Supporting Information

Structural and Reactivity Insights into High-Valent Co(III)-(μ-peroxo)-Co(IV) and Its Electromer Co(III)-(μ-superoxo)-Co(III)

Parkhi Sharma,[a] Sikha Gupta,[a] Rakesh Kumar,[a] Asterios Charisiadis,[b] Maxime Sauvan,[b] Lucia Velasco,[b] Abhishek Saini,[c] and Dooshaye Moonshiram,[b]*Apparao Draksharapu[a,]*

Materials and methods:

All chemicals and reagents were obtained from commercial sources and were used as received. HPLC-grade H_2O, and CH_3CN from Merck were used in the spectroscopic studies. The preparation of tris(4-methoxy-3,5-dimethylpyridyl-2-methyl)amine (TPA*) followed the method previously described. [1] An Agilent 8453 diode-array spectrophotometer was used to record the UV/Vis absorption spectra and conduct the kinetic experiments spectrophotometrically in 1 cm quartz cells (λ = 200–1000 nm range). The ESI-MS was recorded on an Agilent 6546 LC/Q-TOF in the positive-ion mode. The X-band electron paramagnetic resonance (EPR) was measured on a JES-FA200 ESR spectrometer at 77 K in acetonitrile solution. EPR parameters : [frequency, 9136 MHz; power, 0.995 mW; field center, 490.0 mT, width, ± 500.00Mt; sweep time, 30.0 s; modulation frequency, 100.00 kHz, width, 1 mT; amplitude, 1 mT; and time constant, 0.03 s]. The ^{1}H NMR spectra were obtained using a JEOL JNM LA 500 (400 MHz) NMR spectrometer. The cyclic voltammetry experiments were carried out at room temperature using a CH Instruments Electrochemical Analyzer M-600B series. A three-electrode system was used where glassy carbon was used as the working electrode, Pt wire was the auxiliary electrode, and aqueous Ag/AgCl was used as the reference electrode. The solutions used were 1 mM **1**, 1 mM *p*-phenols and 100 mM supporting electrolyte tetra-n-butylammonium perchlorate (TBAP) in acetonitrile and potassium chloride in water. The resonance Raman spectra were obtained at 638 nm (80 mW, Cobolt lasers, HÜBNER Photonics) excitation wavelengths using a Kymera 328i motorized Czerny-Turner Spectrograph (Andor Technology) equipped with a DU 420A-BEX2-DD camera (iDus 420 CCD, Andor Technology). The CCD camera was cooled to −80 °C. The spectral slit width of the instrument was set to 100 μm.

Synthesis of 1a:

A 30 mg sample of [(TPA*)Co(II)Cl]Cl (**1**, 0.05 mmol) was dissolved in 5 mL of water at room temperature, exposed to open air. Upon dissolution, the solution's color changed from green to brown. To this, 21 mg of sodium perchlorate (0.15 mmol) was added, and the mixture was stirred for one hour in an open atmosphere. After an hour, a brown solid precipitate appeared. Gradually, acetonitrile was added to the mixture until the solution became clear. Dark brown crystals of **1a**, suitable for X-ray diffraction analysis, formed over 3–4 days through slow evaporation of the solution. UV/Vis absorption bands: 380 nm and 600 nm, Calcd for $C_{54}H_{83}Cl_3Co_2N_8O_{26}$:C, 43.69; H, 5.64; N, 7.55. Found: C, 43.4; H, 5.3; N, 7.25.

X-ray crystallography:

Single crystals of **1a** were used for X-ray diffraction data collection. Diffraction intensities were collected on a Bruker SMART APEX CCD diffractometer, with graphite-monochromated Mo Kα (0.71073 Å) radiation at 100(2) K. The structures were solved by SHELXT[2] and refined with the SHELXL[3] package incorporated into the Olex2v1.5[4] crystallographic collective package. All non-hydrogen atoms were refined with anisotropic thermal parameters using full-matrix least-squares procedures on F^2. Solvent mask command was used through Olex2, which showcased 184 electrons in a volume of 710 $Å^3$ in 2 voids per unit cell. This electron count corresponds to the presence of 4.6 H_2O per formula unit. CCDC 2381919 contains the supplementary crystallographic data for **1a**.

X-ray Absorption Spectroscopy (XAS) Methods:

X-ray absorption spectra were collected at P65 beamline at DESY (Germany) on mini-undulator beamline at electron energy 7.709 KeV and average current of 100 mA. The radiation was monochromatized by a Si(111) crystal monochromator. The intensity of the X-rays were monitored by three ion chambers (I_0, I_1 and I_2). I_0, placed before the sample, was filled with 92% nitrogen and 8% argon. I_1 and I_2 were placed after the sample. I_1 was filled with 86 % N_2 and 14 % Ar while I_2 was filled with 100 % Kr. Co metal was placed between ion chambers I_1 and I_2 and its absorption was recorded with each scan for energy calibration. Co XAS energy was calibrated by the first maxima in the second derivative of the Cobalt's metal foil's X-ray absorption near edge structure (XANES) spectrum. The samples were kept at 5 K in a He atmosphere at ambient pressure and recorded as fluorescence excitation spectra using a 4-element energy-resolving Silicon drift detector. The solution complexes were measured in the continuous helium flow cryostat in fluorescence mode. Around 24 XAS spectra of each sample were collected. Care was taken to measure at several sample positions on each sample and no more than 5 scans were taken at each sample position. To reduce the risk of sample damage by x-ray radiation, 80% flux was used (beam size 2300 µm (Horizontal) x 300 µm (Vertical)) and no

damage was observed scan after scan to any samples. Co XAS energy was calibrated by the first maxima in the second derivative of the Cobalt's metal X-ray Absorption Near Edge Structure (XANES) spectrum.

Extended X-ray Absorption Fine Structure (EXAFS) Analysis:

Athena software[5] was used for data processing. The energy scale for each scan was normalized using the Cobalt metal standard. Data in energy space were pre-edge corrected, normalized, deglitched (if necessary), and background corrected. The processed data were next converted to the photoelectron wave vector (*k*) space and weighted by *k*. The electron wave number is defined as $k = [2m(E - E_0)/\hbar^2]^{1/2}$, E_0 is the energy origin or the threshold energy. K-space data were truncated near the zero crossings k =2 to 12 Å^{-1}in Co EXAFS before Fourier transformation. The k-space data were transferred into the Artemis Software for curve fitting. To fit the data, the Fourier peaks were isolated separately, grouped together, or the entire (unfiltered) spectrum was used. The individual Fourier peaks were isolated by applying a Hanning window to the first and last 15% of the chosen range, leaving the middle 70% untouched. Curve fitting was performed using *ab initio*-calculated phases and amplitudes from the FEFF8[6] program from the University of Washington. *Ab initio*-calculated phases and amplitudes were used in the EXAFS equation S1.

$$\chi(k) = S_0^2 \sum_j \frac{N_j}{kR_j^2} f_{eff_j}(\pi, k, R_j) e^{-2\sigma_j^2 k^2} e^{\frac{-2R_j}{\lambda_j(k)}} \sin(2kR_j + \phi_{ij}(k)) \quad \textbf{(Eq. S1)}$$

where N_j is the number of atoms in the j^{th} shell; R_j the mean distance between the absorbing atom and the atoms in the j^{th} shell; $f_{eff_j}(\pi, k, R_j)$ is the *ab initio* amplitude function for shell *j*, and the Debye-Waller term $e^{-2\sigma_j^2 k^2}$ accounts for damping due to static and thermal disorder in absorber-backscatterer distances. The mean free path term $e^{\frac{-2R_j}{\lambda_j(k)}}$ reflects losses due to inelastic scattering, where $\lambda_j(k)$, is the electron mean free path. The oscillations in the EXAFS spectrum are reflected in the sinusoidal term $\sin(2kR_j + \phi_{ij}(k))$, where $\phi_{ij}(k)$ is the *ab initio* phase function for shell *j*. This sinusoidal term shows the direct relation between the frequency of the EXAFS oscillations in k-space and the absorber-backscatterer distance. S_0^2 is an amplitude reduction factor.

The EXAFS equation[7] (Eq. S1) was used to fit the experimental Fourier isolated data (q-space) as well as unfiltered data (k-space) and Fourier transformed data (R-space) using *N*, S_0^2, E_0, *R,* and σ^2 as variable parameters. *N* refers to the number of coordination atoms surrounding Co for each shell. The

quality of fit was evaluated by R-factor (Equation S2) and the reduced Chi^2 value. The deviation in E_0 ought to be less than or equal to 10 eV. R-factor less than 2 % denotes that the fit is good enough[7] whereas R-factor between 2 and 5 % denotes that the fit is correct within a consistently broad model. The reduced Chi^2 value is used to compare fits as more absorber-backscatter shells are included to fit the data. A smaller reduced Chi^2 value implies a better fit. Similar results were obtained from fits done in *k*, *q*, and *R*-spaces.

$$R - factor = \frac{\sum_i (difference\ between\ data\ and\ fit_i)^2}{\sum_i (data)^2} \text{ (Eq. S2)}$$

DFT Calculations:

The DFT optimization calculations were performed using the ORCA (Version 5.0) program package developed by Neese[8] and co-workers. The geometry optimizations were carried out using the solid-state (XRD) as a starting point. The calculations were carried out using the BP86 exchange-correlation functional[7] in combination with the triple zeta valance polarization functions (def2-TZVP)[9], and the atom-pairwise dispersion correction with the Becke-Johnson damping scheme (D3BJ).[10,11]

The RI[12] approximation were used to accelerate Coulomb and exchange integrals for the ground and excited state calculations respectively. The default GRID settings were further used for the self-consistent field iterations and for the final energy evaluation. The calculated structures were confirmed to be minima based on a check of the energies and the absence of imaginary frequencies from frequency calculations carried out on the optimized geometries.

Characterization of 1:

The UV-Vis absorption spectrum of **1**, recorded in CH_3CN, displays two d-d bands at 486 and 616 nm (Fig. S1), similar to those observed for [(TPA)Co^{II}Cl]Cl.[13] The ESI-MS analysis of **1** revealed a major peak corresponding to $[(TPA^*)Co(Cl)]^+$ (m/z: 558.2), confirming the presence of the Co(II) complex in solution (Fig. S2). Compound **1** displayed paramagnetically shifted NMR signals in $CDCl_3$ (-5 to 150 ppm), supporting the high spin nature of the Co(II) complex in the solution state as well (Fig. S3).

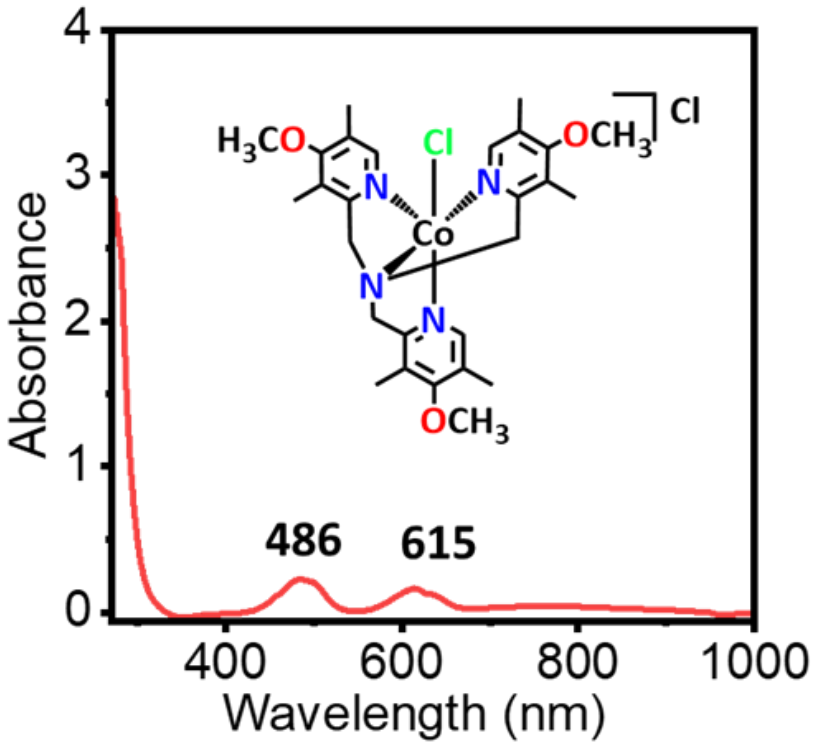


Fig. S1: UV-vis absorption spectra of 1 mM of **1** in CH_3CN**.**

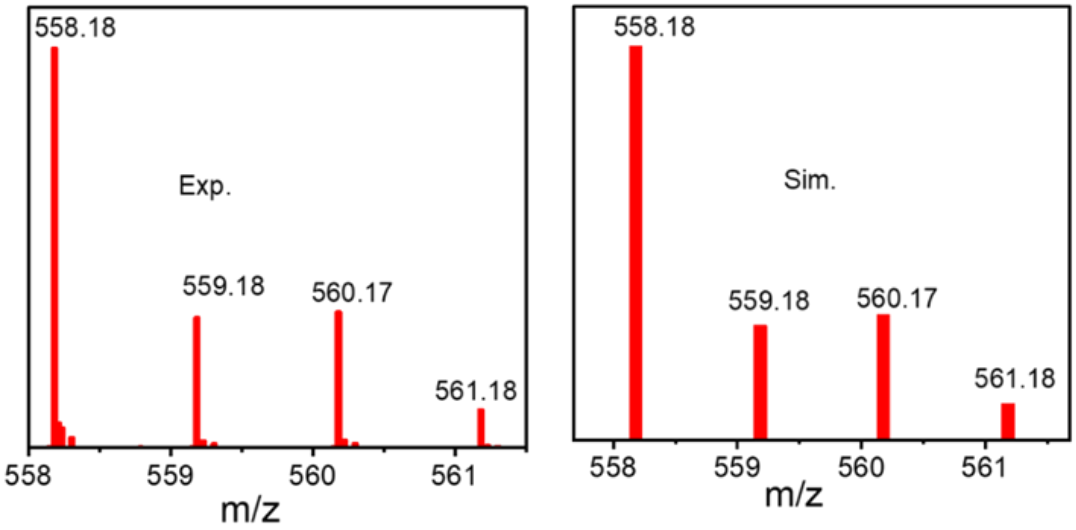


Fig. S2: ESI-mass spectrum of **1** (left) experimental and (right) simulated in CH_3CN.

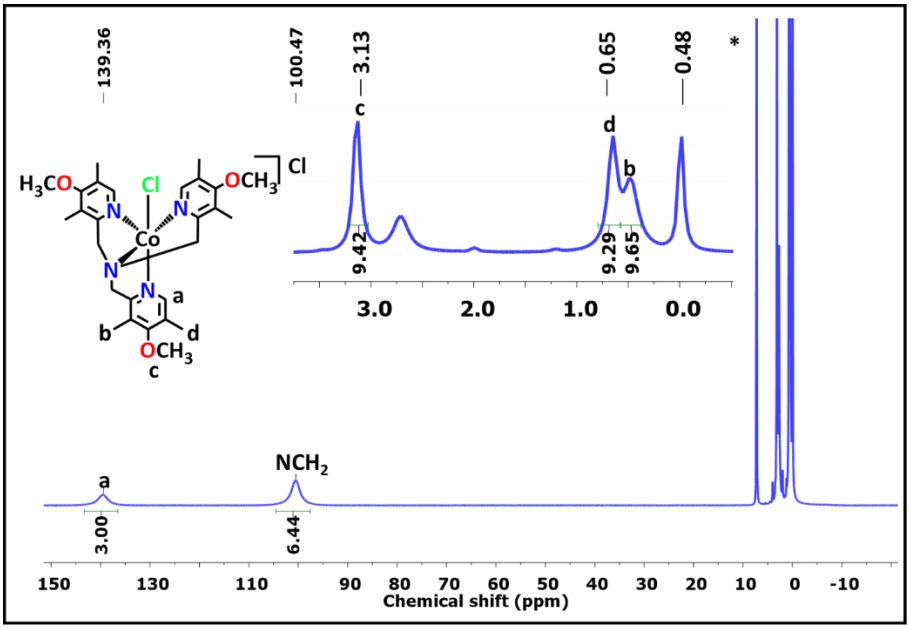


Fig. S3: ^{1}H NMR spectrum of **1** in $CDCl_3$ at 500 MHz. (* peak for solvent).

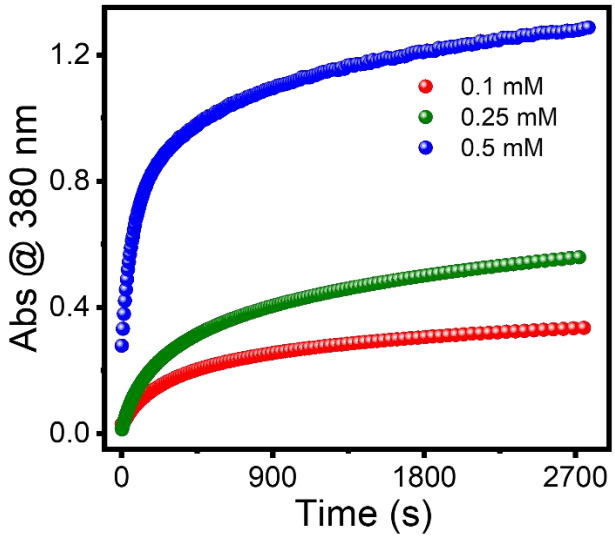


Fig. S4: Changes in the absorbance of **1a** at 380 nm on aerobic oxidation in 1:9 CH_3CN:H_2O at 25 °C.

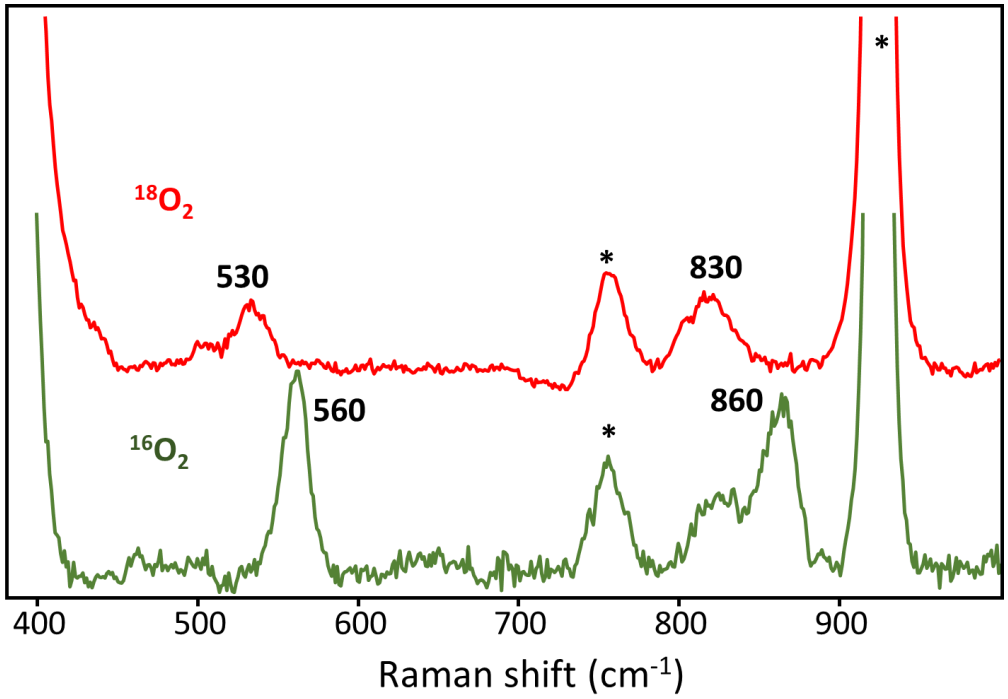


Fig. S5: Resonance Raman spectra (λ_{exc} = 638 nm) of **1a$_{ox}$** (yellow) and **^{18}O-1a$_{ox}$** (green) in 1:9 CH_3CN:H_2O at 25 °C. * Bands from MeCN.

Table S1: Crystal data and structure refinement of **1a**.

	1a
CCDC	2381919
Chemical formula	$C_{54}H_{73}Cl_3Co_2N_8O_{26}$
Formula weight	1476.96
Temperature	100
Wavelength	0.71073
Crystal size	0.21 × 0 × 0
Crystal system	Monoclinic
Space group	$P2_1/n$
α (Å)	90
β (Å)	98.9520(10)
γ (Å)	90
a	15.9896(6)
b	22.9608(8)
c	17.9997(7)
Volume	6527.8(4)
Z	4
Density (calculated)	1.503
Absorption coefficient	0.718
F(000)	3087.0
Goodness-of-fit on F^2	1.124
Final R indices I>2σ(I)	R1 = 0.0777, wR_2 = 0.1653
R indices (all data)	R1 = 0.0974, wR_2 = 0.1742

Table S2: Specific Bond lengths (Å) and bond angles(°) of **1a**.

Bond distance (Å)	**1a**	**Bond Angles** (°)	**1a**
Co1-O1	1.939(3)	Co1-O1-Co2	114.4(2)
Co2-O1	1.938(4)	Co1-O2-O3	110.2(2)
Co1-O2	1.856(3)	O1-Co1-O2	88.3(1)
Co2-O3	1.858(3)	N1-Co1-O2	97.7(1)
Co1-N1	1.929(4)	N2-Co1-O2	179.3(2)
Co1-N2	1.993(5)	N3-Co1-O2	93.5(2)
Co1-N3	1.918(4)	N4-Co1-O2	94.7(2)
Co1-N4	1.917(4)	O1-Co2-O3	88.4(1)
Co2-N5	1.939(5)	O2-O3-Co2	112.3(2)
Co2-N6	1.992(4)	N5-Co2-O3	94.7(2)
Co2-N7	1.912(5)	N6-Co2-O3	176.5(2)
Co2-N8	1.918(4)	N7-Co2-O3	93.0(2)
O2-O3	1.417(5)	N8-Co2-O3	98.1(1)

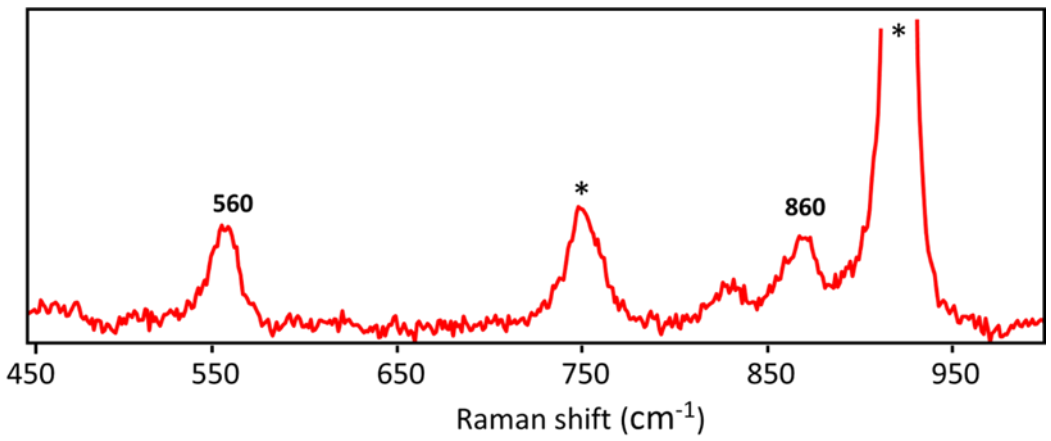


Fig. S6: Resonance Raman spectrum (λ_{exc} = 638 nm) of **1a** (isolated crystals dissolved in MeCN) at 25 °C. * Indicates the solvent peak.

The electrochemical characteristics of the isolated **1a** was investigated in CH_3CN (Fig. S7). **1a** exhibits a reversible redox wave at approximately 0.52 V vs. Fc^+/Fc, indicative of a one-electron process. Whereas the parent $[(TPA)_2Co^{III}_2(\mu\text{-}OH)(\mu\text{-}1,2\text{-}O_2)]^{3+}$ complex displays a reversible redox wave at around 0.73 V vs. Fc^+/Fc (Fig. S7). An approximate 210 mV difference in the redox potential indicates that the incorporation of electron-donating groups in the 2' (OMe) and 3,5(Me) positions of the pyridine rings increases the electron density at the metal center, making it easier to access high valent species. The reversible redox wave observed at 0.52 V vs. Fc^+/Fc for **1a** may originate from $Co^{IV}(O_2)Co^{III}/Co^{III}(O_2)Co^{III}$ or $Co^{III}(O_2^{\bullet-})Co^{III}/Co^{III}(O_2)Co^{III}$ redox couple.

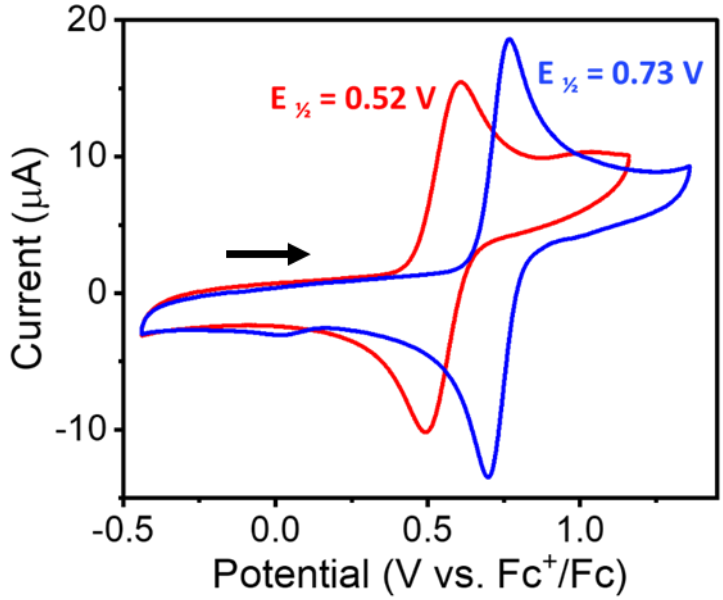


Fig. S7: Cyclic voltammetry of **1a** (red) and $[(TPA)Co(\mu\text{-}OH)(\mu\text{-}O_2)Co(TPA)]^{3+}$ (blue) in CH_3CN at room temperature at a scan rate of 100 mV/s. Arrow indicates the scan direction.

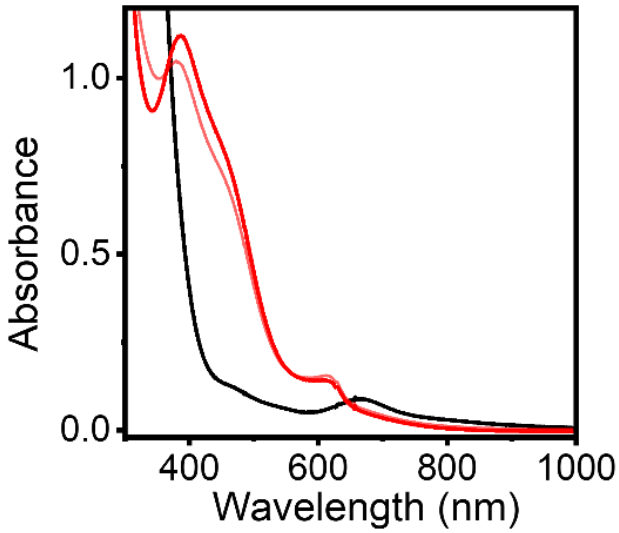


Fig. S8: UV-vis absorption spectra obtained upon addition of 1 eq. of Fc to **1a**$_{ox}$ in CH_3CN at 25 °C. Condition to generate **1a**$_{ox}$: 0.125 mM **1a** + 1 eq. of CAN in CH_3CN at 25 °C.

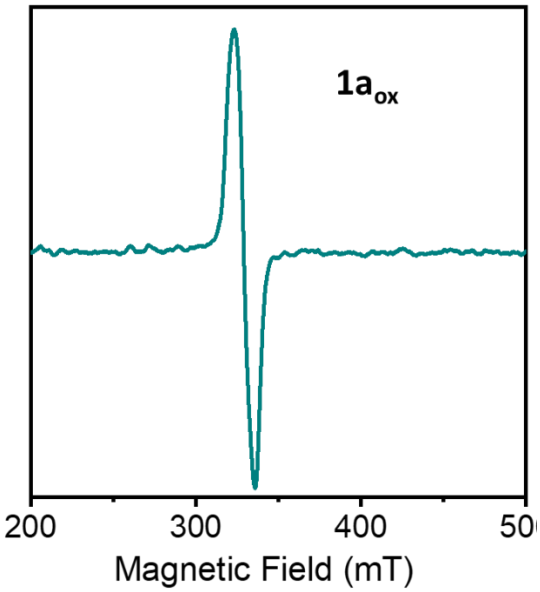


Fig. S9: EPR spectrum of **1a**$_{ox}$ obtained by adding 1 eq. of CAN to 2 mM of **1a** in CH_3CN at room temperature.

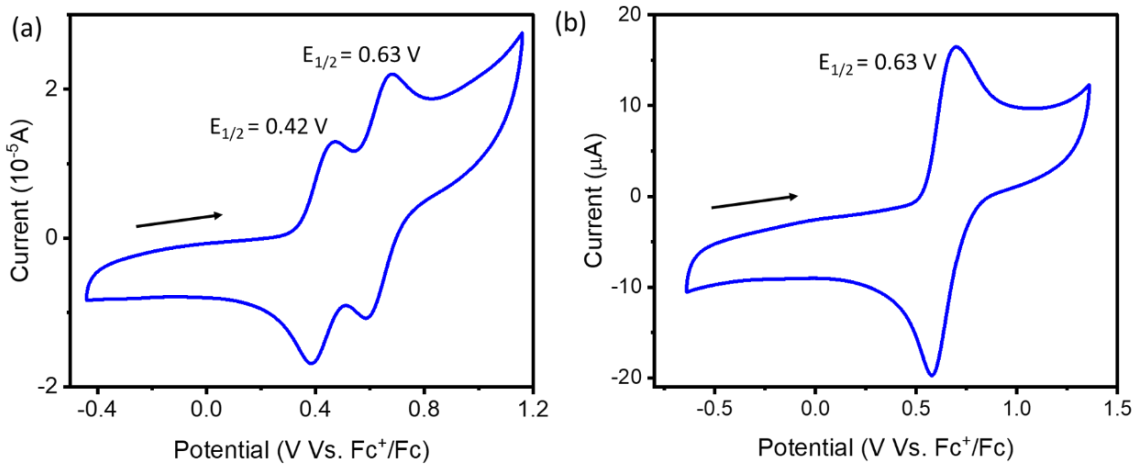


Fig. S10: (a) Cyclic voltammogram of **1b$_{ox}$** in CH_3CN at room temperature at a scan rate of 100 mV/s. Conditions to generate **1b$_{ox}$**: 1 mM **1a** + 1 eq. of CAN + 1 eq. of $^{n}Bu_4NOH$ in CH_3CN at room temperature. (b) Cyclic voltammetry of 1 mM **CAN** in CH_3CN at room temperature at a scan rate of 100 mV/s.

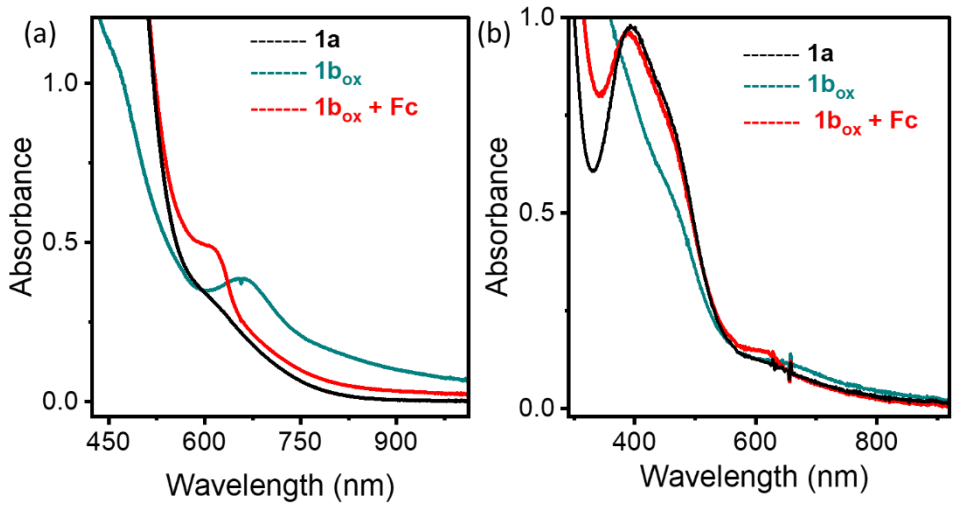


Fig. S11: (a) UV-vis absorption spectra obtained upon addition of 1 eq. of Fc to **1b$_{ox}$** in CH_3CN at 25 °C. Condition to generate **1b$_{ox}$**: 0.5 mM **1a** + 1 eq. of CAN + 1 eq. $^{n}Bu_4NOH$ in CH_3CN at 25 °C. (b) UV-vis absorption spectra obtained upon addition of 1 eq. of Fc to **1b$_{ox}$** in CH_3CN at 25 °C. Condition to generate **1b$_{ox}$**: 0.125 mM **1a** + 1 eq. of CAN + 1 eq. $^{n}Bu_4NOH$ in CH_3CN at 25 °C.

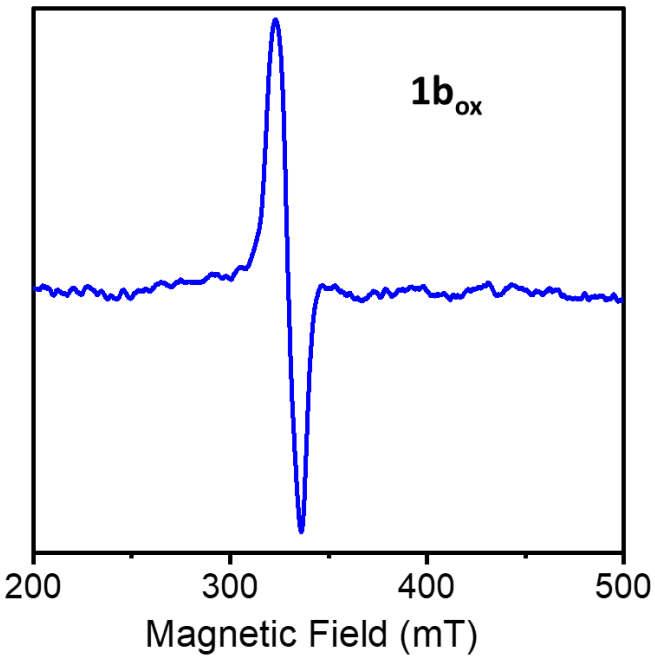


Fig. S12: EPR spectrum of **1b$_{ox}$** obtained by adding 1 eq. of $^{n}Bu_4NOH$ to **1a$_{ox}$** in CH_3CN at room temperature. Condition to generate **1a$_{ox}$**: 1 eq. of CAN to 2 mM of **1a** in CH_3CN.

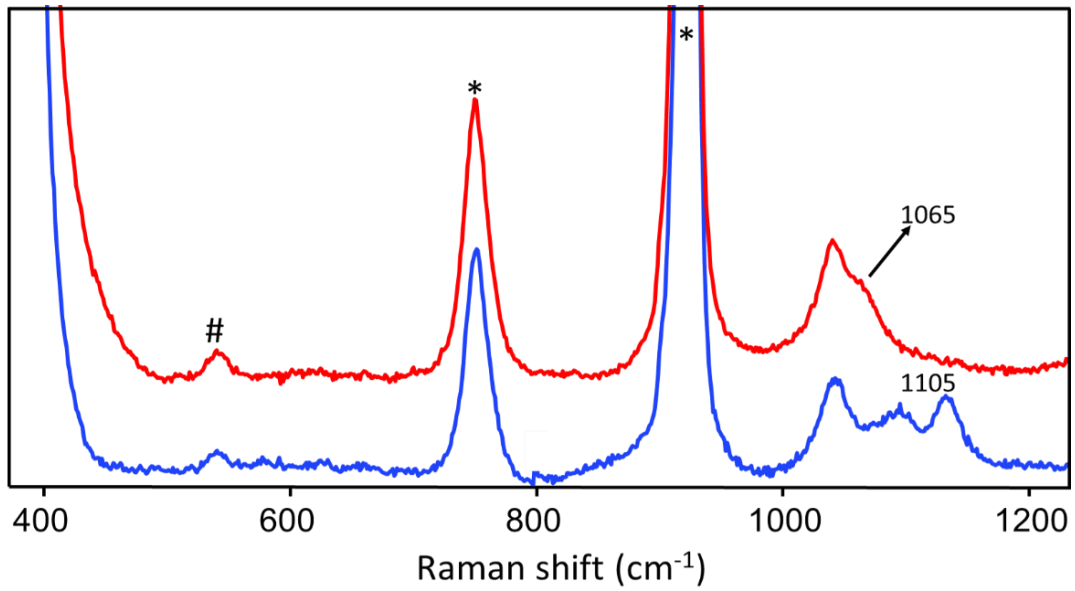


Fig. S13: Resonance Raman spectra (λ_{exc} = 638 nm) obtained after the addition of 5 eq. of $HClO_4$ to **1b$_{ox}$** and **^{18}O-1b$_{ox}$** to form of **1a$_{ox}$** (blue) and **^{18}O-1a$_{ox}$** (red), respectively, in CH_3CN at room temperature. * Bands from CH_3CN and # band from CAN.

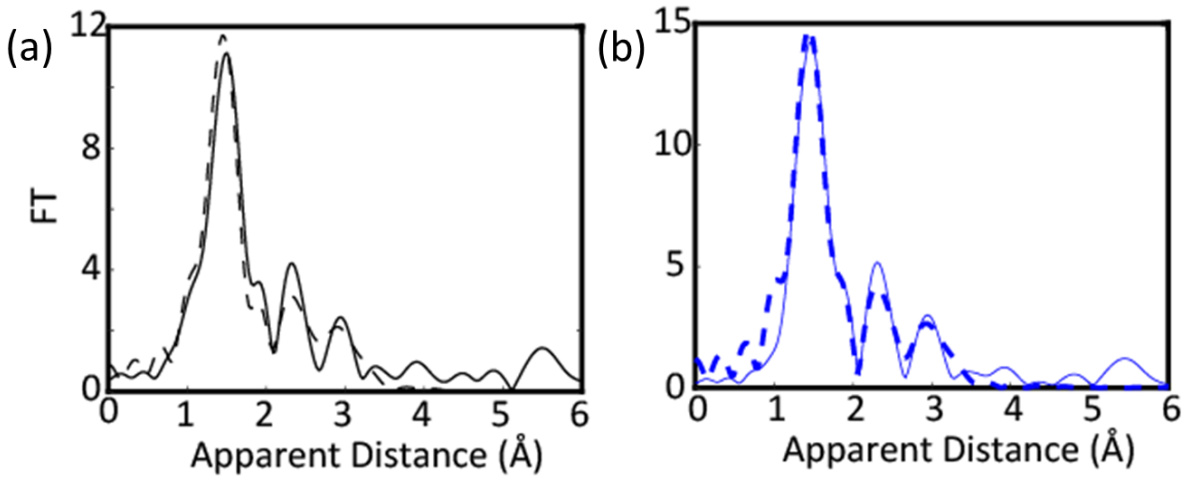


Fig. S14: Fourier transforms of k^3-weighted Co EXAFS of (a) **1a** (black) (b) $\mathbf{1b_{ox}}$ (blue) in solid lines together with their respective fits 2 and 4 in **Table S3** shown in dashed lines.

Table S3. EXAFS Fits parameters.

Sample	**Fit**	**Region**	**Shell,N**	**R, Å**	**E_0**	**ss.^{2} (10^{-3})**	**R-factor**	**Reduced Chi-square**
1a	1	I	Co-N,6	1.92	-3.8	4.2	0.0051	621
	2	**I,II**	**Co-N,6** **Co-C,5** **Co-C, 5** **Co-Co, 1**	**1.92** **2.76** **3.17** **3.33**	**-3.2**	**4.3** **12** **4.1** **4.6**	**0.0074**	**671**
$1b_{ox}$	3	I	**Co-N,6**	1.90	-6.3	2.3	0.0020	303
	4	**I,II**	**Co-N,6** **Co-C,5** **Co-C, 5** **Co-Co, 1**	**1.90** **2.75** **3.16** **3.33**	**-5.8**	**2.3** **10** **2.1** **2.0**	**0.0036**	**247**

* The amplitude reduction factor $S0^2$ was fixed to 1. Region I refers to the EXAFS spectra region between 1.2-2.0 Å Regions I ,II refer to that between 1.2-3.3 Å. We note that the data resolution, the ability to distinguish between 2 bond distances, given by $\pi/2\Delta k$ is ~ 0.157 Å.

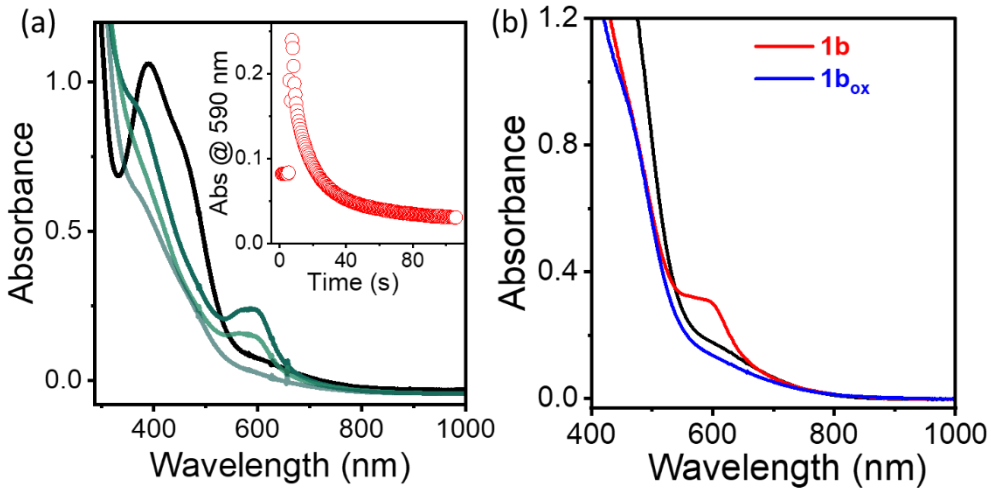


Fig. S15: (a) UV/Vis absorption spectra of the reaction of 0.25 mM **1a** (black) with 2 eq. of $^{n}Bu_4NOH$ to form **1b** at 25 °C (green trace). Inset: Time trace of the absorbance at 590 nm in seconds. (b) UV-vis absorption spectra of the **1b$_{ox}$** (blue trace) obtained by adding 1 eq. of CAN to **1b** (red) in CH_3CN at 25 °C.

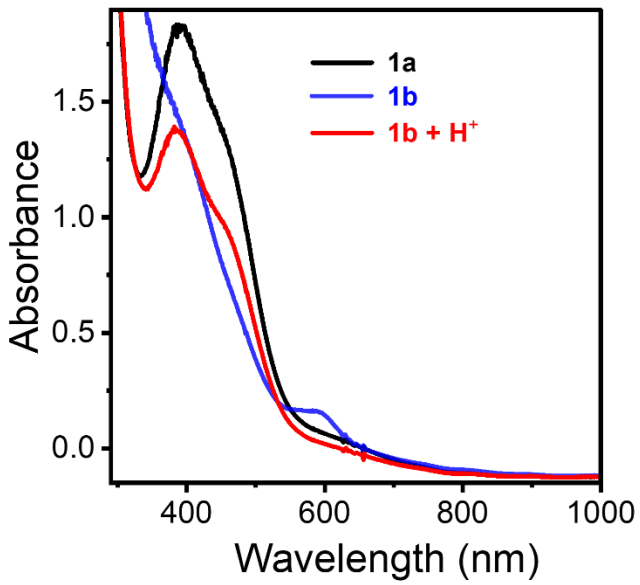


Fig. S16: UV-vis absorption spectra of (black) 0.25 mM **1a** in CH_3CN, (blue) **1a** + 2 eq. of $^{n}Bu_4NOH$ to form **1b** and (red) **1b** + 5 eq. of $HClO_4$ in CH_3CN at 25 °C.

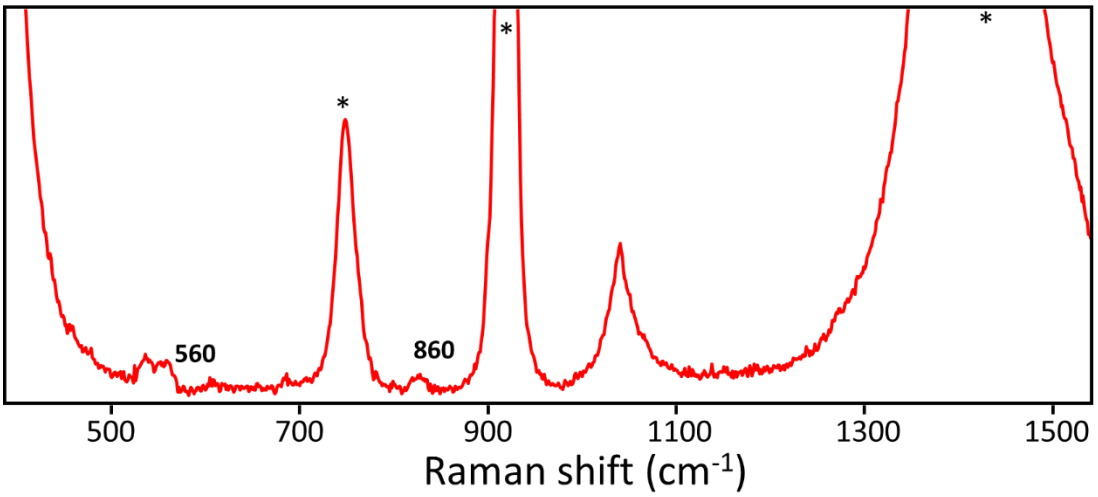


Fig. S17: Resonance Raman spectrum (λ_{exc} = 638 nm) of **1b$_{ox}$** obtained by the addition of 1 eq. of CAN to **1b** at 25 °C. Condition to generate **1b**: 1 mM **1a** + 4 eq. of $^{n}Bu_4NOH$ in CH_3CN at 25 °C. * Bands from CH_3CN.

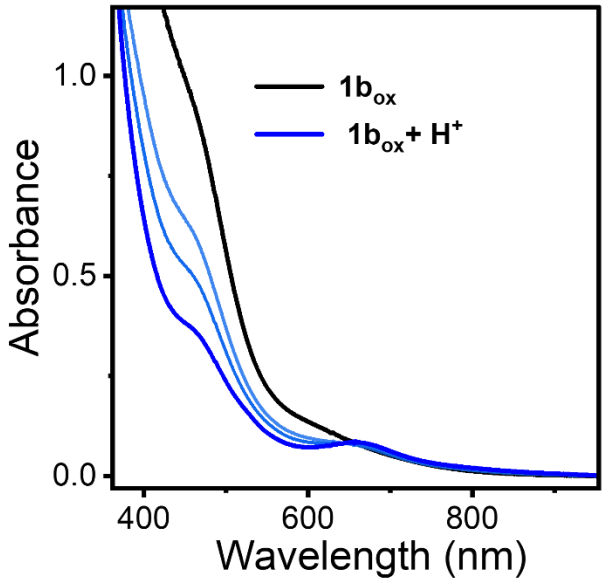


Fig. S18: UV-vis absorption spectra obtained upon the addition of 5 eq. of $HClO_4$ to **1b$_{ox}$** (black) to form **1a$_{ox}$** (blue) in CH_3CN at 25 °C. Condition to generate **1b$_{ox}$**: 0.25 mM **1a** + 2 eq. of $^{n}Bu_4NOH$ + 1 eq. of CAN in CH_3CN at 25 °C.

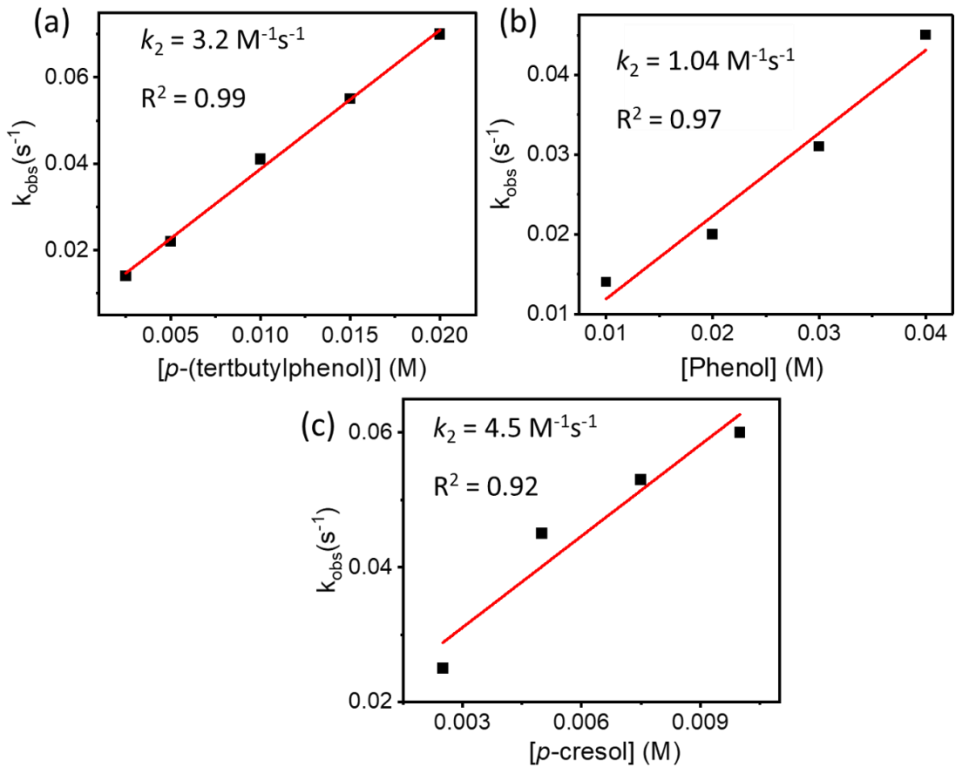


Fig. S19: Plots of k_{obs} for the **1a$_{ox}$** in CH_3CN as a function of (a) [p-tertbutylphenol], (b) [phenol], and (c) [p-Cresol] at 25 °C.

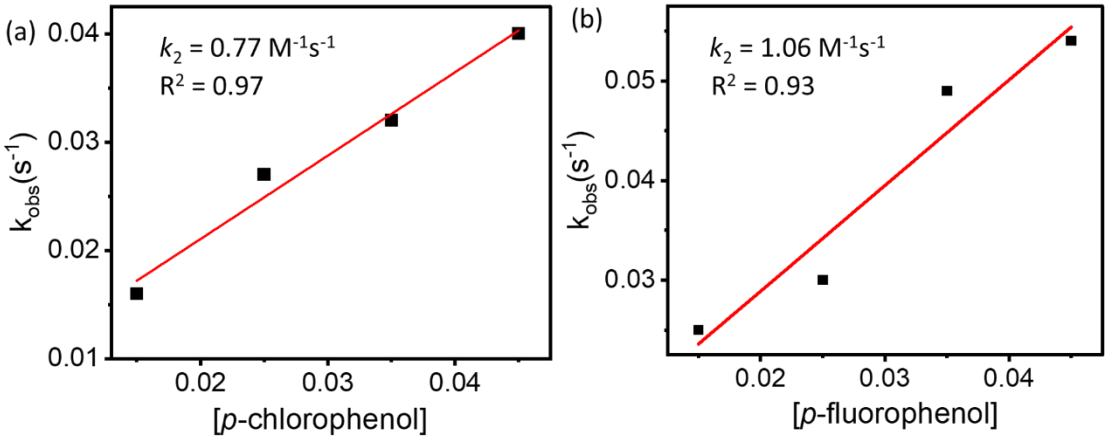


Fig. S20: Plots of k_{obs} for the **1a$_{ox}$** in CH_3CN as a function of (a) [p-chlorophenol] and (b) [p-fluorophenol] at 25 °C.

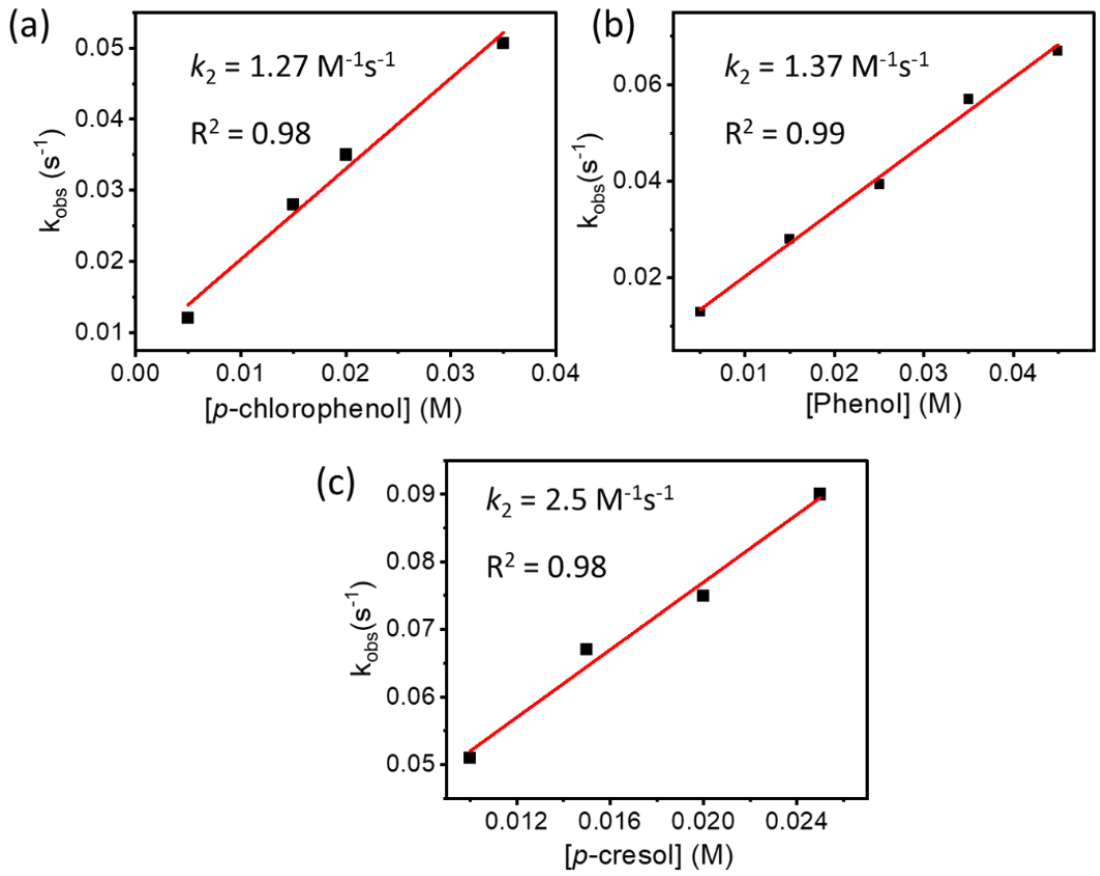


Fig. S21: Plots of k_{obs} for **1b$_{ox}$** in CH_3CN as a function of (a) [p-chlorophenol], (b) [phenol], and (c) [p-cresol] at 25 °C.

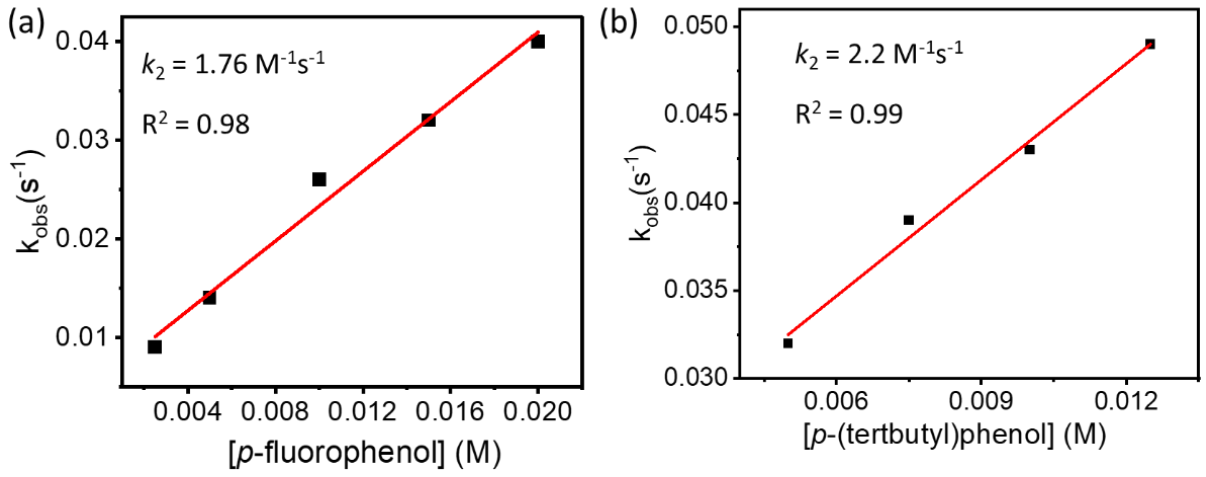


Fig. S22: Plots of k_{obs} for **1b$_{ox}$** in CH_3CN as a function of (a) [p-fluorophenol] and (b) [p-tertbutylphenol] at 25 °C.

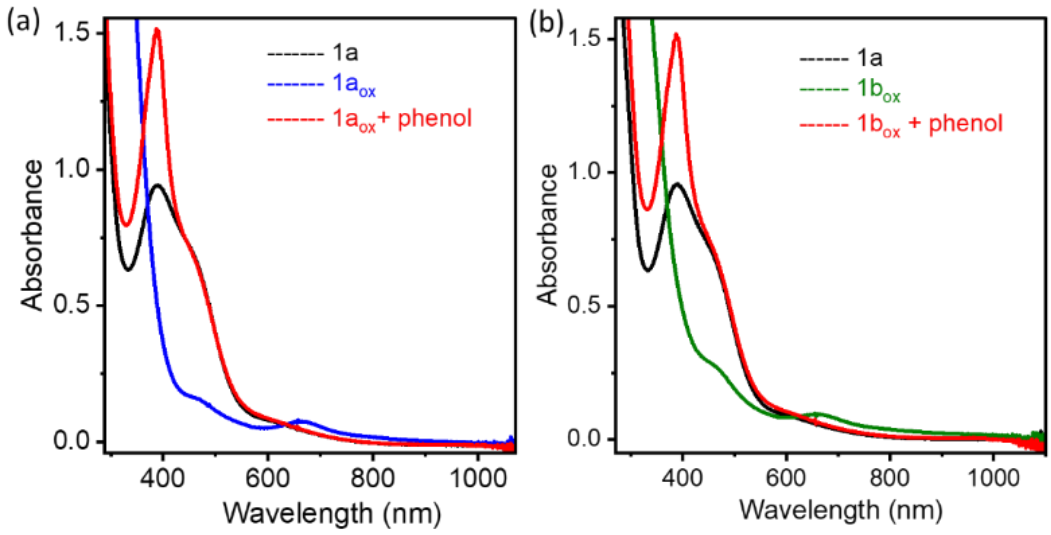


Fig. S23: UV-vis absorption spectra of (a) **1a$_{ox}$** and (b) **1b$_{ox}$** upon reaction with 40 eq. of phenol in CH_3CN at room temperature. Condition to generate **1b$_{ox}$**: 0.125 mM **1a** + 1 eq. of CAN + 1 eq. of $^{n}Bu_4NOH$ in CH_3CN at 25 °C. Condition to generate **1a$_{ox}$**: 0.125 mM **1a** + 1 eq. of CAN in CH_3CN at 25 °C.

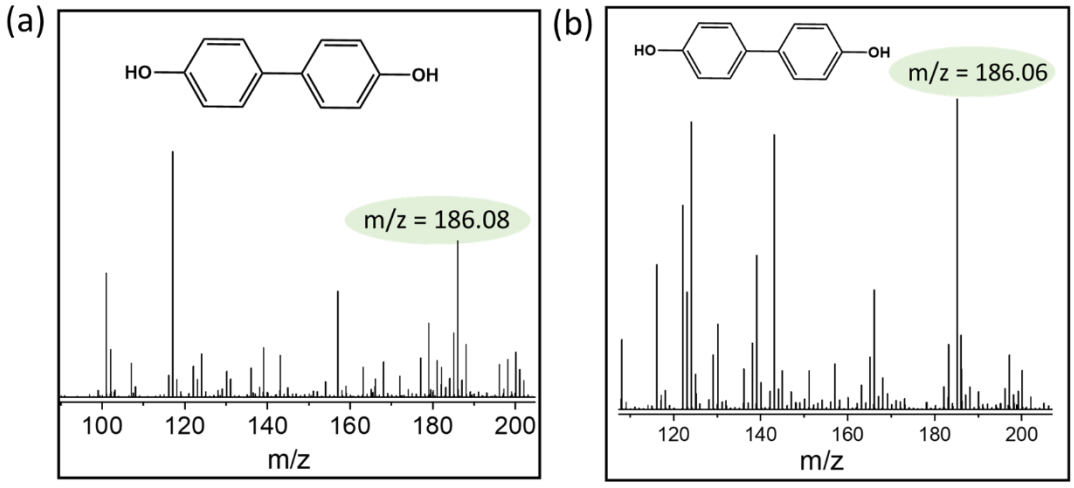


Fig. S24: Product analysis of reaction of (a) **1a$_{ox}$** and (b) **1b$_{ox}$** with 40 eq. of phenol by ESI-MS. Conditions to generate **1a$_{ox}$**: 2.0 mM **1a** in CH_3CN+ 1 eq. CAN in CH_3CN at room temperature. Conditions to generate **1b$_{ox}$**: 2.0 mM **1a** in CH_3CN + 1eq. CAN + 1 eq. $^{n}Bu_4NOH$ in CH_3CN at room temperature.

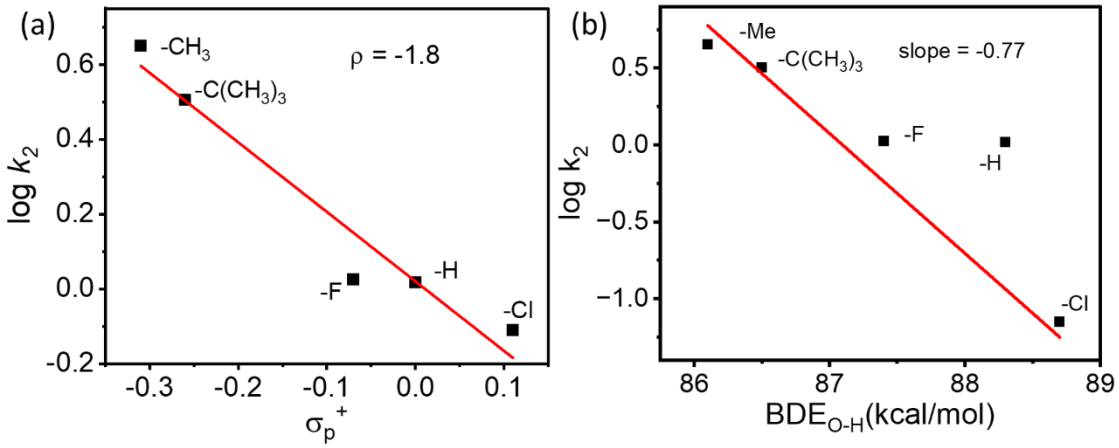


Fig. S25: (a) Hammett plot and (b) BDE plot of log k_2 vs. BDE_{O-H} of the para-X-substituted phenol derivatives for the reaction of **1a$_{ox}$.**

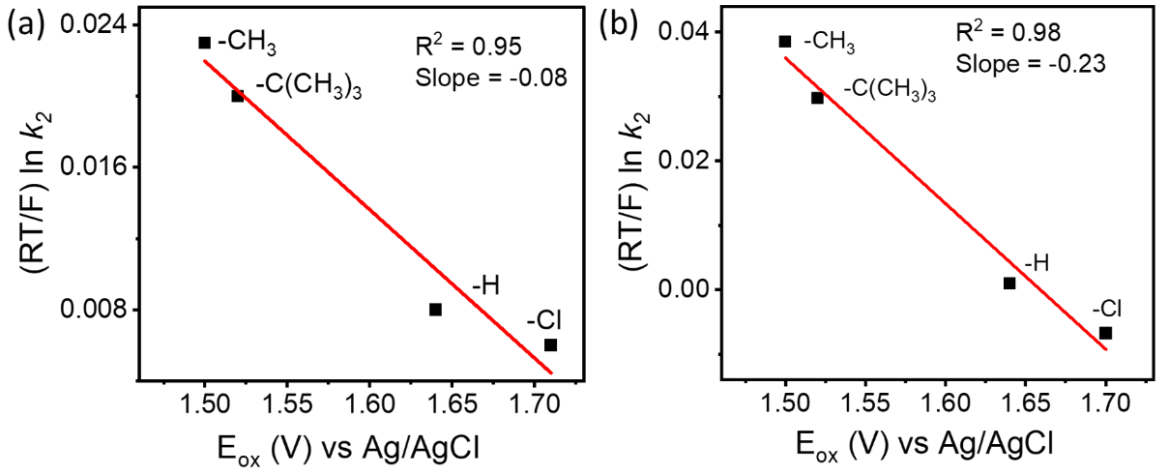


Fig. S26: A plot of (RT/F)ln k_2 vs. E_{OX} (vs. Ag/AgCl) (a) **1b$_{ox}$** and (b) **1a$_{ox}$** of *para*-x-substituted phenol derivatives. Note: E_{ox} values of various phenol derivatives were measured by performing CV of them in acetonitrile at room temperature.

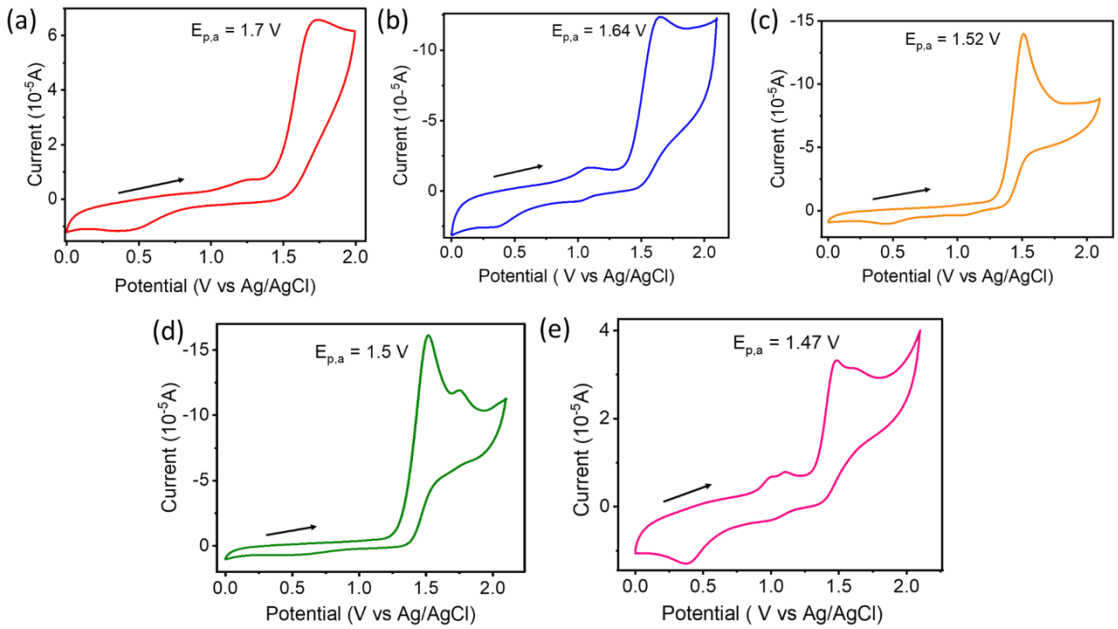


Fig. S27: (a) Cyclic voltammograms of (a) *p*-Cl-phenol, (b) phenol, (c) *p*-tertbutyl-phenol, (d) *p*-Me-phenol, and (e) *p*-F-phenol in CH_3CN at room temperature at a scan rate of 100 mV/s.

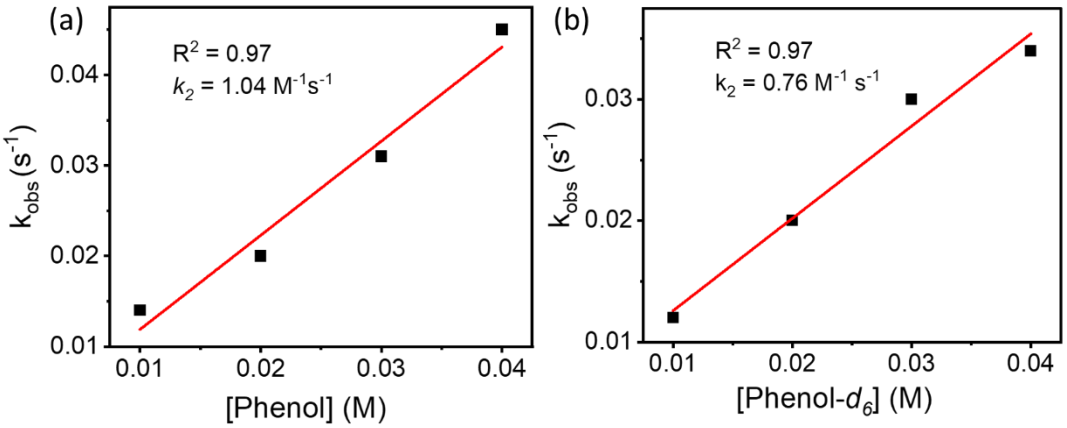


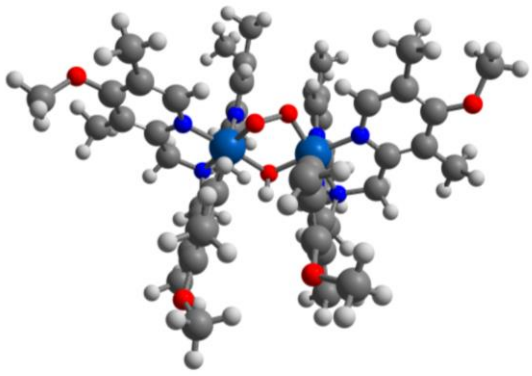
Fig. S28: Plots of k_{obs} as a function of the concentration of (a) phenol and (b) phenol-d_6 for the reaction of **1a$_{ox}$**.

Appendix, DFT Optimized coordinates of 1a, 1b and $1b_{ox}$ using the BP86 exchange-correlation functional[7] in combination with the triple zeta valance polarization functions (def2-TZVP),[9] and the atom-pairwise dispersion correction with the Becke-Johnson damping scheme (D3BJ).[10,11]

Table S4. Summary of the bond distances of calculated Co-based complexes **1a** and $\mathbf{1b_{ox}}$. Bond distances are in Å.

Complexes	Calculated Bond Distances (Å)
1a	Co_1-N: 1.91788, 1.90676, 2.00868, 1.92687 Co_1-O: 1.86864, 1.95871, 2.69591 Co_2-N: 1.92535, 1.90751, 2.00970, 1.91745 Co_2-O: 1.87135, 1.95033, 2.71389 Co-Co: 3.26981 **Co-N/O(6, avg): 1.93**
$\mathbf{1b_{ox}}$	Co_1-N: 1.93087, 1.94433, 2.00952, 1.93774 Co_1-O : 1.79747, 1.86796, 2.67356 Co_2-N: 1.92773, 1.94610, 2.01140, 1.93330 Co_2-O: 1.80087, 1.86530, 2.67846 Co-Co: 3.07983 **Co-N/O(6, avg): 1.91**
$\mathbf{1a_{ox}}$	Co_1-N: 1.93692, 1.91931, 1,97620, 1,94468 Co_1-O : 1.84903, 1.94147, 2.79207 Co_2-N: 1.93138, 1.91376, 1.93672, 1.96767 Co_2-O: 1.84679, 1.95599, 2.76352 Co-Co: 3.27781 **Co-N/O(6, avg): 1.93**

1a



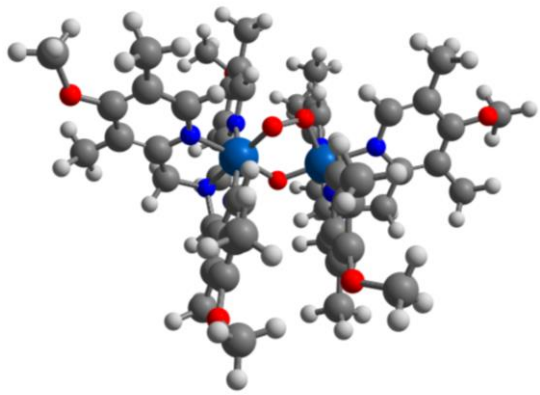
27	4.925245000	9.897737000	13.262350000
27	2.638679000	7.582053000	12.944699000
8	3.987183000	8.674102000	12.054339000
8	3.544671000	9.620261000	14.490694000
8	3.233452000	8.265548000	14.582087000

8	2.252838000	14.061570000	9.829186000
7	6.096655000	8.528589000	13.919230000
8	-1.477723000	11.742118000	11.489376000
8	8.801224000	5.587512000	14.929720000
7	1.279667000	8.894737000	12.618273000
8	-1.678287000	3.931929000	14.991658000
7	2.069275000	6.822941000	11.173138000
7	6.375020000	10.159123000	11.896839000
7	1.322326000	6.442428000	13.723847000
7	3.896249000	6.124326000	12.922152000
7	4.021966000	11.318096000	12.324526000
7	5.848208000	11.190494000	14.317174000
6	2.304165000	12.990635000	12.049264000
6	2.770654000	13.212355000	10.729890000
6	3.935334000	12.539096000	10.259574000
6	6.981123000	8.079804000	12.998785000
6	4.534518000	11.603067000	11.095520000
6	0.877782000	8.971594000	11.327006000
6	6.149478000	8.084324000	15.183544000
1	5.396633000	8.489628000	15.858011000
6	1.225146000	13.782441000	12.739898000
1	1.432203000	14.859695000	12.690996000
1	1.191405000	13.504154000	13.799930000
1	0.228193000	13.611971000	12.315288000
6	-0.286977000	10.599723000	13.250447000
6	0.621709000	5.669965000	12.862331000
6	4.114271000	5.591218000	11.690683000
6	1.532269000	7.977024000	10.395252000
1	0.827541000	7.639829000	9.619402000
1	2.373382000	8.446472000	9.862444000
6	3.317600000	6.249172000	10.588535000
1	3.893831000	7.084253000	10.169197000
1	3.081567000	5.549729000	9.774085000
6	5.403589000	11.646048000	15.504222000
1	4.483640000	11.187980000	15.869220000
6	-0.387301000	4.819092000	13.299663000
6	-0.637156000	10.745659000	11.890883000
6	7.085349000	7.143557000	15.609514000
6	7.953439000	6.615946000	14.630597000
6	-0.057294000	9.920366000	10.901961000
6	5.734922000	10.767762000	10.697569000
1	5.413895000	9.948339000	10.038307000
1	6.464469000	11.363954000	10.131340000
6	0.706397000	9.670909000	13.551783000
6	6.879847000	8.771219000	11.662896000
1	7.844055000	8.778816000	11.132089000
1	6.139373000	8.256250000	11.036312000
8	7.912090000	14.101272000	16.370223000
6	-0.677973000	4.775083000	14.691790000
6	1.028702000	6.412714000	15.034408000
1	1.616901000	7.088229000	15.656967000

6	4.440251000	12.852968000	8.879989000
1	3.663530000	12.647733000	8.129516000
1	5.332807000	12.278671000	8.612148000
1	4.675161000	13.922721000	8.786908000
6	2.968804000	12.009656000	12.782438000
1	2.648442000	11.753874000	13.792664000
6	4.476237000	5.575309000	13.994041000
1	4.211045000	6.025851000	14.950709000
6	7.433958000	11.037343000	12.494284000
1	7.734646000	11.803133000	11.764525000
1	8.327781000	10.422077000	12.681766000
6	7.906253000	7.075597000	13.295989000
6	1.035152000	5.760787000	11.412756000
1	1.450839000	4.795071000	11.089205000
1	0.162376000	5.956554000	10.774023000
6	0.033013000	5.611104000	15.589833000
8	6.539846000	3.034458000	12.334473000
6	8.813916000	6.513649000	12.237223000
1	8.238624000	6.152094000	11.373067000
1	9.396007000	5.676604000	12.633975000
1	9.522179000	7.269924000	11.865853000
6	7.111075000	6.700863000	17.043583000
1	7.807337000	7.314082000	17.635759000
1	7.433232000	5.656964000	17.135856000
1	6.120288000	6.805922000	17.503873000
6	6.989731000	11.675469000	13.786818000
6	5.016245000	4.552066000	11.498646000
6	-0.253583000	5.767872000	17.062063000
1	-1.301004000	6.047950000	17.237248000
1	0.374825000	6.565697000	17.476839000
1	-0.052503000	4.856710000	17.638531000
6	-0.429433000	10.052579000	9.451440000
1	0.459962000	10.174435000	8.816448000
1	-1.078258000	10.920202000	9.298246000
1	-0.967347000	9.162178000	9.090964000
6	-1.167362000	3.937324000	12.366994000
1	-2.234569000	4.202433000	12.381752000
1	-1.109767000	2.889230000	12.692028000
1	-0.813300000	3.994390000	11.332392000
6	-0.905981000	11.423058000	14.342545000
1	-1.183935000	12.421011000	13.983931000
1	-1.819719000	10.945446000	14.727646000
6	6.067179000	12.637704000	16.216711000
6	5.810991000	3.887759000	15.238034000
1	5.558738000	2.820151000	15.286603000
1	5.295017000	4.382494000	16.069862000
6	5.357755000	4.495685000	13.936032000
6	7.244907000	13.171726000	15.646206000
6	0.864673000	14.475701000	9.842593000
1	0.675775000	14.840483000	8.828412000
1	0.699043000	15.288832000	10.557706000

1	0.209590000	13.622730000	10.061378000
6	5.680019000	4.018690000	12.642412000
6	7.745782000	12.664594000	14.425702000
6	-2.897001000	11.538028000	11.731264000
1	-3.257550000	10.684014000	11.140547000
1	-3.389815000	12.456885000	11.400976000
1	-3.098237000	11.368619000	12.797024000
6	5.560672000	13.124613000	17.540957000
1	6.310850000	12.964277000	18.327916000
1	4.636962000	12.606207000	17.824385000
1	5.363274000	14.205335000	17.516457000
6	-1.842379000	3.315537000	16.292212000
1	-2.286848000	4.010856000	17.012317000
1	-0.882487000	2.929397000	16.656780000
1	-2.530476000	2.483116000	16.117412000
6	9.999375000	5.927104000	15.678951000
1	10.641543000	6.586612000	15.077995000
1	10.510491000	4.978824000	15.868741000
1	9.749354000	6.412542000	16.631383000
6	5.327521000	3.970401000	10.148715000
1	6.409613000	3.998887000	9.959278000
1	4.825280000	4.500849000	9.333547000
1	5.041561000	2.909541000	10.103359000
6	9.073839000	13.100291000	13.870767000
1	9.617002000	12.257271000	13.422809000
1	9.704678000	13.511541000	14.667233000
1	8.969571000	13.871930000	13.091937000
6	7.616692000	2.616029000	13.207484000
1	8.298229000	2.060354000	12.556228000
1	7.250203000	1.952399000	13.998389000
6	8.046173000	15.436432000	15.817849000
1	8.480900000	15.422730000	14.810203000
1	8.710939000	15.971727000	16.501668000
1	7.061472000	15.924225000	15.793583000
1	3.444512000	9.333767000	11.583464000

1b$_{ox}$



27	4.861030000	9.827303000	13.336914000

27	2.707693000	7.643985000	13.051185000
8	3.972661000	8.666022000	12.285549000
8	3.565391000	9.599979000	14.659408000
8	3.206352000	8.259143000	14.742991000
8	2.020074000	13.864506000	9.891905000
7	6.105384000	8.519803000	14.013784000
8	-1.385257000	11.836363000	11.599476000
8	8.836197000	5.603705000	15.003224000
7	1.337162000	8.966949000	12.735470000
8	-1.550856000	3.666763000	14.659462000
7	2.201376000	6.990992000	11.219407000
7	6.236326000	10.056202000	11.887116000
7	1.330935000	6.436422000	13.704449000
7	3.932436000	6.142489000	13.032922000
7	3.925583000	11.237480000	12.402036000
7	5.845438000	11.204526000	14.296863000
6	2.227380000	12.930755000	12.171253000
6	2.582725000	13.058199000	10.805469000
6	3.680703000	12.314695000	10.280263000
6	6.963069000	8.055176000	13.077446000
6	4.335089000	11.423944000	11.122628000
6	1.044313000	9.134606000	11.426578000
6	6.184515000	8.098312000	15.283412000
1	5.442884000	8.510717000	15.966247000
6	1.226028000	13.779306000	12.911816000
1	1.480164000	14.845464000	12.844057000
1	1.237354000	13.510165000	13.975032000
1	0.200997000	13.653276000	12.544528000
6	-0.292145000	10.605795000	13.367998000
6	0.682191000	5.720174000	12.759728000
6	4.173372000	5.642960000	11.793595000
6	1.814844000	8.236691000	10.493244000
1	1.247637000	8.006578000	9.578771000
1	2.743647000	8.746517000	10.202724000
6	3.438349000	6.356527000	10.681191000
1	4.069160000	7.166144000	10.289875000
1	3.198133000	5.682090000	9.847356000
6	5.496473000	11.686653000	15.505057000
1	4.620118000	11.225910000	15.963211000
6	-0.294482000	4.788923000	13.091954000
6	-0.550145000	10.833980000	11.999290000
6	7.129774000	7.164043000	15.703347000
6	7.980625000	6.625953000	14.713971000
6	0.124917000	10.097351000	11.000671000
6	5.485376000	10.540521000	10.694017000
1	5.088013000	9.656707000	10.177095000
1	6.159875000	11.057739000	9.996989000
6	0.689989000	9.666810000	13.677029000
1	0.999490000	9.476752000	14.704033000
6	6.791135000	8.680579000	11.717021000
1	7.732803000	8.694390000	11.147616000

1	6.050892000	8.101321000	11.148004000
8	8.005060000	14.221548000	16.076827000
6	-0.604422000	4.596881000	14.468938000
6	1.045857000	6.239004000	15.001745000
1	1.623398000	6.843171000	15.703376000
6	4.066443000	12.517491000	8.842292000
1	3.204078000	12.341602000	8.184043000
1	4.878615000	11.856077000	8.524193000
1	4.374361000	13.557697000	8.662762000
6	2.930922000	11.974591000	12.903484000
1	2.686104000	11.783204000	13.948599000
6	4.488038000	5.573688000	14.105369000
1	4.207481000	6.009868000	15.064748000
6	7.281626000	11.026459000	12.349848000
1	7.456314000	11.778269000	11.566462000
1	8.229953000	10.479936000	12.471425000
6	7.900225000	7.061883000	13.371884000
6	1.064006000	6.018215000	11.327787000
1	1.340375000	5.089572000	10.808631000
1	0.196790000	6.430745000	10.791252000
6	0.098463000	5.327207000	15.462874000
8	6.569031000	3.057207000	12.432132000
6	8.772471000	6.473203000	12.298731000
1	8.162744000	6.023775000	11.501127000
1	9.420764000	5.694505000	12.710746000
1	9.412937000	7.235591000	11.830406000
6	7.171102000	6.730693000	17.139943000
1	7.882499000	7.338029000	17.719910000
1	7.480117000	5.682749000	17.233965000
1	6.187576000	6.850751000	17.611841000
6	6.925728000	11.694123000	13.657321000
6	5.070530000	4.599597000	11.599344000
6	-0.034388000	5.151590000	16.954938000
1	-1.030797000	5.411029000	17.331824000
1	0.688886000	5.798553000	17.466575000
1	0.177467000	4.117291000	17.257447000
6	-0.122833000	10.344730000	9.538805000
1	0.803683000	10.638599000	9.023844000
1	-0.854942000	11.145752000	9.401222000
1	-0.505227000	9.445081000	9.033919000
6	-1.040132000	3.989940000	12.062262000
1	-0.761539000	4.254456000	11.036895000
1	-2.123938000	4.135050000	12.172954000
1	-0.861685000	2.913713000	12.200801000
6	-0.982754000	11.362480000	14.465516000
1	-1.226815000	12.385209000	14.153663000
1	-0.353420000	11.408477000	15.363241000
1	-1.924633000	10.873027000	14.756056000
6	6.195810000	12.711720000	16.129744000
6	5.815264000	3.876028000	15.342324000
1	6.892606000	3.979699000	15.517902000

1	5.569369000	2.806660000	15.379049000
1	5.290057000	4.359326000	16.175180000
6	5.370704000	4.495608000	14.042762000
6	7.305534000	13.254401000	15.440589000
6	0.696216000	14.435339000	10.029637000
1	0.455726000	14.810629000	9.030451000
1	0.695017000	15.268939000	10.739959000
1	-0.028064000	13.665574000	10.324554000
6	5.709334000	4.039192000	12.745069000
6	7.712154000	12.718381000	14.196753000
6	-2.811795000	11.615856000	11.772013000
1	-3.134865000	10.766579000	11.153602000
1	-3.296845000	12.534438000	11.429483000
1	-3.064368000	11.432384000	12.824175000
6	5.796146000	13.229832000	17.478152000
1	6.620024000	13.121093000	18.197219000
1	4.920071000	12.694149000	17.862535000
1	5.561239000	14.302590000	17.436362000
6	-2.352734000	3.555768000	15.860657000
1	-2.779504000	4.530195000	16.127917000
1	-1.774513000	3.136598000	16.690571000
1	-3.156371000	2.864824000	15.589900000
6	10.024688000	5.934583000	15.773418000
1	10.670230000	6.605539000	15.189474000
1	10.535993000	4.984308000	15.951884000
1	9.763787000	6.402780000	16.731016000
6	5.407302000	4.045173000	10.244214000
1	6.493327000	4.069224000	10.077824000
1	4.925230000	4.595191000	9.429901000
1	5.115412000	2.987484000	10.170728000
6	8.978194000	13.160941000	13.515498000
1	9.497604000	12.313524000	13.047940000
1	9.668183000	13.609215000	14.239357000
1	8.789049000	13.903033000	12.724180000
6	7.627375000	2.609879000	13.314148000
1	8.309474000	2.053968000	12.663821000
1	7.239939000	1.940278000	14.089647000
1	8.147800000	3.467519000	13.758337000
6	8.090259000	15.535744000	15.466704000
1	8.438616000	15.486731000	14.427491000
1	8.808182000	16.094793000	16.073372000
1	7.105336000	16.021622000	15.508601000

1b

27	4.831300000	9.895407000	13.141071000
27	2.562920000	7.546069000	12.859866000
8	3.808942000	8.726199000	11.952103000
8	3.607862000	9.562603000	14.483862000
8	2.912528000	8.405979000	14.459001000
8	2.841601000	14.834537000	10.346104000

7	6.045885000	8.525407000	13.755986000
8	-2.447242000	10.447707000	11.180451000
8	9.057153000	5.879941000	14.653231000
7	1.066862000	8.704430000	12.410635000
8	-1.639575000	3.786207000	14.952793000
7	2.124191000	6.629203000	11.165096000
7	6.220029000	10.145875000	11.769782000
7	1.303954000	6.356253000	13.686371000
7	3.937337000	6.183355000	12.935000000
7	3.940813000	11.385533000	12.282337000
7	5.802221000	11.175071000	14.181388000
6	2.487863000	13.316469000	12.262410000
6	3.110188000	13.741615000	11.057178000
6	4.127624000	12.933562000	10.452805000
6	6.900487000	8.071695000	12.800943000
6	4.517801000	11.773910000	11.106163000
6	0.555998000	8.509906000	11.159865000
6	6.222467000	8.169626000	15.037388000
1	5.510814000	8.583324000	15.751241000
6	1.326361000	13.992948000	12.945030000
1	1.570748000	14.996603000	13.312707000
1	1.011050000	13.396340000	13.809956000
1	0.464492000	14.087163000	12.271297000
6	-0.779484000	10.160248000	12.976515000
6	0.726341000	5.449329000	12.860331000
6	4.272629000	5.669079000	11.717623000
6	1.405379000	7.614138000	10.299023000
1	0.819677000	7.087534000	9.535078000
1	2.165264000	8.205246000	9.765947000
6	3.443545000	6.218183000	10.588702000
1	3.906455000	7.115185000	10.158476000
1	3.292346000	5.486195000	9.783270000
6	5.389668000	11.647991000	15.377256000
1	4.474710000	11.217662000	15.783157000
6	-0.263972000	4.583934000	13.302704000
6	-1.323015000	9.937842000	11.683363000
6	7.240149000	7.322169000	15.471766000
6	8.077836000	6.780174000	14.466143000
6	-0.620026000	9.119005000	10.744969000
6	5.557531000	10.804634000	10.601715000
1	5.080100000	10.013451000	10.005659000
1	6.307538000	11.286826000	9.962365000
6	0.409217000	9.497702000	13.273878000
1	0.861333000	9.607778000	14.258935000
6	6.699813000	8.753299000	11.472265000
1	7.619171000	8.787444000	10.871836000
1	5.916041000	8.255469000	10.888305000
8	7.809704000	14.144611000	16.182879000
6	-0.684477000	4.668119000	14.665748000
6	0.914758000	6.422171000	14.971889000
1	1.417185000	7.167853000	15.587366000

6	4.715614000	13.389667000	9.149325000
1	3.933107000	13.460670000	8.379966000
1	5.496832000	12.722030000	8.772692000
1	5.134062000	14.401116000	9.247569000
6	2.969426000	12.137112000	12.825467000
1	2.551231000	11.767400000	13.761995000
6	4.485386000	5.663433000	14.041243000
1	4.132375000	6.072700000	14.987569000
6	7.334938000	10.990506000	12.333649000
1	7.636516000	11.733188000	11.582627000
1	8.204416000	10.336907000	12.500169000
6	7.894807000	7.146948000	13.099816000
6	1.281582000	5.414259000	11.464771000
1	1.919773000	4.526036000	11.346447000
1	0.483477000	5.337875000	10.714846000
6	-0.061278000	5.603799000	15.536929000
8	6.825769000	3.297378000	12.485590000
6	8.795043000	6.551494000	12.057963000
1	8.612669000	6.959868000	11.058612000
1	8.644010000	5.463236000	12.005092000
1	9.852432000	6.700087000	12.315131000
6	7.322669000	7.008898000	16.942485000
1	8.208123000	7.456859000	17.412583000
1	7.360554000	5.930097000	17.134016000
1	6.442835000	7.408997000	17.461200000
6	6.938051000	11.649014000	13.628130000
6	5.258308000	4.704118000	11.580001000
6	-0.323138000	5.757188000	17.014858000
1	-1.363022000	6.022692000	17.237183000
1	0.313345000	6.551742000	17.423650000
1	-0.088128000	4.836240000	17.564294000
6	-1.199786000	8.950080000	9.370835000
1	-0.588124000	8.316467000	8.721274000
1	-1.312372000	9.927089000	8.879477000
1	-2.211033000	8.522816000	9.427943000
6	-0.901782000	3.554753000	12.415743000
1	-0.516279000	3.572732000	11.391186000
1	-1.991426000	3.695546000	12.381604000
1	-0.739390000	2.545696000	12.821574000
6	-1.347847000	11.088586000	14.019360000
1	-1.478376000	12.104849000	13.625491000
1	-0.665634000	11.147875000	14.876780000
1	-2.320811000	10.756935000	14.402050000
6	6.074048000	12.636640000	16.059733000
6	5.877072000	4.102925000	15.372691000
1	6.961013000	4.152483000	15.519923000
1	5.573621000	3.054791000	15.496578000
1	5.397841000	4.673835000	16.177052000
6	5.442341000	4.648326000	14.036526000
6	7.249790000	13.175699000	15.459498000
6	2.152126000	16.014422000	10.846112000

1	2.299339000	16.763671000	10.063472000
1	2.615266000	16.356186000	11.778776000
1	1.082514000	15.821908000	10.974363000
6	5.881579000	4.199012000	12.763605000
6	7.728618000	12.631724000	14.235974000
6	-3.576804000	10.909487000	11.973956000
1	-3.831805000	10.165169000	12.737017000
1	-4.395030000	10.996416000	11.253705000
1	-3.374706000	11.888163000	12.420524000
6	5.593075000	13.148220000	17.382336000
1	6.359834000	13.009404000	18.157906000
1	4.677240000	12.634259000	17.696756000
1	5.396983000	14.228926000	17.335502000
6	-2.431703000	3.753043000	16.171350000
1	-2.952863000	4.706624000	16.312435000
1	-1.813477000	3.499193000	17.037839000
1	-3.160843000	2.957632000	15.994723000
6	9.921433000	5.884774000	15.829389000
1	10.161996000	6.914566000	16.117023000
1	10.830698000	5.369410000	15.506385000
1	9.464225000	5.339443000	16.661517000
6	5.684955000	4.154559000	10.249425000
1	6.766658000	4.288488000	10.108138000
1	5.173339000	4.633262000	9.408375000
1	5.507804000	3.070578000	10.197680000
6	9.057402000	12.988145000	13.613902000
1	9.479102000	12.135195000	13.067568000
1	9.793731000	13.260436000	14.374950000
1	8.984848000	13.826927000	12.905762000
6	7.681527000	2.633393000	13.452853000
1	8.326531000	1.992828000	12.844919000
1	7.095258000	2.014146000	14.138978000
1	8.289499000	3.370353000	13.990350000
6	8.677518000	15.185666000	15.654375000
1	9.728710000	14.893567000	15.754441000
1	8.482527000	16.056593000	16.287656000
1	8.423103000	15.416247000	14.614160000
1	3.207641000	9.395508000	11.569026000

References:

1. G. Xue, D. Wang, R. De Hont, A.T. Fiedler, X. Shan, E. Münck and L. Que, Jr., *Proc. Natl. Acad. Sci.* U. S. A, 2007, **104**, 20713–20718.
2. G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Adv.*, 2015, **71**, 3–8.
3. G. M. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, **71**, 3–8.
4. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339–341.

5. B. Ravel and M. Newville, *J. Synchrotron Radiat.*, 2005, **12**, 537–541.
6. J. J. Rehr and R. C. Albers, *Rev. Mod. Phys.*, 2000, **72**, 621–654.
7. A. D. Becke, *Phys. Rev A*., 1988, **38**, 3098-3100.
8. F. Neese, *Wiley Interdiscip. Rev. Comput. Mol. Sci.*, 2012, **2**, 73–78.
9. F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297–3305.
10. S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010**, 132**, 154104.
11. S. Grimme, S. Ehrlich and L. Goerigk, *Journal of Computational Chemistry.,* 2011**, 32**, 1456-1465.
12. S. Kossmann and F. Neese, *J. Chem. Theory Comput.*, 2010, **6**, 2325–2338.
13. S. L. F. Chan, T. L. Lam, C. Yang, S. C. Yan and N. M. Cheng, *Chem. Commun.,* 2015, **51**, 7799–7801.