

Supporting Information for:

Synthesis and Characterization of $V^V(3,6\text{-DBSQ})(3,6\text{-DBCat})_2$, a d^0 Metal Complex with Dioxygenase Catalytic Activity

Aimee M. Morris,[†] Cortlandt G. Pierpont,^{*,‡} and Richard G. Finke^{*,†}

[†]*Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523 and* [‡]*Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309*

Corresponding authors: CGP: pierpont@colorado.edu; RGF: rfinke@lamar.colostate.edu

EXPERIMENTAL

Materials

The following were obtained from the indicated sources, then used as received: TiCl_4 (Aldrich, 99.9%), Ag_2O (Aldrich, 99%), catechol (Aldrich, $\geq 99\%$), toluene (Aldrich, 99.8%, anhydrous), xylenes (Fisher Scientific, ACS grade), isobutylene (Aldrich, 99%), hexanes (Fisher Scientific, ACS grade), methylene chloride (Fisher, ACS grade), diethyl ether (Aldrich, HPLC grade), n-pentane (Fisher, pesticide grade), and $\text{VO}(\text{acac})_2$ (Aldrich, 95%; stored in a Vacuum Atmospheres N_2 drybox).

Instrumentation

^1H NMR was run on a Varian Inova (JS-300) nuclear magnetic resonance (NMR) spectrometer using CDCl_3 as the solvent. The ^1H NMR was referenced to the residual proton impurity in the deuterated solvent. Diffraction data were collected on a Bruker APEX2 diffractometer employing Mo $\text{K}\alpha$ radiation. Standard Bruker APEX2 control and integration software was employed, and Bruker SHELXTLⁱ software was used for structure solution, refinement, and graphics. SADABSⁱⁱ correction was employed and the structure was solved by direct methods and refined by a full-matrix, weighted least-squares process. In addition, PLATON's SQUEEZE function was used to refine the disordered methanol solvent. The IR spectrum was collected on an Avatar 360 FT-IR spectrometer with a solid KBr sample pellet. The near IR spectrum was obtained with a solid KBr sample pellet on a Perkin-Elmer Lambda 9 UV-visible near-IR spectrophotometer. Solution UV/vis measurements were obtained on a Hewlett-Packard 8452A diode spectrometer in glass, Schlenk UV cells (i.e., cells with a Teflon valve glass-blown onto a standard pyrex glass cuvette). Electron paramagnetic resonance (EPR) spectra were recorded on a Bruker ESP-300E spectrometer using a 5-mm o.d.

quartz j-young EPR tube with 2,2-diphenyl-1-picrylhydrazyl (DPPH) as the reference compound ($g=2.0037$). Elemental Analyses were performed by Galbraith Laboratories, Inc. (Knoxville, TN). Positive and negative ion electrospray ionization mass spectrometry analyses were performed on an Agilent model 6220 TOF mass spectrometer.

Synthesis of 3,6-di-tert-butylcatechol (3,6-DBCat)

The 3,6-DBCat synthesis was carried out in a Parr pressure reactor (model 4561) made of Monel 400 alloy. The reactor is equipped with a pressure gauge and automatic temperature controller. The interior of the reactor contains an impeller, thermocouple, cooling loop, and dip tube, all of which are in contact with the reaction solution. A glass liner was dried overnight at 160 °C and used to avoid contact of the solution with the interior of the reactor. 3,6-DBCat was synthesized according to previously published literature methods,ⁱⁱⁱ but with the following changes: (i) the reaction was scaled down by a factor of five in order to accommodate our Parr bomb reactor volume (~300 mL) and not exceed a pressure of 16 atm, as described in the literature,ⁱⁱⁱ (ii) the reaction was run at 150 °C instead of 100 °C, and the reaction time was extended from 1.5 hours to 4 hours because the reaction is not complete at 1.5 hours as monitored by the pressure loss. In addition, following the vacuum distillation, the product was purified by recrystallizing twice in hot n-pentane (purified yield 4 g (12 %)). The purified product was characterized by ¹H NMR in CDCl₃ and MS. Observed [previously reportedⁱⁱⁱ]: 6.75 [6.59]; 5.33 [5.11]; and 1.39 [1.31] ppm in a 1:1:9 ratio. GC-MS found for C₁₄H₂₁O₂, m/z 221 (3,6-DBCat-H⁺).

Synthesis of 3,6-Di-tert-butyl-1,2-benzoquinone (3,6-DBBQ)

3,6-DBBQ was synthesized according to the literature procedure.^{iv} Specifically, 0.899 g (4.04 mmol) of pure 3,6-DBCat was dissolved in ~10 mL of diethyl ether with stirring. Upon addition of 2.000 g (8.63 mmol) of Ag₂O (in excess), the solution immediately turns green. Stirring was continued for ~5 minutes and then the grey solid (Ag) was filtered off using a medium frit. The solution was rotovapped to dryness yielding crude 3,6-DBBQ. The crude 3,6-DBBQ was then purified by column chromatography. The column (450 × 30 mm) was packed with a slurry of silica gel (Aldrich 70-230 mesh, 100 g, suspended in ~200 mL of n-hexanes). The crude 3,6-DBBQ was dissolved in ~3 mL of CH₂Cl₂, placed on top of the column and eluted with ~500 mL of CH₂Cl₂. The green colored fractions were combined and rotovapped to dryness. The purified 3,6-DBBQ was then dried under vacuum at room temperature overnight. Yield 0.127 g (14 %). ¹H NMR in CDCl₃ observed [previously reported^{iv}]: 6.81 [6.17] and 1.27 [1.21] ppm in a 1:9 ratio. GC-MS found for C₁₄H₂₀O₂Na, *m/z* 243 (3,6-DBBQ+Na⁺).

Synthesis of V(3,6-DBSQ)(3,6-DBCat)₂

V(3,6-DBSQ)(3,6-DBCat)₂ was synthesized under Ar by distilling at 70 °C dry methanol over the stirring mixture of VO(acac)₂ (68.0 mg, 0.256 mmol), 3,6-DBCat (114 mg, 0.511 mmol), and 3,6-DBBQ (58.3 mg, 0.265 mmol) over the course of ~2 hours. The resultant solution was deep blue. The entire apparatus was sealed and placed in the freezer to induce crystallization which occurred overnight. The apparatus was then

transferred into a N₂ atmosphere drybox and the resultant deep-blue solid was filtered over a medium frit and dried under vacuum at room temperature overnight. Yield 121 mg (66 %). Elemental analysis (Galbraith Laboratories, Inc. Knoxville, TN) was consistent with V(3,6-DBSQ)(3,6-DBCat)₂•CH₃OH. Calc. [found]: V, 6.85 [6.58]; C, 69.43 [69.91]; H 8.67 [8.90].

CHARACTERIZATION

X-ray Diffraction

The single crystal was removed from the mother liquor after the freezer induced crystallization (*vide supra*), mounted on a goniometer, and data collection was started. The X-ray data, atomic coordinates, anisotropic displacement, bond length, and bond angle tables for the structure solution of V(3,6-DBSQ)(3,6-DBCat)₂ can be seen in Tables S1-S4 below.

Table S1. Crystal data and structure refinement for V(3,6-DBSQ)(3,6-DBCat)₂.

| | | |
|---|-------------|--|
| Identification code: rfl10r_0m | | |
| Empirical formula: C ₄₂ H ₆₀ O ₆ V | | |
| Formula weight: 711.84 | | |
| Temperature: 296(2) K | | |
| Wavelength: 0.71073 | | |
| Crystal system: orthorhombic | | |
| Space group: Ccca | | |
| Unit cell dimensions: | | |
| a: = 19.9969(17) Å | alpha = 90° | |
| b: = 23.740(2) Å | beta = 90° | |
| c: = 18.1741(16) Å | gamma = 90° | |
| Volume, Z: 8627.8(13) Å ³ , 8 | | |
| Density (calculated): 1.096 mg/m ³ | | |
| Absorption coefficient: 0.270 mm ⁻¹ | | |
| F(000): 3064 | | |
| Crystal size: 0.36 x 0.10 x 0.07 mm | | |
| Erange for data collection: 1.74 to 23.53° | | |

Limiting indices: $-22 < \theta < 22$, $-26 < \theta < 26$, $-20 < \theta < 20$
 Reflections collected: 14529
 Independent reflections: 3222 ($R(\text{int}) = 0.0819$)
 Completeness to 23.53° , 99.9 %
 Max. and min. transmission: 0.9826 and 0.9080
 Refinement method: Full-matrix least-squares on F^2
 Data / restraints / parameters: 3222 / 0 / 331
 Goodness-of-fit on F^2 : 1.071
 Final R indices: $R1 = 0.0540$, $wR2 = 0.1195$
 R indices (all data): $R1 = 0.0840$, $wR2 = 0.1325$
 Largest diff. peak and hole: 0.436 and -0.356

Table 2. Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$\times 10^3$] for $V(3,6\text{-DBSQ})(3,6\text{-DBCat})_2$. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized tensor.

| | x | y | z | $U(\text{eq})$ |
|-------|---------|---------|----------|----------------|
| V(1) | 2500 | 5000 | 385(1) | 23(1) |
| O(1) | 2995(1) | 4533(1) | 1008(1) | 24(1) |
| O(2) | 1924(1) | 4364(1) | 405(1) | 25(1) |
| O(3) | 1992(1) | 5311(1) | -451(1) | 26(1) |
| C(1) | 2825(2) | 3991(1) | 1007(2) | 30(1) |
| C(2) | 2191(2) | 3897(1) | 678(2) | 26(1) |
| C(3) | 1900(2) | 3359(1) | 632(2) | 40(1) |
| C(4) | 2279(3) | 2943(2) | 956(3) | 68(2) |
| C(5) | 2906(3) | 3032(2) | 1278(3) | 75(2) |
| C(6) | 3207(2) | 3551(2) | 1307(2) | 48(1) |
| C(7) | 1240(2) | 3261(2) | 226(2) | 44(1) |
| C(8) | 1038(4) | 2634(2) | 242(4) | 78(2) |
| C(9) | 677(2) | 3601(2) | 590(3) | 56(1) |
| C(10) | 1314(2) | 3437(2) | -581(2) | 41(1) |
| C(11) | 3921(3) | 3660(2) | 1598(3) | 65(2) |
| C(12) | 3880(3) | 4028(2) | 2285(3) | 58(1) |
| C(13) | 4257(3) | 3097(2) | 1815(4) | 162(4) |
| C(14) | 4344(3) | 3931(4) | 1004(4) | 102(3) |
| C(15) | 2204(2) | 5182(1) | -1104(2) | 23(1) |
| C(16) | 1912(2) | 5372(1) | -1769(2) | 25(1) |
| C(17) | 2219(2) | 5185(1) | -2394(2) | 29(1) |
| C(18) | 1291(2) | 5750(2) | -1757(2) | 34(1) |
| C(19) | 712(2) | 5429(2) | -1392(2) | 44(1) |
| C(20) | 1078(2) | 5909(2) | -2544(2) | 47(1) |

| | | | | |
|-------|---------|---------|----------|-------|
| C(21) | 1441(3) | 6296(2) | -1340(2) | 47(1) |
|-------|---------|---------|----------|-------|

Table S3. Bond lengths [Å] and angles [°] for V(3,6-DBSQ)(3,6-DBCat)₂.

| | |
|--------------------|------------|
| V(1)-O(1) | 1.868(2) |
| V(1)-O(1)#1 | 1.868(2) |
| V(1)-O(2) | 1.898(2) |
| V(1)-O(2)#1 | 1.898(2) |
| V(1)-O(3) | 1.971(2) |
| V(1)-O(3)#1 | 1.971(2) |
| O(1)-C(1) | 1.330(4) |
| O(2)-C(2) | 1.326(4) |
| O(3)-C(15) | 1.298(3) |
| C(1)-C(6) | 1.404(5) |
| C(1)-C(2) | 1.421(5) |
| C(2)-C(3) | 1.406(5) |
| C(3)-C(4) | 1.376(5) |
| C(3)-C(7) | 1.530(5) |
| C(4)-C(5) | 1.399(7) |
| C(5)-C(6) | 1.373(6) |
| C(6)-C(11) | 1.543(6) |
| C(7)-C(10) | 1.533(5) |
| C(7)-C(9) | 1.534(6) |
| C(7)-C(8) | 1.543(6) |
| C(11)-C(14) | 1.514(9) |
| C(11)-C(12) | 1.527(6) |
| C(11)-C(13) | 1.548(6) |
| C(15)-C(16) | 1.415(4) |
| C(15)-C(15)#1 | 1.466(6) |
| C(16)-C(17) | 1.364(4) |
| C(16)-C(18) | 1.533(5) |
| C(17)-C(17)#1 | 1.428(7) |
| C(18)-C(21) | 1.532(5) |
| C(18)-C(19) | 1.536(5) |
| C(18)-C(20) | 1.539(5) |
| | |
| O(1)-V(1)-O(1)#1 | 105.38(12) |
| O(1)-V(1)-O(2) | 80.66(9) |
| O(1)#1-V(1)-O(2) | 97.99(9) |
| O(1)-V(1)-O(2)#1 | 97.99(9) |
| O(1)#1-V(1)-O(2)#1 | 80.66(9) |
| O(2)-V(1)-O(2)#1 | 177.80(13) |

| | |
|---------------------|------------|
| O(1)-V(1)-O(3) | 164.25(9) |
| O(1)#1-V(1)-O(3) | 88.39(8) |
| O(2)-V(1)-O(3) | 90.01(9) |
| O(2)#1-V(1)-O(3) | 91.68(9) |
| O(1)-V(1)-O(3)#1 | 88.39(8) |
| O(1)#1-V(1)-O(3)#1 | 164.25(9) |
| O(2)-V(1)-O(3)#1 | 91.68(9) |
| O(2)#1-V(1)-O(3)#1 | 90.01(9) |
| O(3)-V(1)-O(3)#1 | 79.16(12) |
| C(1)-O(1)-V(1) | 116.01(19) |
| C(2)-O(2)-V(1) | 115.4(2) |
| C(15)-O(3)-V(1) | 116.67(19) |
| O(1)-C(1)-C(6) | 125.5(3) |
| O(1)-C(1)-C(2) | 112.3(3) |
| C(6)-C(1)-C(2) | 122.2(3) |
| O(2)-C(2)-C(3) | 124.9(3) |
| O(2)-C(2)-C(1) | 112.7(3) |
| C(3)-C(2)-C(1) | 122.4(3) |
| C(4)-C(3)-C(2) | 113.6(4) |
| C(4)-C(3)-C(7) | 124.9(3) |
| C(2)-C(3)-C(7) | 121.5(3) |
| C(3)-C(4)-C(5) | 124.3(4) |
| C(6)-C(5)-C(4) | 123.0(4) |
| C(5)-C(6)-C(1) | 114.4(4) |
| C(5)-C(6)-C(11) | 124.7(4) |
| C(1)-C(6)-C(11) | 120.7(4) |
| C(3)-C(7)-C(10) | 109.7(3) |
| C(3)-C(7)-C(9) | 110.2(3) |
| C(10)-C(7)-C(9) | 109.9(4) |
| C(3)-C(7)-C(8) | 111.3(4) |
| C(10)-C(7)-C(8) | 107.8(4) |
| C(9)-C(7)-C(8) | 107.9(5) |
| C(14)-C(11)-C(12) | 111.7(5) |
| C(14)-C(11)-C(6) | 110.1(4) |
| C(12)-C(11)-C(6) | 109.1(4) |
| C(14)-C(11)-C(13) | 107.8(6) |
| C(12)-C(11)-C(13) | 107.9(4) |
| C(6)-C(11)-C(13) | 110.2(4) |
| O(3)-C(15)-C(16) | 124.9(3) |
| O(3)-C(15)-C(15)#1 | 113.75(17) |
| C(16)-C(15)-C(15)#1 | 121.39(18) |
| C(17)-C(16)-C(15) | 114.9(3) |
| C(17)-C(16)-C(18) | 124.5(3) |
| C(15)-C(16)-C(18) | 120.5(3) |
| C(16)-C(17)-C(17)#1 | 123.66(19) |
| C(21)-C(18)-C(16) | 110.1(3) |

| | |
|-------------------|----------|
| C(21)-C(18)-C(19) | 110.8(3) |
| C(16)-C(18)-C(19) | 109.1(3) |
| C(21)-C(18)-C(20) | 107.8(3) |
| C(16)-C(18)-C(20) | 110.7(3) |
| C(19)-C(18)-C(20) | 108.4(3) |

Symmetry transformations used to generate equivalent atoms#1: $-x+1/2, -y+1, z$

Table S4. Anisotropic displacement parameters [$\times 10^3$] for V(3,6-DBSQ)(3,6-DBCat)₂.

| | U11 | U22 | U33 | U23 | U13 | U12 |
|-------|--------|--------|--------|--------|---------|--------|
| V(1) | 27(1) | 26(1) | 16(1) | 0 | 0 | 4(1) |
| O(1) | 25(1) | 28(1) | 17(1) | -2(1) | 0(1) | 3(1) |
| O(2) | 26(1) | 27(1) | 22(1) | 2(1) | -4(1) | 5(1) |
| O(3) | 31(1) | 28(1) | 18(1) | 0(1) | 3(1) | 8(1) |
| C(1) | 39(2) | 28(2) | 21(2) | -3(2) | -7(2) | 6(2) |
| C(2) | 33(2) | 28(2) | 17(2) | 0(1) | -3(2) | 5(2) |
| C(3) | 61(3) | 27(2) | 31(2) | -1(2) | -12(2) | -8(2) |
| C(4) | 113(4) | 20(2) | 69(3) | 3(2) | -43(3) | -9(2) |
| C(5) | 122(5) | 30(2) | 73(3) | 0(2) | -69(3) | 12(3) |
| C(6) | 69(3) | 32(2) | 42(2) | -6(2) | -29(2) | 16(2) |
| C(7) | 55(3) | 40(2) | 36(2) | -6(2) | -12(2) | -14(2) |
| C(8) | 112(5) | 59(4) | 62(4) | -1(3) | -32(4) | -45(4) |
| C(9) | 46(3) | 80(4) | 41(3) | -12(3) | -4(2) | -28(3) |
| C(10) | 47(3) | 40(3) | 35(2) | -9(2) | -7(2) | -3(2) |
| C(11) | 76(3) | 50(3) | 69(3) | -29(2) | -53(3) | 35(2) |
| C(12) | 64(4) | 64(3) | 47(3) | -13(3) | -25(3) | 9(3) |
| C(13) | 184(7) | 71(4) | 229(8) | -65(5) | -179(7) | 80(4) |
| C(14) | 44(4) | 172(8) | 90(5) | -66(5) | -24(3) | 54(4) |
| C(15) | 27(2) | 20(2) | 22(2) | -2(1) | 2(2) | -3(1) |
| C(16) | 25(2) | 28(2) | 22(2) | -1(2) | -1(2) | 1(2) |
| C(17) | 28(2) | 38(2) | 20(2) | 5(2) | -6(2) | 0(2) |
| C(18) | 36(2) | 43(2) | 23(2) | 0(2) | -3(2) | 13(2) |
| C(19) | 32(2) | 68(3) | 31(2) | 2(2) | 5(2) | 14(2) |
| C(20) | 47(3) | 61(3) | 31(2) | 3(2) | -7(2) | 20(3) |
| C(21) | 61(3) | 42(2) | 37(3) | 0(2) | -10(2) | 21(2) |

Near IR Spectrum

The room temperature near IR region was scanned to look for ligand-ligand charge-transfer bands; none were observed from 300 to 3000 nm, Figure S1.

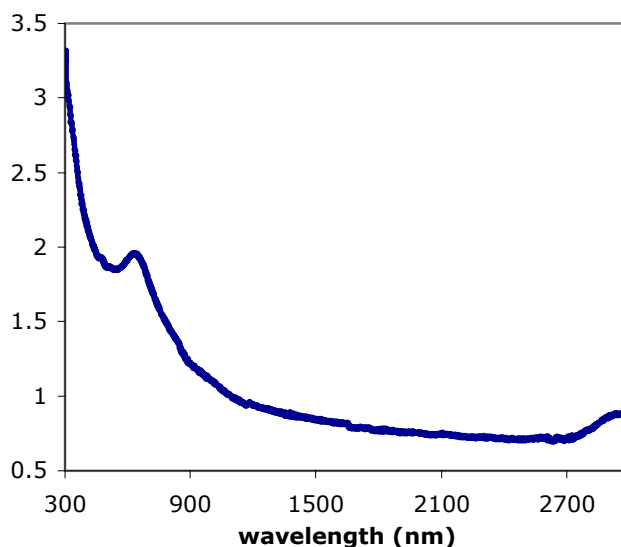


Figure S1. The near IR region of $V(3,6\text{-DBSQ})(3,6\text{-DBCat})_2$ at room temperature. No ligand-ligand charge transfer bands are present from 300 to 3000 nm. The small peak observed near 3000 nm is due to the residual water OH stretching from the KBr.

IR Spectrum

In order to test for a low energy ligand-ligand charge transfer band, the IR region was also scanned at room temperature. Again, no ligand-ligand charge transfer band is observed from 400 to 4000 cm^{-1} indicating that the charge is localized on a single semiquinone ligand of $V(3,6\text{-DBSQ})(3,6\text{-DBCat})_2$.

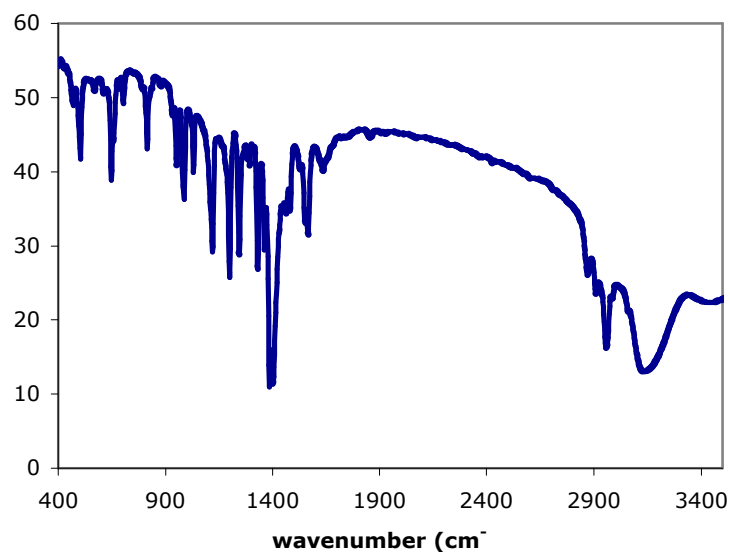


Figure S2. The IR region of $V(3,6\text{-DBSQ})(3,6\text{-DBCat})_2$ at room temperature. The normal C-O, C-C, and C-H stretching bands are present, but no ligand-ligand charge transfer band is observed, at least at room temperature.

Solid-State and Solution UV/Visible Spectra

The solid-state UV/Visible spectrum is shown in Figure S3. Note that the same peaks are present as in the solution spectrum (Figure 2 of the main text and Figure S4), but the peaks around ~300 and 405 nm are not as pronounced in the solid-state spectrum.

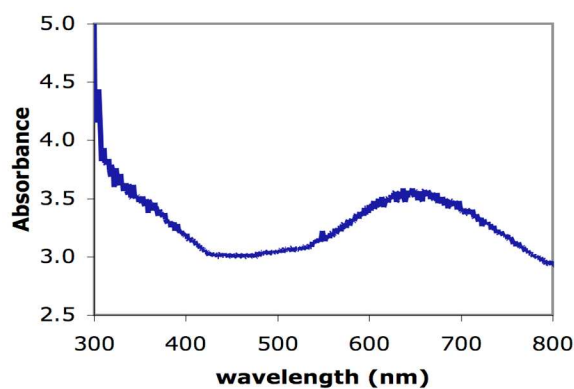


Figure S3. UV/Vis spectrum of $V(3,6\text{-DBSQ})(3,6\text{-DBCat})_2$ prepared as a KBr pellet and at room temperature.

The UV/Vis of $V(3,6\text{-DBSQ})(3,6\text{-DBCat})_2$ was taken in toluene, both under an inert N_2 atmosphere and after bubbling the solution with O_2 , all at room temperature. The solution spectra can be seen in Figure S3 below. Note that upon exposure to O_2 , the peak at ~ 670 nm diminishes, but the peaks at ~ 405 and 300 nm remain. This is analogous to what is observed with $[VO(3,5\text{-DBSQ})(3,5\text{-DBCat})]_2$.^v That is, the peak at 668 nm diminishes upon exposure to O_2 while the peak at 294 nm remains. The products of this reaction with just O_2 (i.e., and in the absence of additional, non-bound substrate) have not been characterized, in part since they are under non-catalytic conditions, but still may be of interest for further studies.

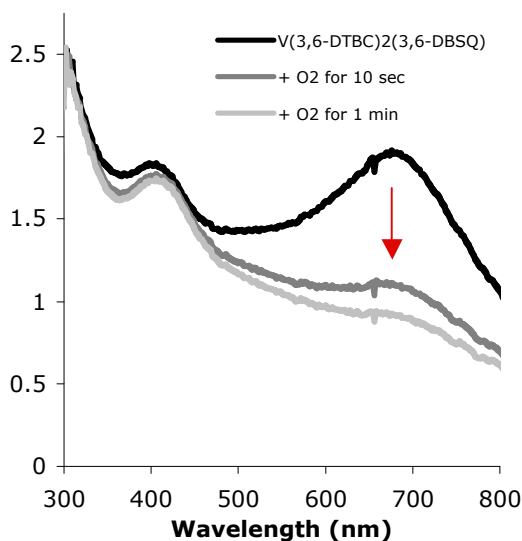


Figure S4. UV/Vis spectra of $V(3,6\text{-DBSQ})(3,6\text{-DBCat})_2$ in toluene under an inert atmosphere and after bubbling with O_2 , all at room temperature. The spectra show the disappearance of the 670 nm band and also the retention of the 300 and 405 nm bands with exposure to O_2 . The products of this reaction under non-catalytic conditions remains to be identified.

ⁱ Sheldrick, G. M. *Acta Cryst. A* **2008**, 64, 112-122.

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- ^{iv} Wheeler, D. E.; McCusker, J. K. *Inorg. Chem.* **1998**, *37*, 2296-2307.
- ^v Yin, C.-X.; Finke, R. G. *J. Am. Chem. Soc.* **2005**, *127*, 9003-9013.