

Supplementary Information

Table S1. Crystallographic data for CuV16

	CuV16
formula	C ₃₂ H ₇₈ Cu ₂ N ₁₂ O ₄₇ V ₁₆
fw	2325.18
crystal system	monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i> (#14)
<i>a</i> (Å)	15.3809(3)
<i>b</i> (Å)	24.2793(4)
<i>c</i> (Å)	21.5471(3)
β (deg)	102.3660(10)
<i>V</i> (Å ³)	7859.8(2)
<i>Z</i>	4
μ (mm ⁻¹)	16.603
<i>R</i> ₁ (<i>I</i> > 2 σ (<i>I</i>))	0.0519
<i>wR</i> ₂	0.1349

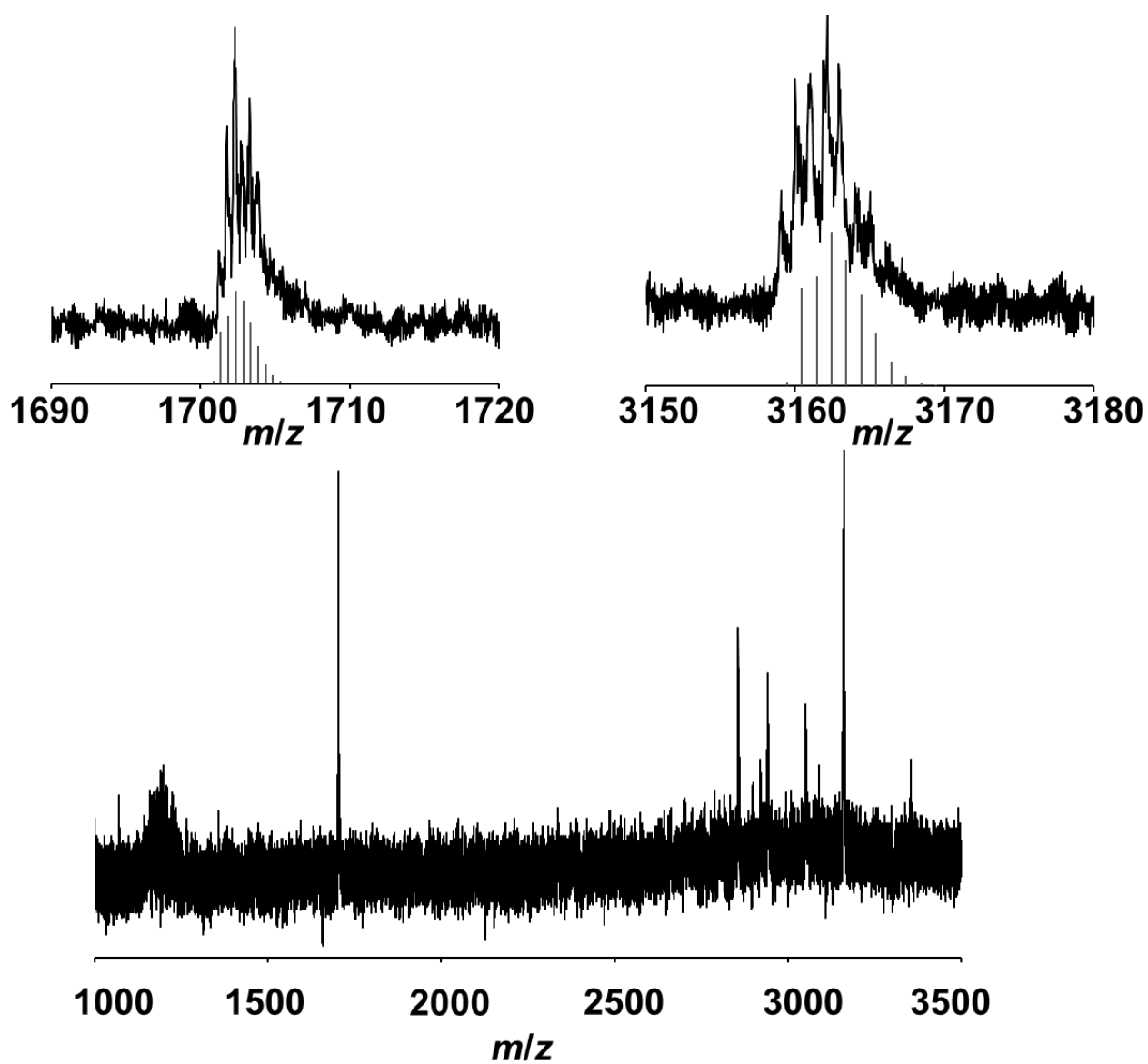


Figure S1. Electrospray-ionization mass spectra of Cu₂V₁₆ in acetonitrile.

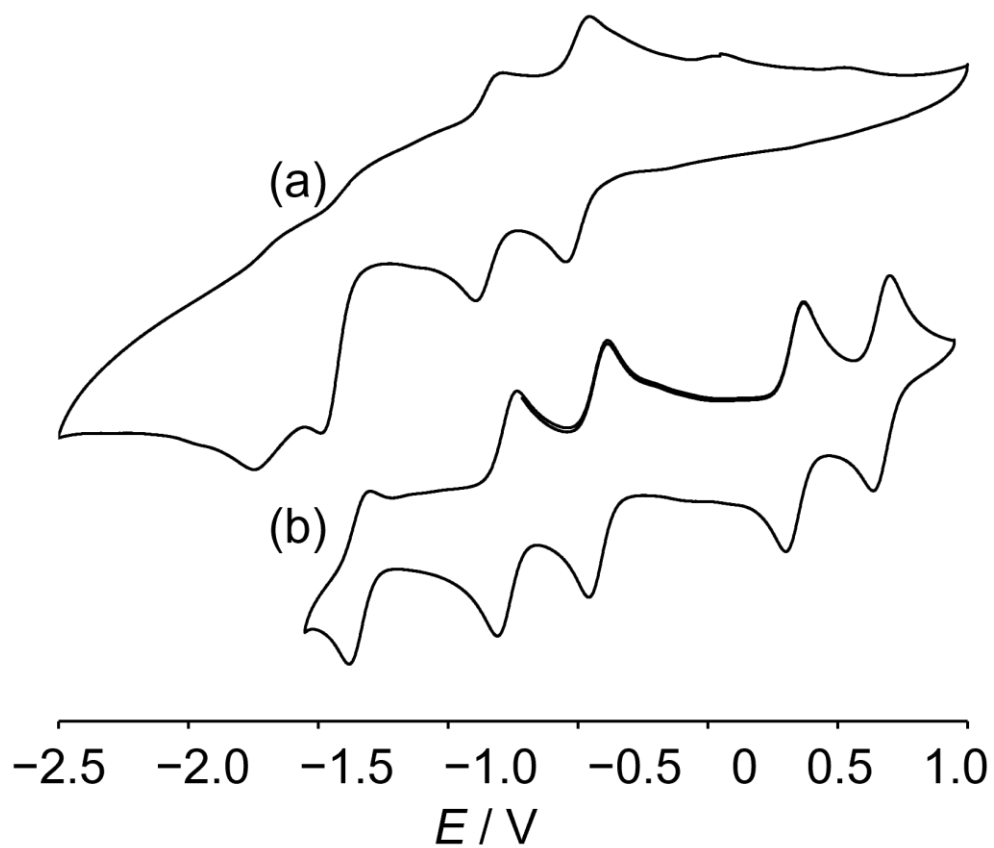


Figure S2. Cyclicvoltamogram of (a) $\text{Cu}_2\text{V16}$ and (b) V18 in acetonitrile. Scan rate was 100 mV s^{-1} . The working electrode was glassy carbon and the reference electrode was the Ag/Ag^+ electrode. The supporting electrolyte was $(^n\text{Bu}_4\text{N})\text{PF}_6$.

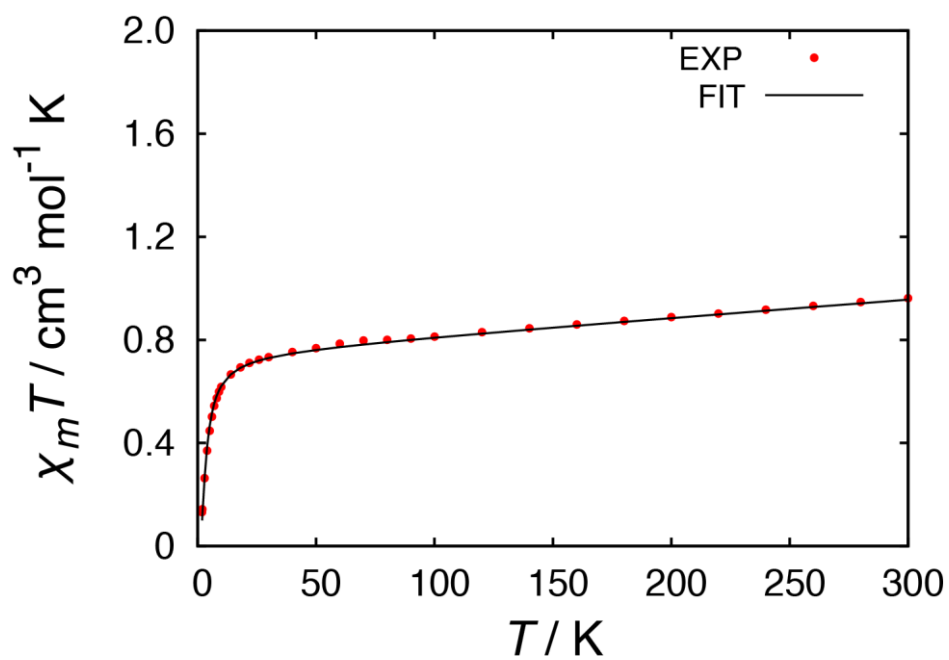


Figure S3. $\chi_m T$ versus T plot of Cu₂V₁₆ in applied field of 5000 Oe (red points). The solid line corresponds to the fit by PHI program assuming the isotropic exchange interaction with the Hamiltonian: $\mathbf{H} = -J \mathbf{S}_1 \cdot \mathbf{S}_2$ ($S_1 = S_2 = 1/2$). The best-fitting parameter was $J = -2.2 \text{ cm}^{-1}$. The temperature independent paramagnetism was fixed to $0.0007 \text{ cm}^3 \text{ mol}^{-1}$.

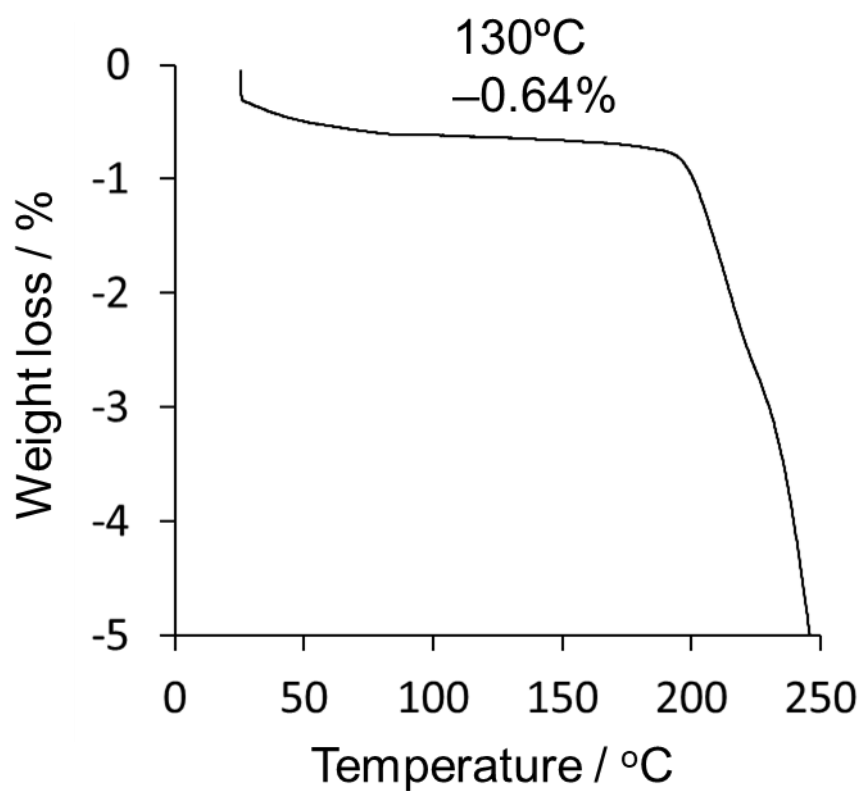


Figure S4. Thermogravimetric data of Cu₂V16. The weight loss is -0.64% at 130°C due to 1 molecule of water. The weight loss over 200°C is due to the decomposition of tetra-*n*-butyl ammonium.

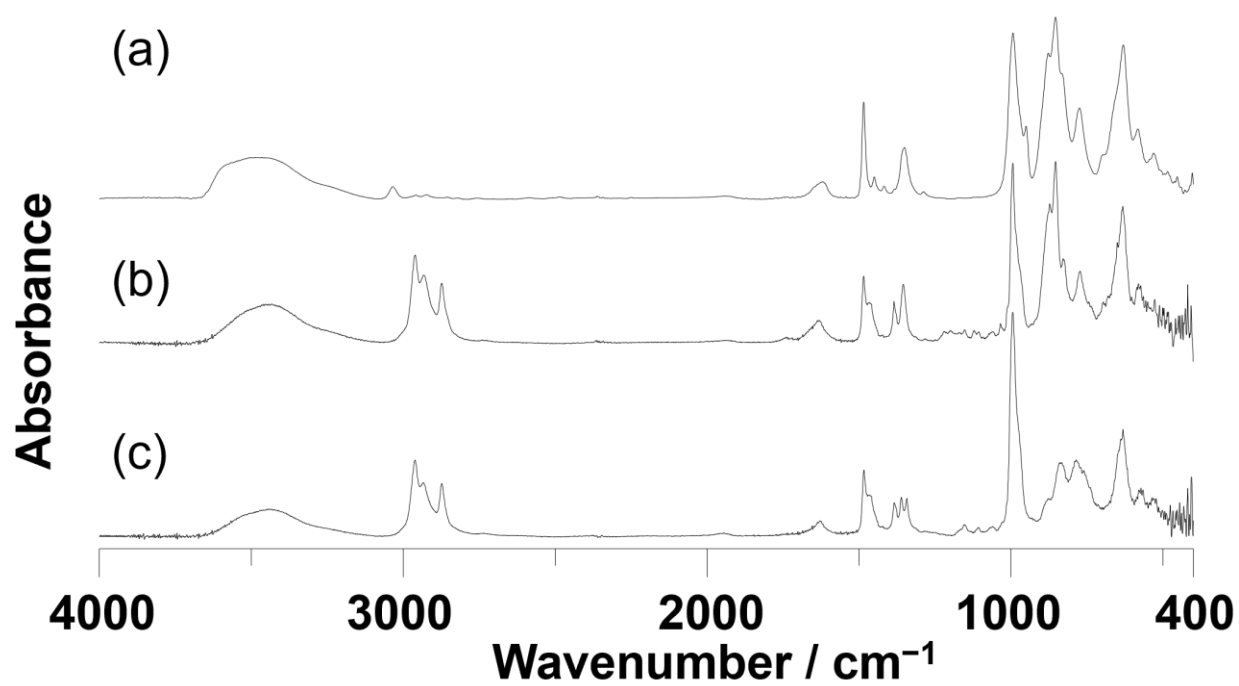


Figure S5. IR spectra of (a) tetramethyl ammonium salts of Cu₂V16, (b) tetra-*n*-butyl ammonium salts of Cu₂V16, and (c) V18.

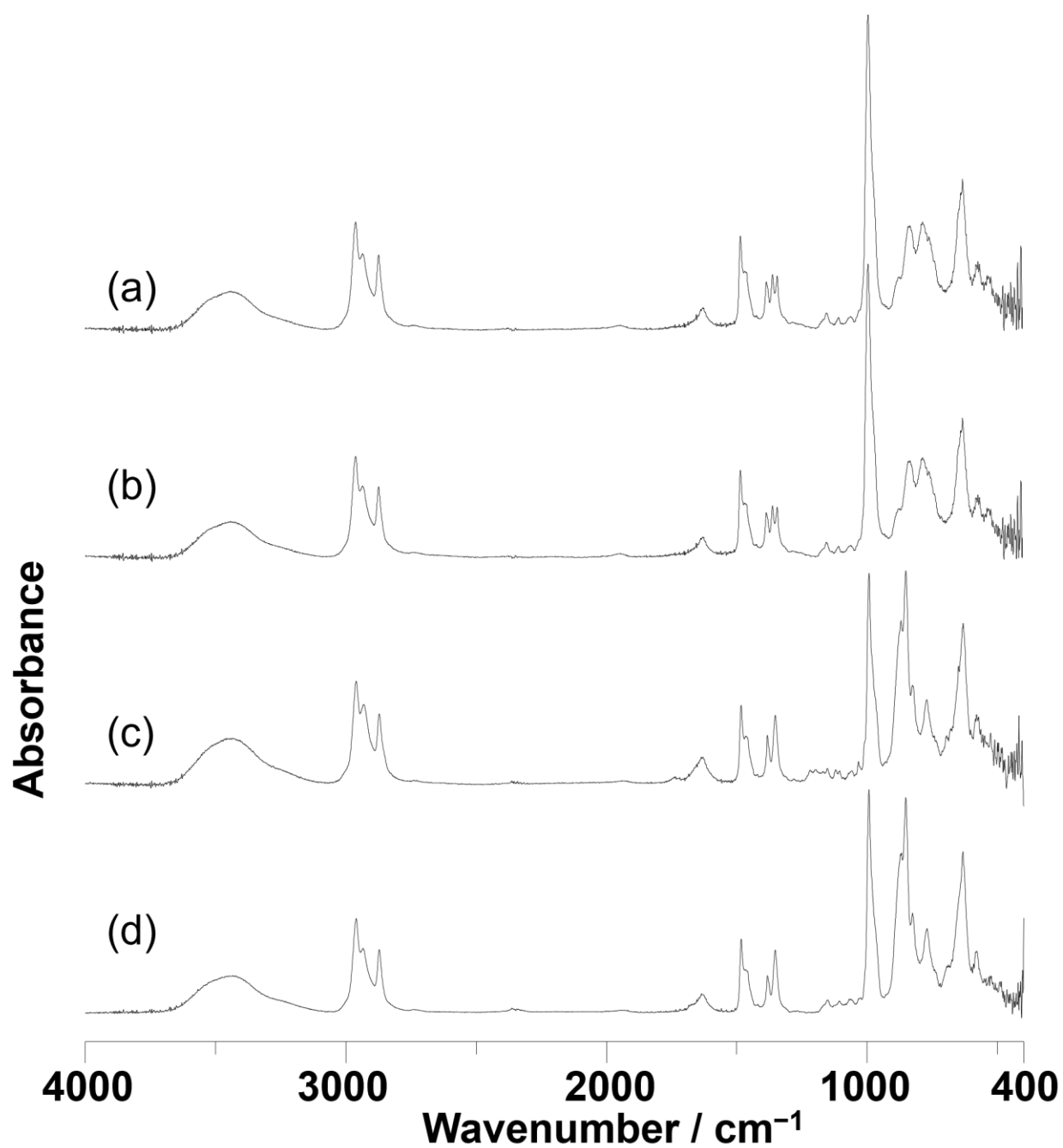


Figure S6. IR spectra of (a) V18 before the catalytic reaction, (b) V18 after the catalytic reaction, (c) Cu₂V16 before the catalytic reaction, and (d) Cu₂V16 after the catalytic reaction.