

**Supporting Information**

**Enhanced Catalytic Activity of Oxovanadium Complexes in Oxidative  
Polymerization of Diphenyl Disulfide**

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## Experimental

Diphenyl disulfide (PhSSPh), VO(salen), oxovanadium(IV) acetylacetonate (VO(acac)<sub>2</sub>), TrB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>, bromanil and 1,1,2,2-tetrafluoroethanesulfonic acid (CHF<sub>2</sub>CF<sub>2</sub>SO<sub>3</sub>H) were purchased from Tokyo Kasei Corp. and used as received. Molecular weight measurements were done by gel permeation chromatography using an AGILENT PL-220 and 1-chloronaphthalene as the eluent (1 ml/min) maintained at 210 °C. Calibration was done with polystyrene standards.

### Polymerization Procedure

#### Entry 2 in Table 1

To a 10-ml flask, 1.0870 g of PhSSPh (4.98 mmol), 84.0 mg of VO(salen) (5 mol%), and 461.3 mg of TrB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> (10 mol%) were introduced. The mixture was stirred for 20 hours at 100 °C, under 101 kPa of oxygen flow. The reaction mixture was cooled to room temperature and dispersed into 50 ml of CH<sub>2</sub>Cl<sub>2</sub>. The dispersion was poured into 300 ml of MeOH-HCl mixture (MeOH/HCl = 95/5, in v/v). The precipitation was collected with a glass filter. The solid was washed with MeOH, H<sub>2</sub>O, and MeOH thoroughly and dried under vacuum to give purified PPS 52% yield. Melting point was measured and found to be  $T_m = 149$  °C.

#### Entry 3 in Table 1

To a 100-ml flask, 20 g of PhSSPh (91.6 mmol), 0.305 g of VO(salen) (1 mol%), and 95.5 μL 1,1,2,2-tetrafluoroethanesulfonic acid (1 mol%) were introduced. The mixture was stirred for 80 hour at 130 °C, under 101 kPa of oxygen flow. 1 g of the final reaction mixture was taken and cooled to room temperature. The cooled mixture was dispersed into 50 ml of CH<sub>2</sub>Cl<sub>2</sub>. The dispersion was poured into 300 ml of MeOH-HCl mixture (MeOH/HCl = 95/5, in v/v). The precipitation was collected with a glass filter. The solid was washed with MeOH, H<sub>2</sub>O, and MeOH thoroughly and dried under vacuum to give purified PPS in 70% yield. Molecular weight and melting point were measured and found to be as follows,  $M_n = 1200$ ,  $M_w = 1600$ , and  $T_m = 163$  °C.

#### Entry 4 in Table 1

To a 10-ml flask, 1.0914 g of PhSSPh (5.00 mmol), 83.4 mg of VO(salen) (5 mol%), and 469.9 mg of TrB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> (10 mol%) were introduced. The

mixture was stirred for 20 hours at 160 °C, under 101 kPa of oxygen flow. The reaction mixture was cooled to room temperature and dispersed into 50 ml of CH<sub>2</sub>Cl<sub>2</sub>. The dispersion was poured into 300 ml of MeOH-HCl mixture (MeOH/HCl = 95/5, in v/v). The precipitation was collected with a glass filter. The solid was washed with MeOH, H<sub>2</sub>O, and MeOH thoroughly and dried under vacuum to give purified PPS in 69% yield. Molecular weight and melting point were measured and found to be as follows,  $M_n = 880$ ,  $M_w = 1800$ , and  $T_m = 254$  °C.

#### Entry 5 in Table 1

To a 10-ml flask, 1.0900 g of PhSSPh (5.00 mmol), 83.9 mg of VO(salen) (5 mol%), and 75 mg of 1,1,2,2-tetrafluoroethanesulfonic acid (10 mol%) were introduced. The mixture was stirred for 20 hours at 160 °C, under 101 kPa of oxygen flow. The reaction mixture was cooled to room temperature and dispersed into 50 ml of CH<sub>2</sub>Cl<sub>2</sub>. The dispersion was poured into 300 ml of MeOH-HCl mixture (MeOH/HCl = 95/5, in v/v). The precipitation was collected with a glass filter. The solid was washed with MeOH, H<sub>2</sub>O, and MeOH thoroughly and dried under vacuum to give purified PPS in 69% yield. Molecular weight and melting point were measured and found to be as follows,  $M_n = 1500$ ,  $M_w = 3400$ , and  $T_m = 198$  °C.

#### Entry 6 in Table 1

To a 100-ml flask, 20 g of PhSSPh (91.7 mmol), 0.305 g of VO(salen) (1 mol%), and 95.5 μL of 1,1,2,2-tetrafluoroethanesulfonic acid (1 mol%) were introduced. The mixture was mechanically stirred for 40 hours at 160 °C, under 101 kPa of oxygen flow. The reaction mixture was cooled to room temperature and dispersed into 50 ml of CH<sub>2</sub>Cl<sub>2</sub>. The dispersion was poured into 1000 ml of MeOH-HCl mixture (MeOH/HCl = 95/5, in v/v). The precipitation was collected with a glass filter. The solid was washed with MeOH, H<sub>2</sub>O, and MeOH thoroughly and dried under vacuum to give purified PPS in 82% yield. Molecular weight and melting point were measured and found to be as follows,  $M_n = 1100$ ,  $M_w = 1500$ , and  $T_m = 175$  °C.

#### Entry 7 in Table 1

To a 50-ml autoclave with Teflon® inner tube, 6.758 g of PhSSPh (31

mmol), 103 mg of VO(salen) (1 mol%), and 32.3  $\mu\text{L}$  of 1,1,2,2-tetrafluoroethanesulfonic acid (1 mol%) were introduced. The mixture was heated, pressurized with 0.45 MPa of oxygen and stirred for 20 hours at 160  $^{\circ}\text{C}$ . At every 1 hour, the reaction mixture was depressurized to ambient pressure and pressurized to 0.45 MPa again with oxygen. After the reaction, oxygen was depressurized and purged with nitrogen. Then the autoclave was cooled down to room temperature. The reaction mixture was dispersed into 50 ml of  $\text{CH}_2\text{Cl}_2$  and the dispersion was poured into 300 ml of MeOH-HCl mixture (MeOH/HCl = 95/5, in v/v). The precipitation was collected with a glass filter. The solid was washed with MeOH,  $\text{H}_2\text{O}$ , and MeOH thoroughly and dried under vacuum to give PPS in 82% yield. Molecular weight and melting point were measured and found to be as follows,  $M_n = 1800$ ,  $M_w = 4400$ , and  $T_m = 205$   $^{\circ}\text{C}$ .

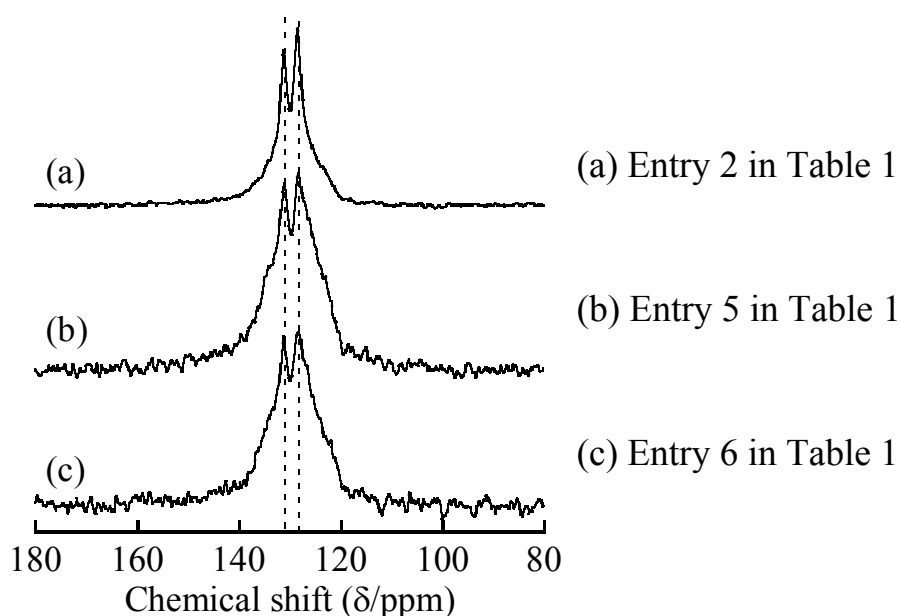


Fig S1. CP-MAS spectra of the PPS

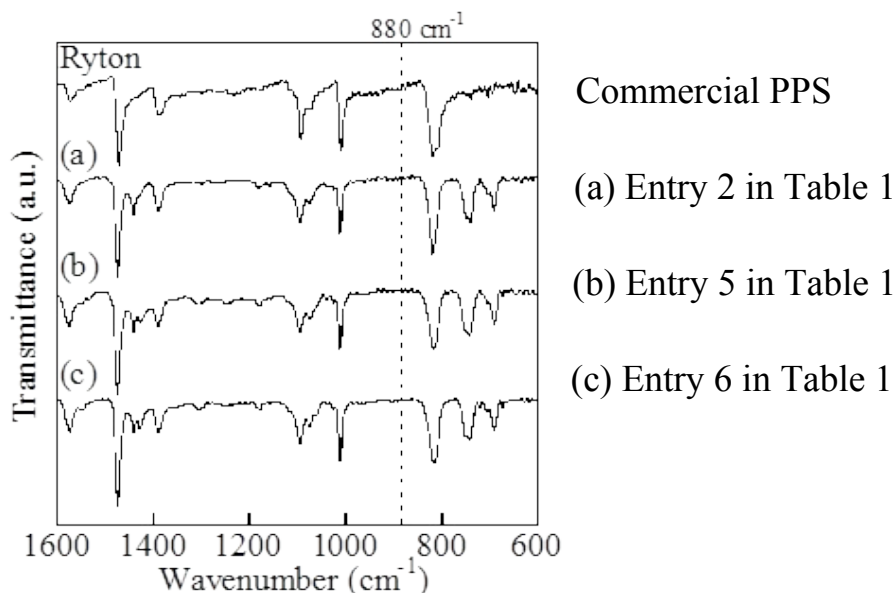


Fig S2. IR spectra of the PPS

#### Entry 1 in Table 2

To a 10-ml flask, 1.0900 g of PhSSPh (4.99 mmol), 52.5 mg of bromanil (2.5 mol%), and 26.0  $\mu$ L of 1,1,2,2-tetrafluoroethanesulfonic acid (5 mol%) were introduced. The mixture was stirred for 4 hours at 160  $^{\circ}$ C, under 101 kPa of oxygen flow. The reaction mixture was cooled to room temperature and dispersed into 50 ml of  $\text{CH}_2\text{Cl}_2$ . The dispersion was poured into 300 ml of MeOH-HCl mixture (MeOH/HCl = 95/5, in v/v). The precipitation was collected with a glass filter. The solid was washed with MeOH,  $\text{H}_2\text{O}$  and MeOH thoroughly and dried under vacuum to give trace amount of polymer.

#### Entry 2 in Table 2

To a 10-ml flask, 1.0914 g of PhSSPh (5.00 mmol), 33.1 mg of  $\text{VO}(\text{acac})_2$  (2.5 mol%), 53.0 mg of bromanil (2.5 mol%), and 26.0  $\mu$ L of 1,1,2,2-tetrafluoroethanesulfonic acid (5 mol%) were introduced. The mixture was stirred for 1 hour at 160  $^{\circ}$ C, under 101 kPa of oxygen flow. The reaction

mixture was cooled to room temperature and dispersed into 50 ml of  $\text{CH}_2\text{Cl}_2$ . The dispersion was poured into 300 ml of MeOH-HCl mixture (MeOH/HCl = 95/5, in v/v). The precipitation was collected with a glass filter. The solid was washed with MeOH, 0.1 N of aqueous KOH solution,  $\text{H}_2\text{O}$ , and MeOH thoroughly and dried under vacuum to give purified PPS in 51% yield. Molecular weight was measured and found to be as follows,  $M_n = 900$  and  $M_w = 1100$ .

#### Entry 3 in Table 2

To a 10-ml flask, 1.0898 g of PhSSPh (4.99 mmol), 33.6 mg of  $\text{VO}(\text{acac})_2$  (2.5 mol%), 53.9 mg of bromanil (2.5 mol%), and 26.0  $\mu\text{L}$  of 1,1,2,2-tetrafluoroethanesulfonic acid (5 mol%) were introduced. The mixture was stirred for 4 hours at 160  $^\circ\text{C}$ , under 101 kPa of oxygen flow. The reaction mixture was cooled to room temperature and dispersed into 50 ml of  $\text{CH}_2\text{Cl}_2$ . The dispersion was poured into 300 ml of MeOH-HCl mixture (MeOH/HCl = 95/5, in v/v). The precipitation was collected with glass filter. The solid was washed with MeOH, 0.1 N of aqueous KOH solution,  $\text{H}_2\text{O}$ , and MeOH thoroughly and dried under vacuum to give purified PPS in 82% yield. Molecular weight was measured and found to be as follows,  $M_n = 1600$  and  $M_w = 2400$ .

#### Entry 4 in Table 2

To a 10-ml flask, 1.0903 g of PhSSPh (4.99 mmol), 66.0 mg of  $\text{VO}(\text{acac})_2$  (5 mol%), and 52.0  $\mu\text{L}$  of 1,1,2,2-tetrafluoroethanesulfonic acid (10 mol%) were introduced. The mixture was stirred for 1 hour at 160  $^\circ\text{C}$ , under 101 kPa of oxygen flow. The reaction mixture was cooled to room temperature and dispersed into 50 ml of  $\text{CH}_2\text{Cl}_2$ . The dispersion was poured into 300 ml of MeOH-HCl mixture (MeOH/HCl = 95/5, in v/v). The precipitation was collected with glass filter. The solid was washed with MeOH,  $\text{H}_2\text{O}$ , and MeOH thoroughly and dried under vacuum to give purified PPS in 22% yield. Molecular weight was measured and found to be as follows,  $M_n = 680$  and  $M_w = 850$ .

#### Entry 5 in Table 2

To a 10-ml flask, 1.0908 g of PhSSPh (5.00 mmol), 66.2 mg of  $\text{VO}(\text{acac})_2$  (5 mol%), and 52.0  $\mu\text{L}$  of 1,1,2,2-tetrafluoroethanesulfonic acid (10 mol%)

were introduced. The mixture was stirred for 4 hours at 160 °C, under 101 kPa of oxygen flow. The reaction mixture was cooled to room temperature and dispersed into 50 ml of CH<sub>2</sub>Cl<sub>2</sub>. The dispersion was poured into 300 ml of MeOH-HCl mixture (MeOH/HCl = 95/5, in v/v). The precipitation was collected with glass filter. The solid was washed with MeOH, H<sub>2</sub>O, and MeOH thoroughly and dried under vacuum to give purified PPS in 74% yield. Molecular weight was measured and found to be as follows,  $M_n = 1300$  and  $M_w = 1600$ .

#### Entry 6 in Table 2

To a 10-ml flask, 1.090 g of PhSSPh (5.0 mmol), 41.7 mg of VO(salen) (2.5 mol%), 53 mg of bromanil (2.5 mol%), and 26.0 μL of 1,1,2,2-tetrafluoroethanesulfonic acid (5 mol%) were introduced. The mixture was stirred for 4 hours at 160 °C, under 101 kPa of oxygen flow. The reaction mixture was cooled to room temperature and dispersed into 50 ml of CH<sub>2</sub>Cl<sub>2</sub>. The dispersion was poured into 300 ml of MeOH-HCl mixture (MeOH/HCl = 95/5, in v/v). The precipitation was collected with glass filter. The solid was washed with MeOH, 0.1 N of aqueous KOH solution, H<sub>2</sub>O and MeOH thoroughly and dried under vacuum to give purified PPS in 56% yield. Molecular weight was measured and found to be as follows,  $M_n = 960$  and  $M_w = 1300$ .

#### Entry 7 in Table 2

To a 10-ml flask, 1.0908 g of PhSSPh (5.00 mmol), 83.4 mg of VO(salen) (5 mol%), and 52.0 μL of 1,1,2,2-tetrafluoroethanesulfonic acid (10 mol%) were introduced. The mixture was stirred for 4 hours at 160 °C, under 101 kPa of oxygen flow. The reaction mixture was cooled to room temperature and dispersed into 50 ml of CH<sub>2</sub>Cl<sub>2</sub>. The dispersion was poured into 300 ml of MeOH-HCl mixture (MeOH/HCl = 95/5, in v/v). The precipitation was collected with glass filter. The solid was washed with MeOH, H<sub>2</sub>O, and MeOH thoroughly and dried under vacuum to give purified PPS in 24% yield.

#### Cyclic Voltammetry of VO(salen)

Cyclic voltammetry was performed 1mM solution of VO(salen) in 1,2-dichloroethane with 0.1 M solutions of tetrabutylammonium

tetrafluoroborate (TBABF<sub>4</sub>), with Pt electrodes vs. Ag/AgCl at a scan speed of 100 mV/s, using an ALS/CH Instruments Electrochemical Analyzer (Model 660Dx), at -10, 20, and 70 °C (Table S1). Then correlation between temperature and redox potential ( $E_{1/2}$ ) was determined as follows.

$$E_{1/2} \text{ (V, vs. Ag/AgCl)} = 0.0015 \times (\text{Temp, } ^\circ\text{C}) + 0.4492$$

Table S1. Redox potential of VO(salen)

Temperature (°C)	V ( $E_{1/2}$ , vs. Ag/AgCl)
-10	0.44
20	0.47
70	0.56

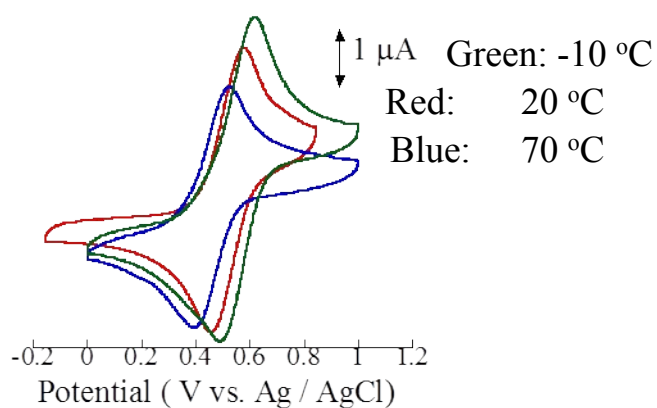


Fig S3. Cyclic voltammogram of VO(salen) under various temperatures

#### Cyclic Voltammetry of bromanil

Cyclic voltammetry was performed 1mM solution of bromanil in nitrobenzene with 0.1 M solutions of tetrabutylammonium tetrafluoroborate (TBABF<sub>4</sub>), with Pt electrodes vs. Ag/AgCl at a scan speed of 100 mV/s, using an ALS/CH Instruments Electrochemical Analyzer



(Model 660Dx), at ambient temperature.

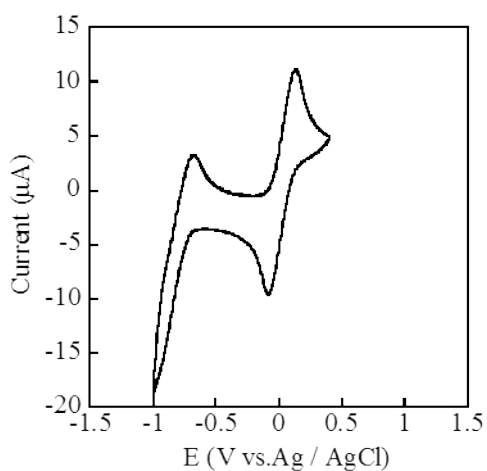


Fig S4. Cyclic voltammogram of bromanil under neutral condition

#### Cyclic Voltammetry of bromanil under acidic conditions

Cyclic voltammetry was performed 1mM solution of bromanil and 2 or 5 molar of  $C_2HF_4SO_3H$  in nitrobenzene with 0.1 M solutions of tetrabutylammonium tetrafluoroborate (TBABF<sub>4</sub>), with Pt electrodes vs. Ag/AgCl at a scan speed of 100 mV/s, using an ALS/CH Instruments Electrochemical Analyzer (Model 660Dx), at ambient temperature.

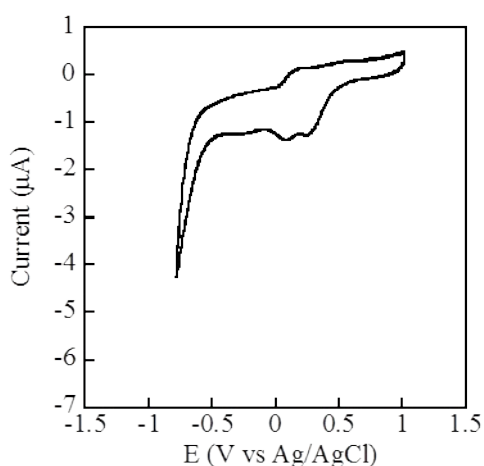


Fig S5. Cyclic voltammogram of bromanil with 2 molar of  $C_2HF_4SO_3H$

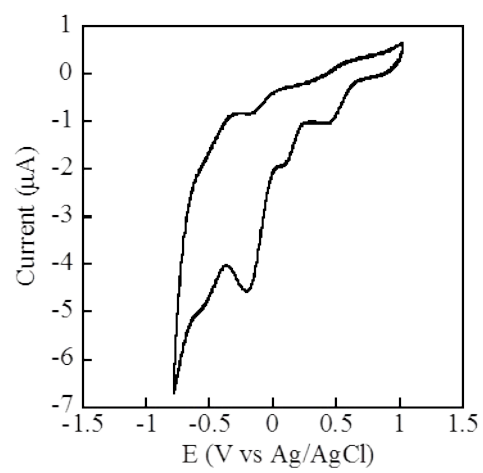


Fig S6. Cyclic voltammogram of bromanil with 5 molar equivalents of  $C_2HF_4SO_3H$