

Supplementary information for

Reactivity Control of Nitrate-Incorporated Octadecavanadates by the Oxidation State and Metal-Substitution

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Experimental Section

Instruments: NMR spectra were recorded with JEOL JNM-LA400. IR spectra were measured on Jasco FT/IR-4200 using KBr method. Temperature-dependent IR spectra were measured on Jasco FT/IR-6600 using transmission method with a sample-coated Si disk in the gas-cell with a heater. The sample-coated Si disk was prepared by the drop of acetonitrile solution of tetra-*n*-butyl ammonium salts of polyoxovanadates on the surface of Si disk and the evaporation of acetonitrile. The window of the gas-cell was Si disks. The temperature was measured by the thermocouple set on the surface of the gas-cell. Elemental analyses of C, H, and N were performed by the Research Institute for Instrumental Analysis at Kanazawa University. Elemental analysis of V was measured by Thermo Fisher Scientific inductively coupled plasma atomic emission spectroscopy iCAP6300. UV-vis spectrum were measured on Jasco V770. Thermogravimetry data were collected on a Rigaku Thermo plus EVO2 instrument with a temperature sweep rate of 10 °C/min under 0.2 L/min N₂ flow. GC analysis was performed on Shimadzu GC-2014 with a flame ionization detector (FID) equipped with ZB-WAXplus capillary column (phenomenex, internal diameter = 0.25 mm, length = 30 m) and Neutrabond-1 capillary column (GL Sciences, internal diameter = 0.25 mm, length = 30 m). GC-MS spectra were measured on Shimadzu GCMS-QP2010. An ALS/CH Instruments electrochemical analyzer (Model 600A) was used for voltammetric experiments under N₂ gas flow condition. The working electrode was glassy carbon, the counter electrode was Pt wire, and the reference electrode was Ag/Ag⁺. The voltage scan rate was set at 100 mV s⁻¹. The concentration of the sample and the supporting electrolyte, {*n*-Bu₄N}PF₆ was 1 mM and 100 mM, respectively. The potentials in all voltammetric experiments were converted using data derived from the oxidation of Fc (Fc/Fc⁺, Fc = ferrocene) as an external reference. The distillation of the small amount of reagent was performed by glass tube oven SIBATA GTO-1000.

Reagents: Solvents and reagents were commercially available and used as received.

X-ray Crystallographic analysis: Single crystal structure analysis was performed at -190°C by using a Rigaku/MSC Mercury diffractometer with graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$) and with 0.5° ω -scans at 0° and 90° in φ . The crystal data is summarized in Table S1. Data were collected and processed by using the CrystalClear program.^{S1} Numerical absorption corrections were applied by using CrystalClear and corrections for Lorenz and polarization effects were performed. The structure analysis was performed using CrystalStructure.^{S2} All structures were solved by SHELXS-97 (direct methods) and refined by SHELXL-2017.^{S3,S4} Non-hydrogen atoms were refined anisotropically. Hydrogen atoms are positioned geometrically and refined using a riding model. The structural analysis were performed using winGX for Windows software.^{S5}

Catalytic reaction: Substrate 1 mmol, catalyst 5 μmol , acetonitrile 2 mL were put in the glass test tube with the screw cap. For GC analysis, internal standard 0.2 mmol were added. The solution was kept at 32°C under Ar atmosphere. The solution was stirred at 800 rpm with the Teflon-coated magnetic stir bar. The reaction started with the addition of 5.5 M TBHP in decane solution 1 mmol to the reaction solution. Yields were determined by GC with internal standard method and/or ^1H NMR. The products were determined by the retention time of the commercially available authentic chemicals unless otherwise mentioned. 7-Oxabicyclo[4.1.0]heptan-2-ol (2,3-Epoxy cyclohexanol) was obtained by the reaction with V18. After the reaction, the catalyst was removed by addition of excess amount of diethyl ether and solvent were removed by evaporation. The products were distilled. The products were determined by GC-MS and ^1H NMR. After the reaction of thioanisole with V18ox and V18, excess amount of diethyl ether was added to the reaction solution and the precipitates were collected by filtration and dried. The collected solids were characterized by IR spectroscopic analysis (Figure S10). Samples for the characterization via ^1H NMR were obtained as follows: The reaction under the catalytic conditions without an internal standard was carried out. Addition of diethyl ether to the reaction solution to remove the catalysts and evaporation gave the samples. They are dissolved in CDCl_3 .

p-Methoxy(methylsulfinyl)benzene: 7.57-7.55 (d, 2H), 7.00-6.98 (d, 2H), 3.82 (s, 3H), 2.66 (s, 3H). *p*-Mesylmethoxybenzene: 7.85-78.1 (d, 2H), 7.00-6.97 (d, 2H), 3.84 (s, 3H), 2.99 (s, 3H)

p-(Methylsulfinyl)toluene: 7.10-7.08 (d, 2H), 7.02-7.00 (d, 2H), 2.37 (s, 3H), 2.22 (s, 3H). *p*-Mesyltoluene: 7.47-7.45 (d, 2H), 7.26-7.24 (d, 2H), 2.62 (s, 3H), 2.33 (s, 3H)

(Methylsulfinyl)benzene: 7.37-7.33(d, 2H), 7.14-7.10 (t, 2H), 7.00-6.97 (t, 1H), 2.32 (s, 3H). Mesylbenzene: 7.52-7.51(d, 2H), 7.40-7.37 (t, 2H), 7.16-7.12 (t, 1H), 2.57 (s, 3H)

p-Bromo(methylsulfinyl)benzene: 7.21-7.19 (d, 2H), 6.94-6.92 (d, 2H), 2.28 (s, 3H). *p*-Bromomesylbenzene: 7.50-7.48(d, 2H), 7.38-7.36 (d, 2H), 2.55 (s, 3H)

p-(Methylsulfinyl)benzotrile: 7.85-7.82 (d, 2H), 7.78-7.76 (d, 2H), 2.76 (s, 3H). *p*-Mesylbenzotrile: 8.09-8.07 (d, 2H), 7.90-7.88 (d, 2H), 3.09 (s, 3H)

p-(Methylsulfinyl)nitrobenzene: 8.08-8.06 (d, 2H), 7.35-7.33 (d, 2H), 2.52 (s, 3H). *p*-Mesylnitrobenzene: 8.32-8.30 (d, 2H), 7.84-7.81(d, 2H), 2.71 (s, 3H)

(Vinylsulfinyl)benzene: 7.52-7.50 (m, 2H), 7.42-7.38 (m, 3H), 6.52-6.46 (dd, 1H), 6.10-6.06 (d, 1H), 5.78-5.76 (d, 1H)

(Phenylsulfinyl)benzene: 7.60-7.59 (d, 2H), 7.46-7.33(m, 3H)

1-(Butylsulfinyl)butane: 2.60-2.48 (m, 4H), 1.66-1.58 (m, 4H), 1.38-1.33(m, 4H), 0.85-0.82 (t, 6H)

2,3,4,5-Tetrahydro-1 λ 4-1-thiophenone: 2.77-2.67 (m, 4H), 2.34-2.27 (m, 2H), 1.93-1.86 (m, 2H)

1-Phenyl-1-ethanone: 7.95-7.92 (m, 2H), 7.57-7.53(m, 1H), 7.47-7.42 (m, 2H), 2.56 (s, 3H)

9-Oxabicyclo[6.1.0]nonane: 2.84-2.80 (m, 2H), 2.09-2.05 (m, 2H), 1.57-1.37 (m, 8H), 1.25-1.16 (m, 2H)

2-Cyclohexen-1-one: 6.98-6.97 (d, 1H), 5.99-5.97 (d, 1H), 2.51-1.22 (m, 6H). 7-Oxabicyclo[4.1.0]heptan-2-ol: 3.96 (s, 1H), 3.29-2.87 (m, 2H), 2.51-1.22 (m, 7H)

Additional references:

S1. *CrystalClear*, version 1.3.5, Rigaku Corporation, Tokyo, Japan.

S2. *CrystalStructure*, version 4.1, Rigaku Corporation, Tokyo, Japan.

S3. G. M. Sheldrick, *Acta Cryst.* 2008, A64, 112.

S4. G. M. Sheldrick SHELXL 2017/1. University of Göttingen: Göttingen, Germany, 2017.

S5. L. J. Farrugia, *J. Appl. Crystallogr.* 1999, **32**, 837.

Table S1. Crystallographic data for V18ox.

| | |
|---|---|
| formula | C ₅₄ H ₁₂₁ N ₈ O ₄₉ V ₁₈ |
| fw | 2583.50 |
| crystal system | orthorhombic |
| space group | <i>P</i> 2 ₁ 2 ₁ 2 (#18) |
| <i>a</i> (Å) | 14.9504(3) |
| <i>b</i> (Å) | 16.4998(3) |
| <i>c</i> (Å) | 19.5731(3) |
| <i>V</i> (Å ³) | 4828.26(15) |
| <i>Z</i> | 2 |
| μ (mm ⁻¹) | 1.742 |
| <i>R</i> ₁ (<i>I</i> > 2 σ (<i>I</i>)) | 0.0362 |
| <i>wR</i> ₂ | 0.1020 |
| Flack parameter | -0.030(8) |

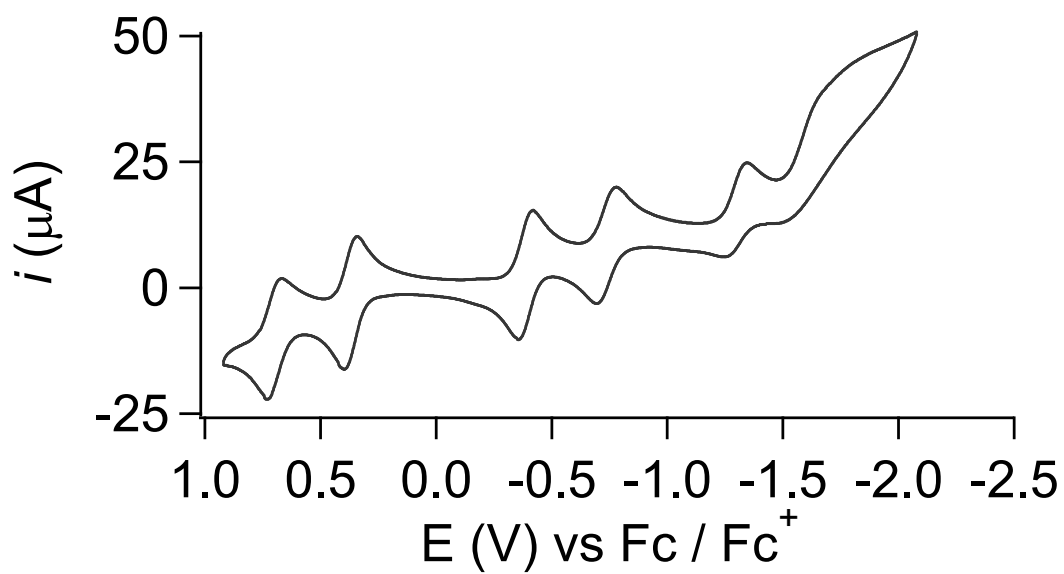


Figure S1. Cyclic voltammogram of V18 in acetonitrile.

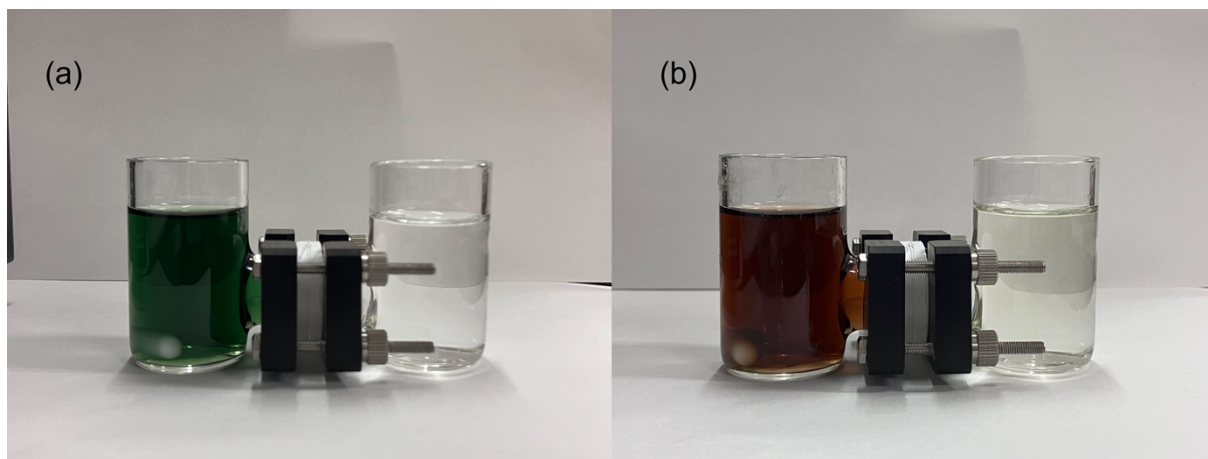


Figure S2. Photos of the solution (a) before and (b) after the controlled potential electrolysis.

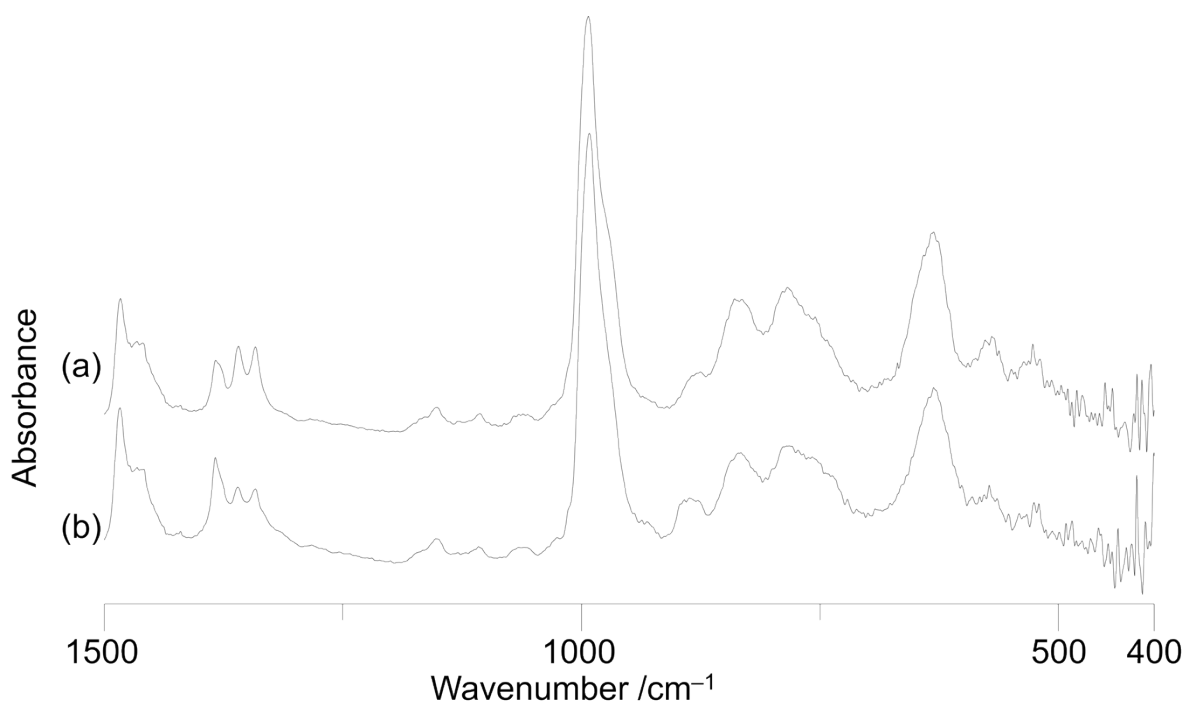


Figure S3. IR spectra of (a) authentic samples of V18 and (b) product obtained without addition of nitrate. The identical spectra of (b) to (a) suggested the formation of V18. The typical peaks at 1342 and 1359 cm⁻¹ was due to the incorporated NO₃⁻ in V18.

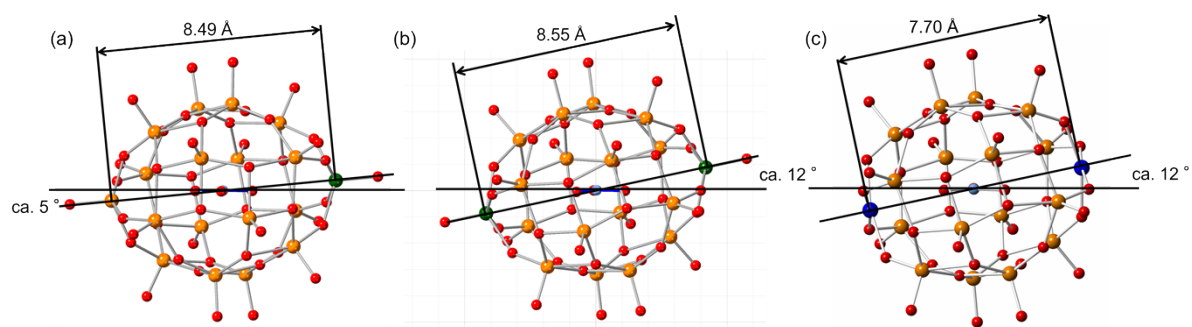


Figure S4. Ball-and-stick representations of (a) V18ox, (b) V18, and (c) Cu₂V16. Orange, green, red, blue, and light blue spheres represent pentavalent vanadium, tetravalent vanadium, oxygen, copper, and nitrogen atoms, respectively.

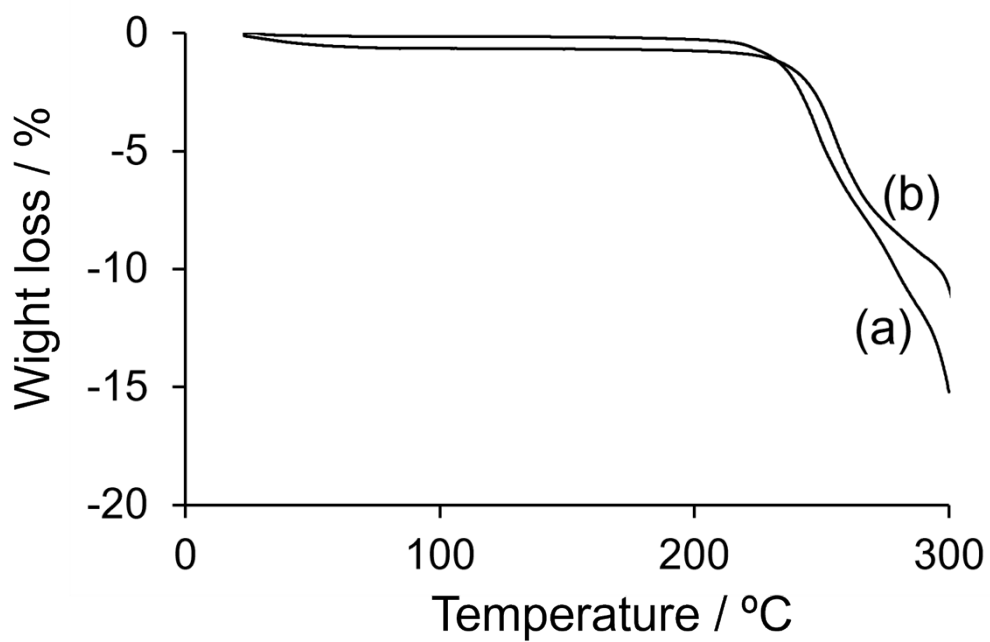


Figure S5. Thermogravimetry analysis of (a) V18ox and V18. V18 possess one hydrated water respective to an anion.

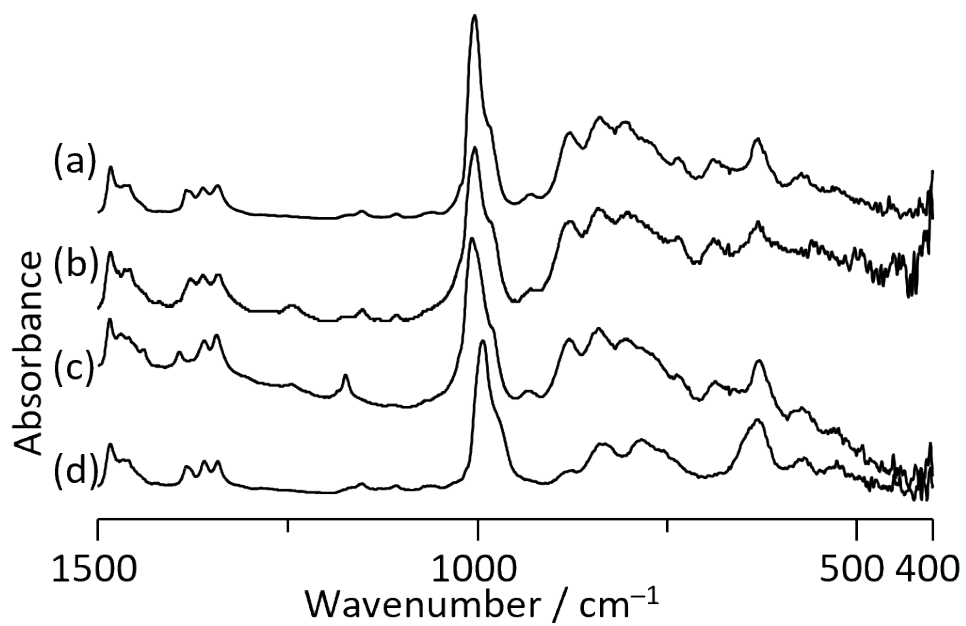


Figure S6. IR spectra of (a) TBA salts of V18ox prepared by chemical reaction, (b) V18ox prepared by electrolysis, (c) crystalline samples of TBA and TEA salts of V18ox and (d) authentic samples of V18.

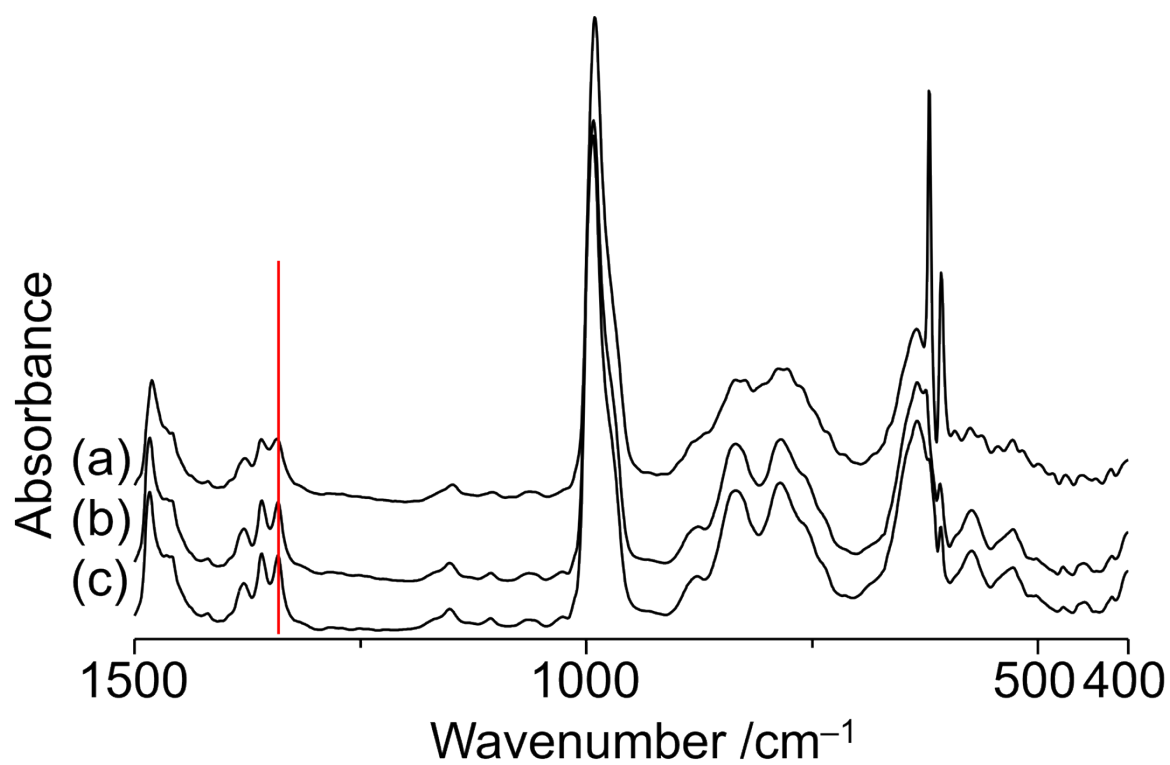


Figure S7. Temperature-dependent IR spectra of V18 (a) at 200°C, (b) after cooling from 200°C to room temperature, and (c) at room temperature under vacuum condition. The red line represents the peak at 1342 cm⁻¹. No peak shift at 1342 cm⁻¹ was observed.

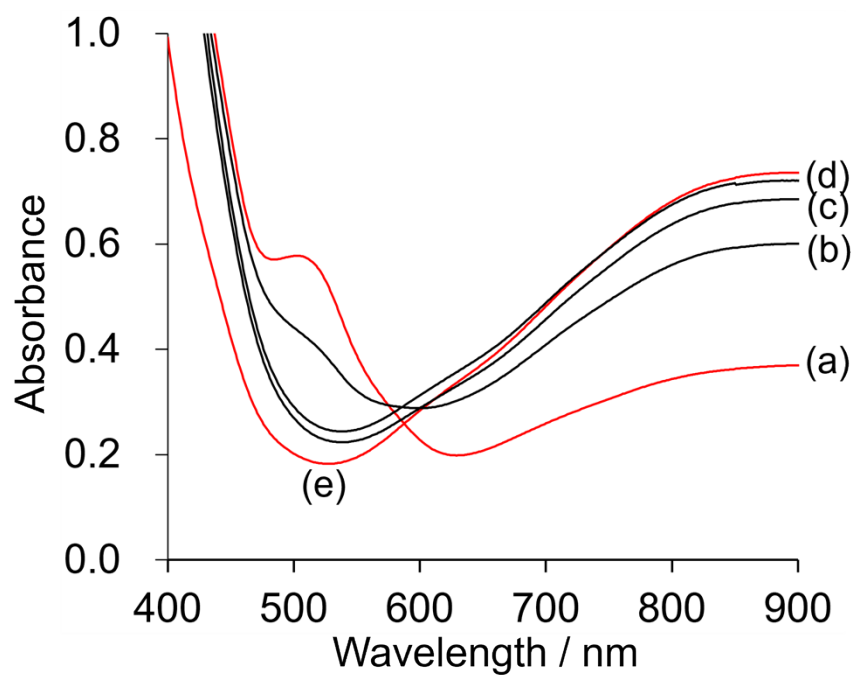


Figure S8. UV/Vis spectra of V18ox in the presence of (a) 0, (b) 0.75 equiv, (c) 1.5 equiv, (d) 2.25 equiv of TBAI. (e) UV/vis spectrum of V18. The high peak intensity below 650 nm was due to the formation of I_2 and/or $TBAI_3$.

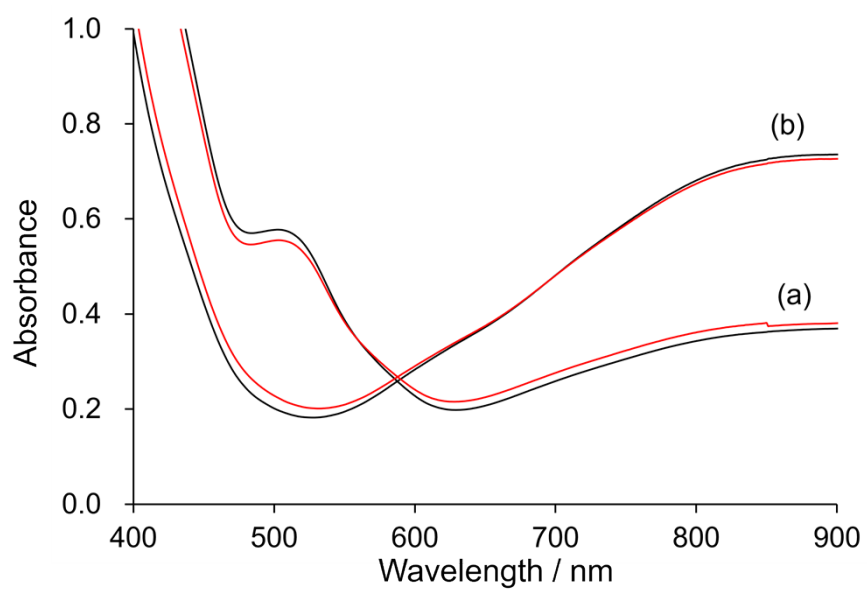


Figure S9. UV/Vis spectra of (a) V18ox and (b) V18. The red-lined spectra were measured in the presence of 200 equiv of TBHP.

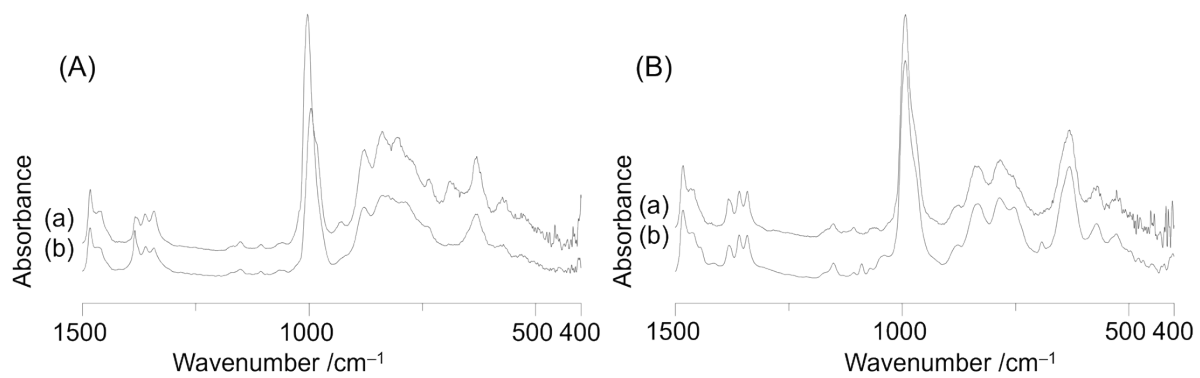


Figure S10. IR spectra of (A) V18ox and (B) V18 (a) before and (b) after the thioanisole oxidation.