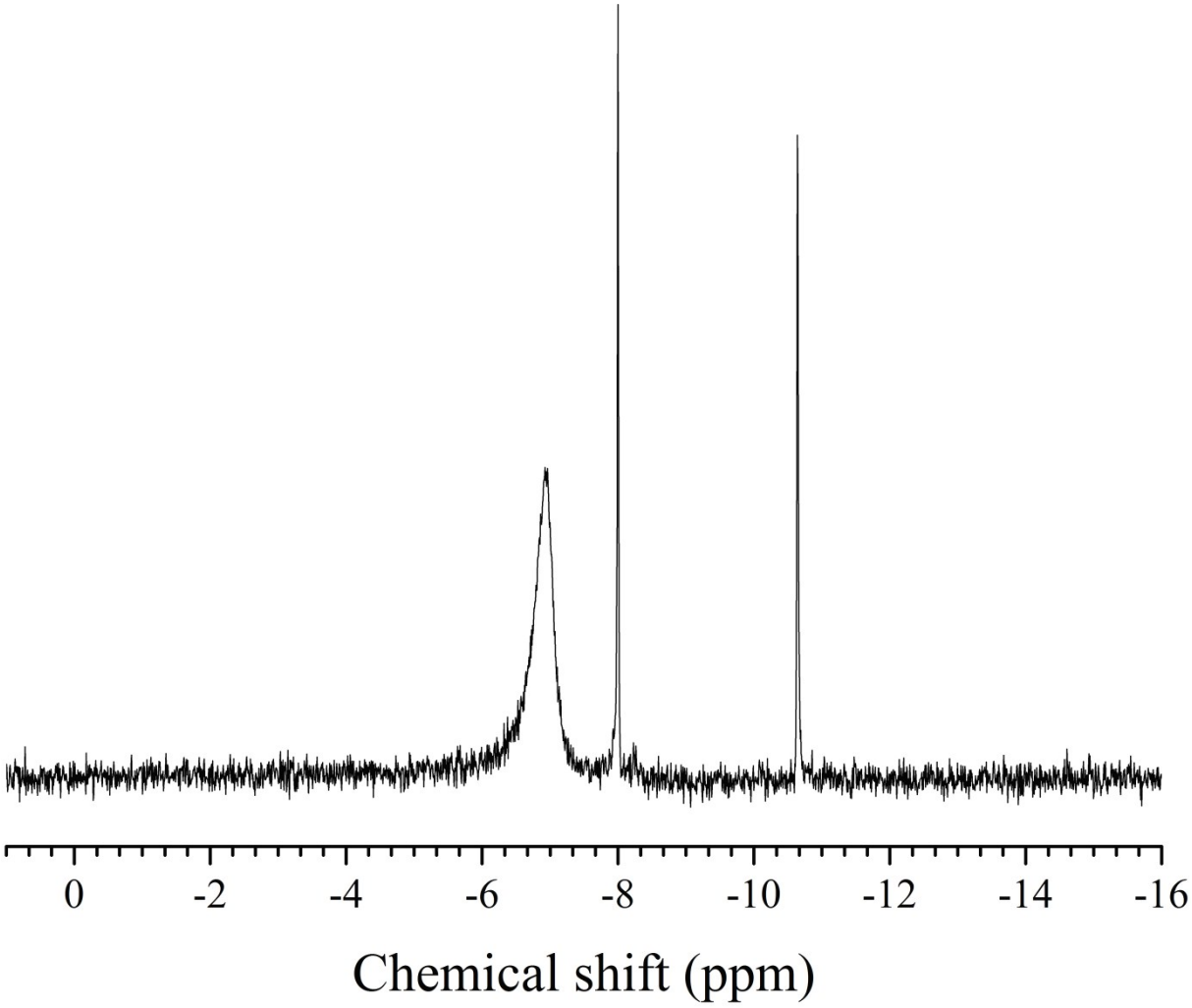


Figure S10. Room temperature UV-Vis spectrum of **KLi-1** solution in 2 M Li_2SO_4 buffer (pH 3.0).

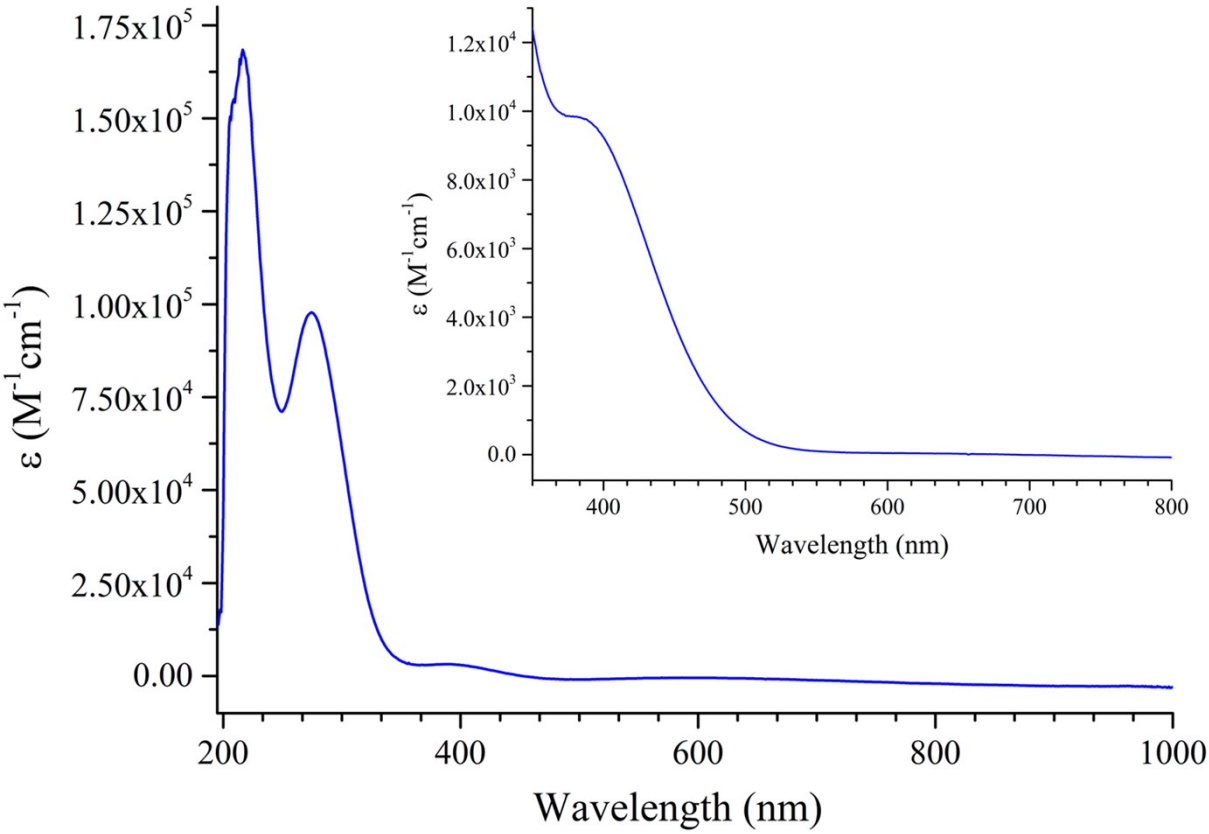


Figure S11. Time-dependent room temperature UV-vis spectra of 1.0×10^{-4} M solution of **KLi-1** in 2 M Li_2SO_4 buffer (pH 3.0).

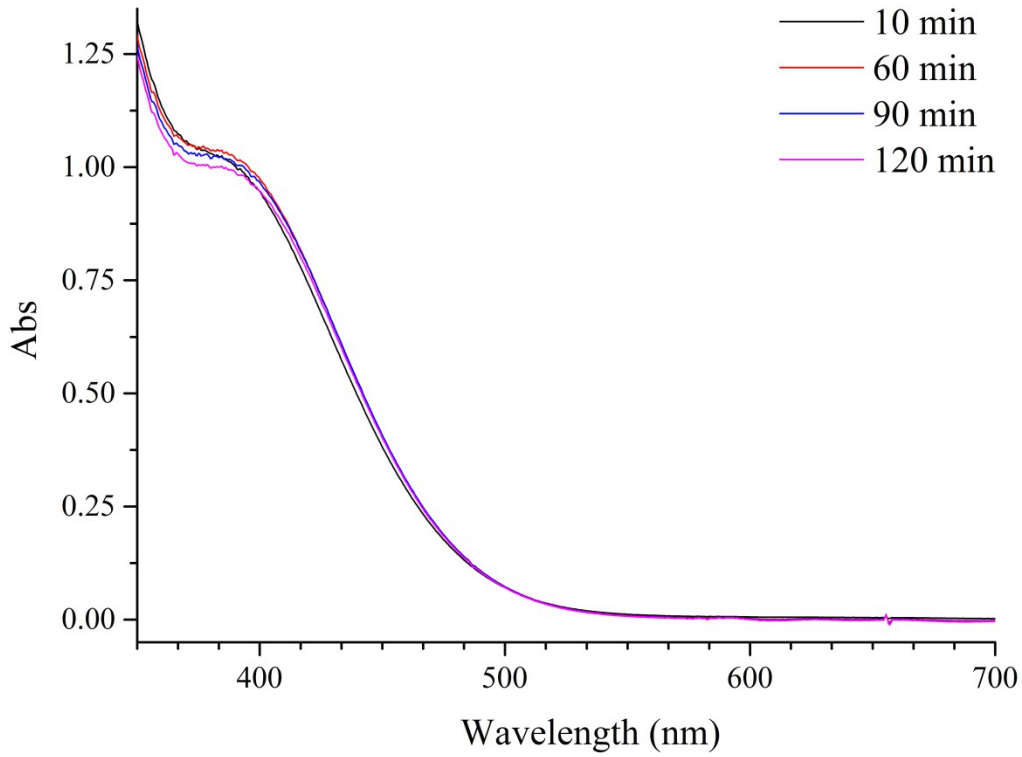


Figure S12. Time-dependent room temperature UV-vis spectra of 1.0×10^{-4} M solution of **KLi-1** in 2 M Li_2SO_4 buffer (pH 3.0).

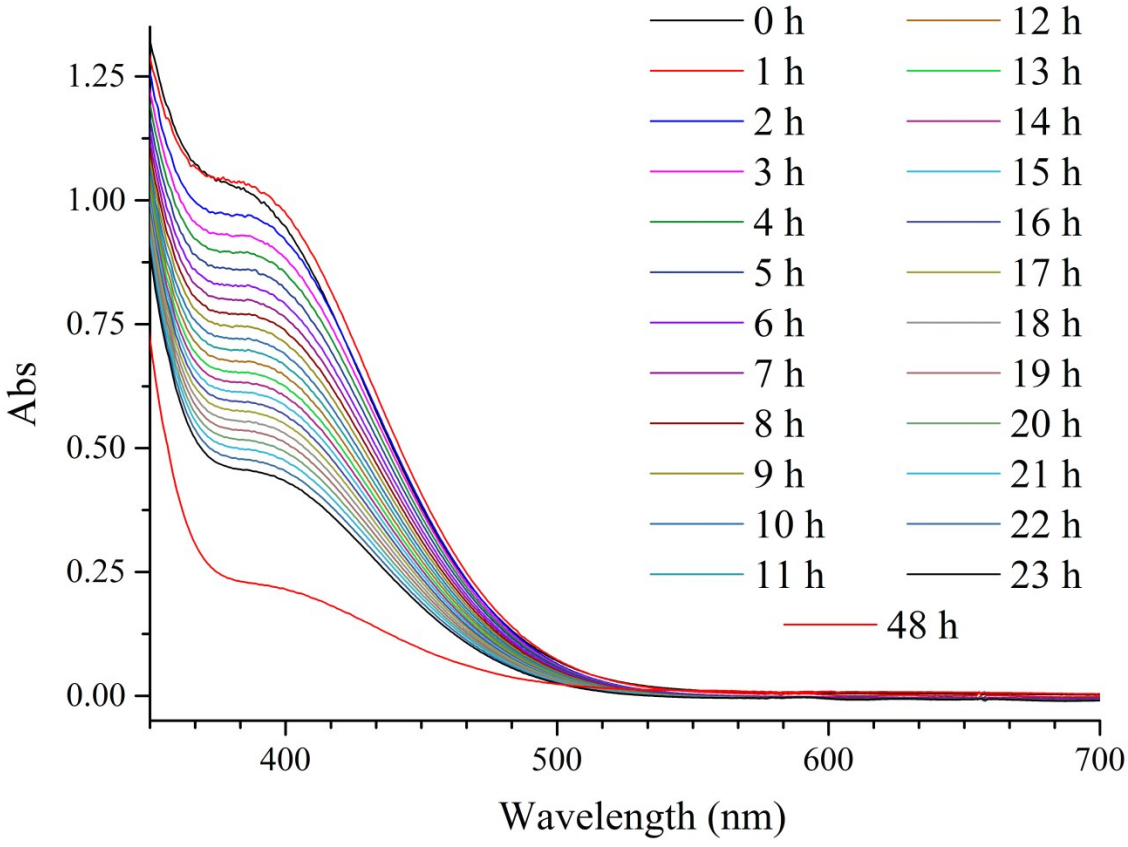


Figure S13. Room temperature UV-Vis spectrum of **KLi-1** solution in 0.5 M Li_2SO_4 buffer (pH 2.0).

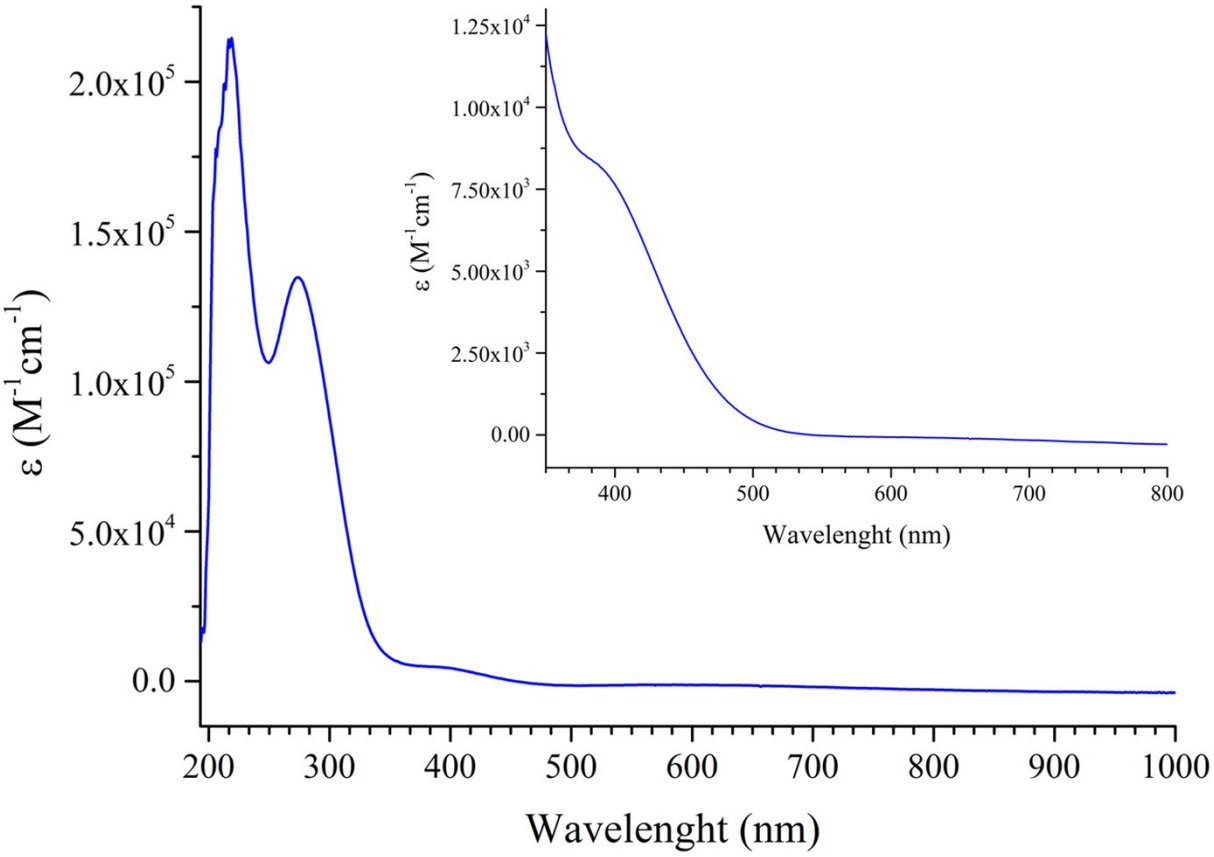


Figure S14. Time-dependent room temperature UV-vis spectra of 9.0×10^{-5} M solution of **KLi-1** in 0.5 M Li_2SO_4 buffer (pH 2.0).

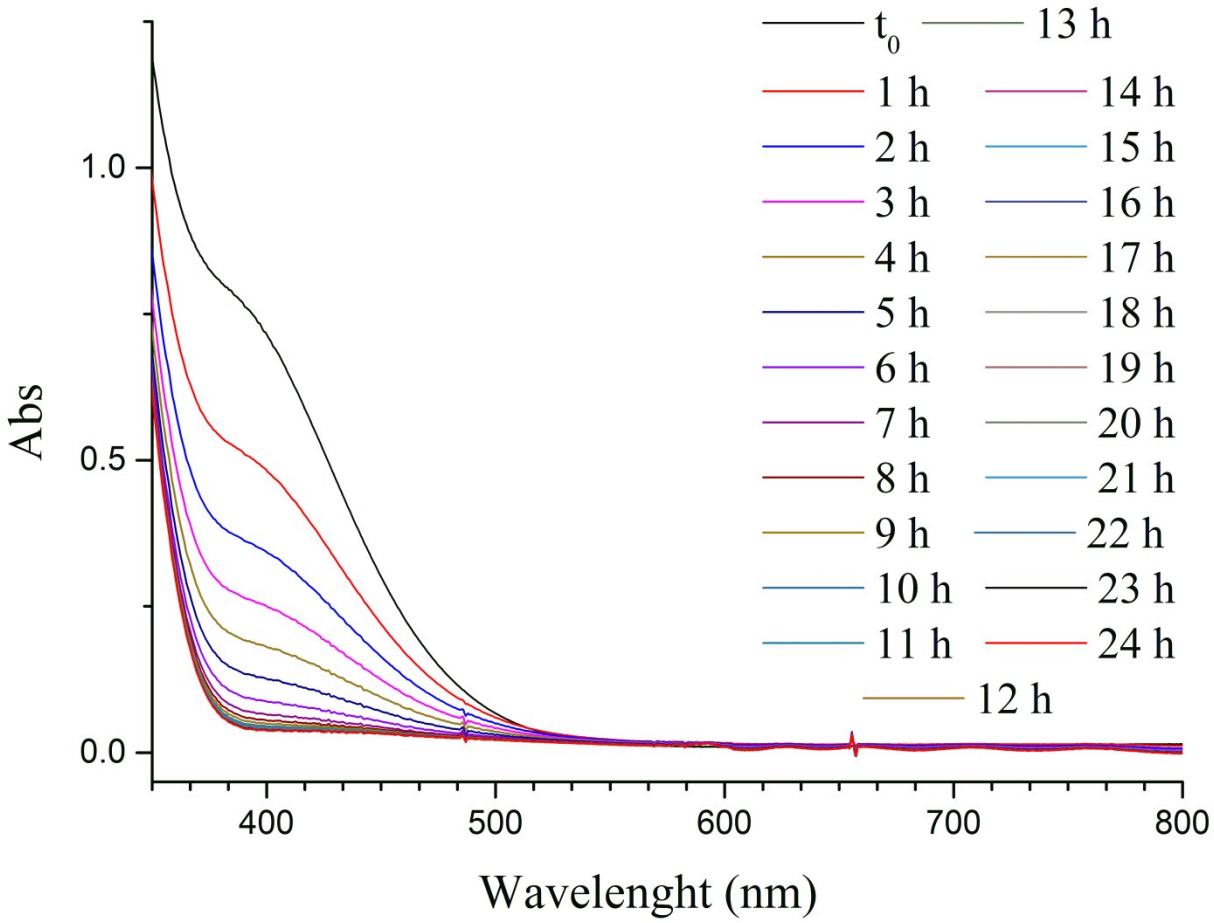


Figure S15. CV of 0.5 mM **KLi-1** solutions in 1 M LiCl/HCl buffer at pH 2.0 (black line); 0.5 M Li_2SO_4/H_2SO_4 buffer at pH 2.0 (red) and non-buffered 2 M LiCl (blue) *vs*. SCE

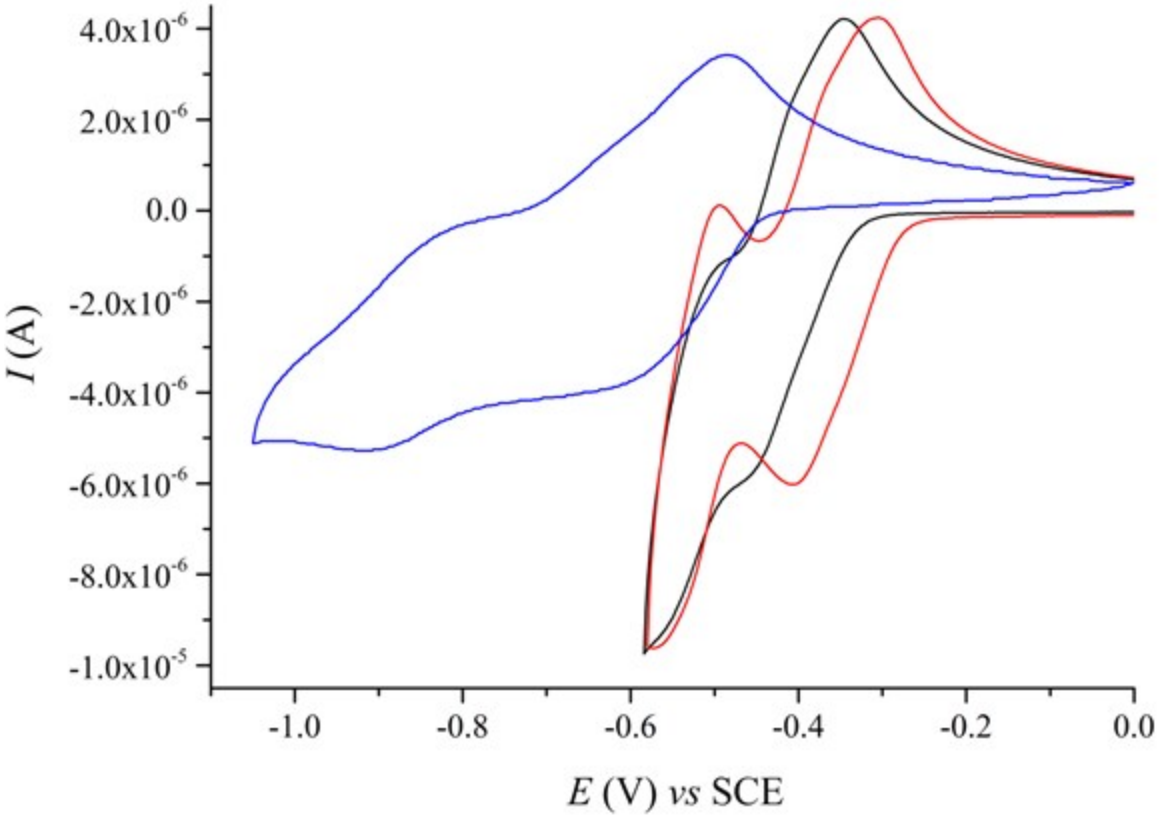


Figure S16. CVs of **KLi-1** with the following reverse potentials: E_r = –0.75 V (black) and E_r = –0.58 V (red). Electrolyte: 0.5 M $Li_2SO_4 + H_2SO_4$ (pH 2.0). POM concentration: 0.5mM. Scan rate: 10 mV s^{-1}; working electrode: glassy carbon; reference electrode: SCE.

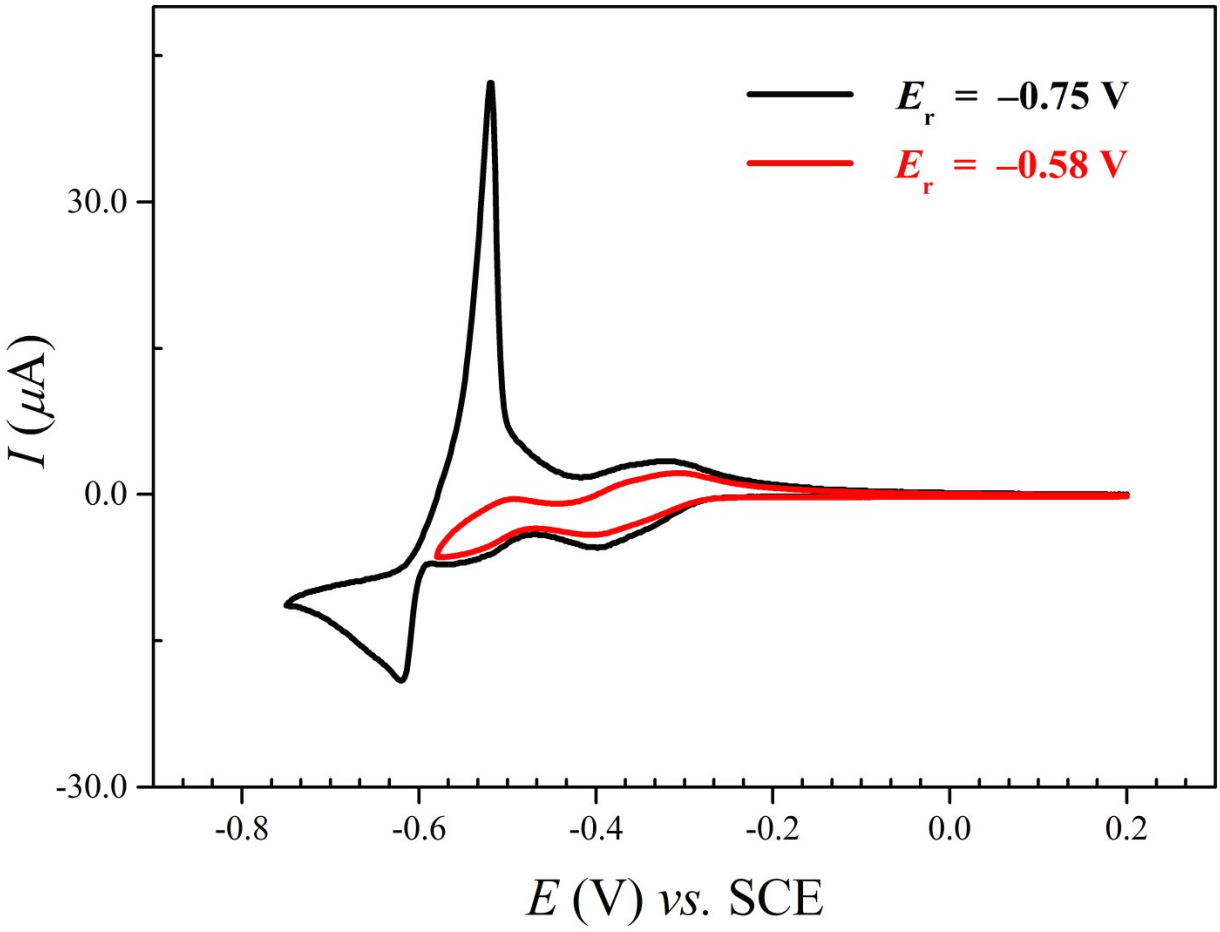
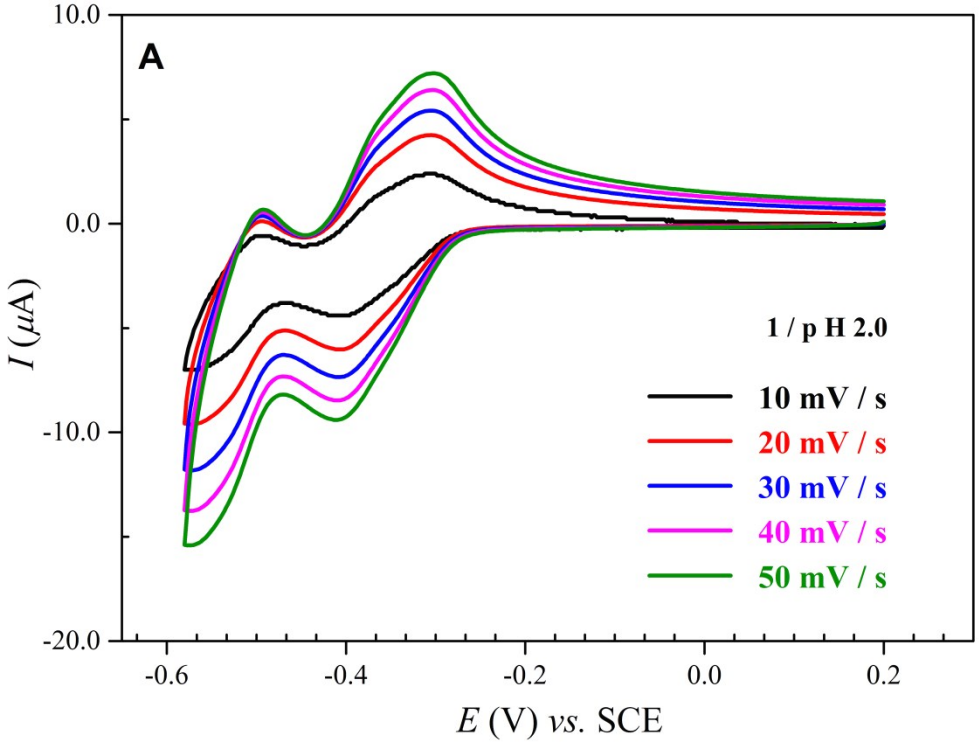
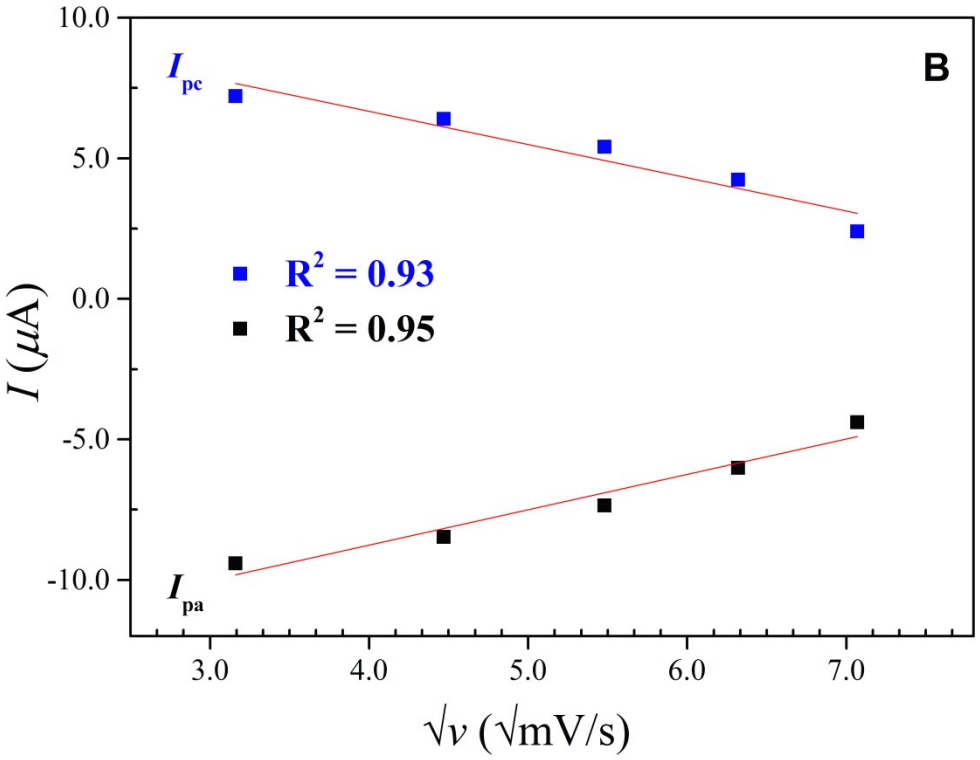


Figure S17. (A) CVs of **KLi-1** as a function of the scan rate, the potential range being restricted to the waves of the W centers. Electrolyte: 0.5 M $Li_2SO_4 + H_2SO_4$ (pH 2.0). POM concentration: 0.5mM; working electrode: glassy carbon; reference electrode: SCE. (B) Reduction peak currents, I_{pc}, and oxidation peak currents, I_{pa}, for the first wave assigned to the W centers as a function of the scan rate. The values were collected from the CVs in Figure A.





References

1. I. D. Brown, D. Altermatt, *Acta Crystallogr., Sect. B* **1985**, *41*, 244-247.

2. K. Knížek, Kalvados – Software for crystal structure and powder diffraction; see http://www.fzu.cz/~knizek/kalvados/index.html.