

## Supporting Information

### **Nitric oxide monooxygenation (NOM) reaction of a Cobalt-nitrosyl $\{\text{Co}(\text{NO})\}^8$ to Co-nitrito $\{\text{Co}(\text{NO}_2^-)\}$ : Acid induced hydrogen gas ( $\text{H}_2$ ) evolution**

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## Experimental Section

**Materials.** All reagents and solvents obtained from commercial sources (Sigma Aldrich Chemical Co. and Tokyo Chemical Industry) were of the best available purity and used without further purification unless otherwise indicated. Solvents were dried according to reported literature and distilled under inert atmosphere before use.<sup>S1</sup> Na<sup>15</sup>NO<sub>2</sub> (99.2% <sup>15</sup>N-enriched) was purchased from ICON Services Inc. (Summit, NJ, USA). The 12TMC ligand was prepared by reacting excess amounts of formaldehyde and formic acid with 1,4,7,10-tetraazacyclododecane as reported previously.<sup>S2</sup>

**Instrumentation.** UV-vis spectra were recorded on a Hewlett-Packard 8453 diode array spectrometer equipped with a thermostat cell holder (UNISOKU Scientific Instruments) designed for low-temperature experiments. FT-IR spectra in solid form were recorded on the Bruker-Alpha Eco-ATR FTIR spectrometer using the standard KBr disk method. The solution IR spectra were recorded on the Cary 630 spectrophotometer in the frequency range of 400 – 4000 cm<sup>-1</sup> using a demountable liquid-cell kit having a round KBr cell window (32 mm). <sup>1</sup>H-NMR spectra were measured with a Bruker model Ascend 400 FT-NMR spectrometer. Electrospray ionization mass spectra (ESI-MS) were recorded on an Agilent Mass Spectrometer (6200 series TOF/6500 series Q-TOF B.08.00), by infusing samples directly into the source using a manual method. The spray voltage was set at 4.2 kV and the capillary temperature at 80 °C. We have determined the composition of gases (H<sub>2</sub>, m/z = 2; HD, m/z = 3 and D<sub>2</sub>, m/z = 4) using an on-line MS with an OmniStar™ Gas Analysis System GSD 320 (Pfeiffer) quadrupole mass spectrometer apparatus. The GC-MS analysis was recorded on an Agilent 7890B GC system equipped with a 5977B MSD Mass analyzer.

**Synthesis of [(12TMC)Co<sup>II</sup>(NO<sub>2</sub>)](BF<sub>4</sub>).** Prepared by the following procedure as reported earlier.<sup>S2</sup> [(12TMC)Co<sup>II</sup>(ACN)](BF<sub>4</sub>)<sub>2</sub> (100 mg in 10 ml CH<sub>3</sub>CN, 0.2 mmol) was reacted with

1 mL aqueous solution of NaNO<sub>2</sub> (14 mg, 0.2 mmol) with constant stirring at RT. The reaction mixture was stirred for one hour until the color of the solution changed from wine red to light pink, indicating completion of the reaction. The volume of the reaction mixture was decreased to 2 mL over a rotary vacuum and then layered with diethyl ether and kept for crystallization at -20 °C. Yield: 85 mg (~ 90%). UV:  $\lambda_{max} = 535$  nm ( $\epsilon = 24$  M<sup>-1</sup> cm<sup>-1</sup>). FT-IR (KBr pellet): 2925, 1271, 1085, 754 cm<sup>-1</sup>. Mass (*m/z*): Calcd: 333.2, Found: 333.2.

**Synthesis of [(12TMC)Co<sup>III</sup>(NO)](BF<sub>4</sub>)<sub>2</sub> (1).** Complex **1** was prepared by the following already reported procedure.<sup>S2</sup> The Ar saturated CH<sub>3</sub>CN solution (15 mL) containing [(12TMC)Co<sup>II</sup>(CH<sub>3</sub>CN)](BF<sub>4</sub>)<sub>2</sub> (0.502 g, 1 mmol) was purged with an excess of NO for 10 min; the color of the solution was changed from light pink to wine red color. The reaction mixture was purged with Ar gas for 10 min to remove the excess NO gas from the solution and then layered with Ar saturated ether. Deep wine red colored crystals of [(12TMC)Co<sup>III</sup>(NO)](BF<sub>4</sub>)<sub>2</sub> were obtained by slow diffusion after several days by at -20 °C. UV:  $\lambda_{max} = 370$  nm ( $\epsilon = 800$  M<sup>-1</sup> cm<sup>-1</sup>). FT-IR (KBr pellet): 2925, 1703, 1084 cm<sup>-1</sup>. Mass (*m/z*): Calcd: 404.2, Found: 404.2 ([[(12TMC)Co<sup>III</sup>(NO)](BF<sub>4</sub>)<sub>2</sub>]<sup>+</sup>). EPR: Silent. <sup>1</sup>H NMR (400 MHz, Acetonitrile-*d*<sub>3</sub>)  $\delta$  (*ppm*) = 3.66 – 3.54 (m, 8H), 3.16 – 3.04 (m, 8H), 2.33 (s, 12H) (Figure S5a).

**Synthesis of [(12TMC)Co<sup>II</sup>(<sup>15</sup>NO)](BF<sub>4</sub>)<sub>2</sub> (1-<sup>15</sup>NO).** The synthetic procedure of 1-<sup>15</sup>NO is similar to that of 1-<sup>14</sup>NO. Initial cobalt complex [(12TMC)Co<sup>II</sup>(CH<sub>3</sub>CN)](BF<sub>4</sub>)<sub>2</sub> (100 mg, 0.2 mmol) was dissolved in 5 ml distilled and degassed CH<sub>3</sub>CN, to this <sup>15</sup>NO gas (prepared by reacting with Na<sup>15</sup>NO<sub>2</sub> with H<sub>2</sub>SO<sub>4</sub>, A schematic diagram of NO setup is shown in Figure S1) was purged slowly with constant stirring. The mixture was then stirred for 30 minutes at RT; after reaction completion, the color of the solution changed from light brown to dark pink. Deep wine red colored crystals [(12TMC)Co<sup>III</sup>(<sup>15</sup>NO)](BF<sub>4</sub>)<sub>2</sub> were obtained by slow diffusion after several days by at -20 °C. UV:  $\lambda_{max} = 370$  nm ( $\epsilon = 800$  M<sup>-1</sup> cm<sup>-1</sup>). FT-IR (KBr pellet):

2924, 1637, 1084  $\text{cm}^{-1}$ . Mass ( $m/z$ ): Calcd: 405.2, Found: 405.2 ( $[(12\text{TMC})\text{Co}^{\text{III}}(\text{NO})(\text{BF}_4)]^+$ ).  
EPR: Silent.  $^1\text{H-NMR}$ : active.

**Synthesis of complex  $[(12\text{TMC})\text{Co}^{\text{II}}(\text{NO}_2)](\text{BF}_4)$  (**3**) in the reaction of  $[(12\text{TMC})\text{Co}^{\text{III}}(\text{NO})](\text{BF}_4)_2$  (**1**) + 1 equivalent Base ( $\text{OH}^-$ ).** Complex **1** was reacted with an equimolar amount of base ( $\text{Bu}_4\text{NOH}$ ,  $\text{OH}^-$  source) in  $\text{CH}_3\text{CN}$  to determine the product of NOM reaction. In this regard, complex **1** (98 mg, 0.2 mmol) was reacted with one equivalent  $\text{Bu}_4\text{NOH}$  (52 mg, 0.2 mmol) in  $\text{CH}_3\text{CN}$  at RT. Upon reaction with  $\text{Bu}_4\text{NOH}$ , the color of the reaction mixture changed to light pink from wine red over a time period of 2 minutes, indicating the formation of a new product (**3**). The reaction mixture was then stirred for 30 minutes at RT. The end product (**3**), obtained in the reaction of **1** and  $\text{OH}^-$ , was determined to be  $[(12\text{TMC})\text{Co}^{\text{II}}(\text{NO}_2)](\text{BF}_4)$  from various spectroscopic and structural characterization. The deep pink colored crystals were obtained on keeping the solution layered with  $\text{Et}_2\text{O}$ , at  $-20\text{ }^\circ\text{C}$  for 5 days. UV:  $\lambda_{\text{max}} = 535\text{ nm}$  ( $\epsilon = 24\text{ M}^{-1}\text{ cm}^{-1}$ ). FT-IR (KBr pellet): 2925, 1271, 1084, 755  $\text{cm}^{-1}$ . Mass ( $m/z$ ): Calcd: 333.2, Found: 333.2.

**Reaction of  $[(12\text{TMC})\text{Co}^{\text{III}}(\text{NO})](\text{BF}_4)_2$  with sodium oxide ( $\text{Na}_2\text{O}$ ).** This reaction is very sensitive and needs precautions to avoid any interference, as to remove Sodium ion ( $\text{Na}^+$ ) from sodium oxide, we have used the crown ether (15-Crown-5). For all NOM reactions of **1** with oxide ( $\text{Na}_2\text{O}$ ,  $\text{O}^{2-}$  source), we have prepared the solution of  $\text{Na}_2\text{O}$  (1 equiv.) in the presence of 15-Crown-5 (5 equiv.) under Argon atmosphere. We have to use the  $\text{Na}_2\text{O}$  solution within 1 hour of its preparation, neither it decomposes. Therefore, to avoid any interference, we have used one sample at a time under the Argon atmosphere. The experiments were done in triplicate to observed the reproducibility. Complex **1** was reacted with an equimolar amount of  $\text{O}^{2-}$  in  $\text{CH}_3\text{CN}$  to determine the end product of NOM reaction. In this regard, for the isolation and characterization of the reaction product of the **1** with  $\text{Na}_2\text{O}$ , complex **1** (196 mg, 0.4 mmol)

was reacted with Na<sub>2</sub>O (26 mg, 0.4 mmol) in presence 15-Crown-5 (440 mg, 2 mmol) in CH<sub>3</sub>CN at RT. The color of the reaction mixture was changed to light pink from wine red over a time period of 2 - 3 minutes, indicating the completion of the reaction. The reaction mixture was then stirred for 15 more minutes at RT. The end product, obtained in the reaction of **1** with Na<sub>2</sub>O (in the presence of 15-Crown-5), was isolated as a precipitate using ether and crystallized by the solvent diffusion method. The light pink colored crystals were obtained on keeping the solution layered with Et<sub>2</sub>O, at -20 °C for 5 days. The isolated product was determined to be [(12TMC)Co<sup>II</sup>(NO<sub>2</sub>)](BF<sub>4</sub>) (**3**) from the various spectroscopic and structural characterization.

**Reactivity Studies.** All UV-vis spectral measurements were run in a UV cuvette in CH<sub>3</sub>CN or aqueous solutions at RT. We have performed the reactions under the Ar atmosphere wherever required. All kinetic reactions were run at least three times, and the data reported here are the average outcome for these reactions. We have performed all the reactions either at RT or 273 K as the initial Co<sup>III</sup>-nitrosyl complex (**1**) is very stable even at 298 K. The formation of complex **3** and H<sub>2</sub> gas in the above reactions, were identified by comparing them with authentic samples. The final yields of different products were determined by comparing them against the standard curves prepared using authentic samples.

**<sup>15</sup>N-labeling Experiments by FT-IR Spectroscopy.** We have recorded the FT-IR spectrum of the different complexes, in their solid-state as KBr pellets, to follow the source of nitrogen in the NOM reactions of complex **1**. The FT-IR spectrum of complex **3**, isolated in the reaction of [(12TMC)Co<sup>III</sup>(<sup>14</sup>NO)](BF<sub>4</sub>)<sub>2</sub> (98 mg, 0.2 mmol) with Bu<sub>4</sub>NOH (52mg, 0.2 mmol) under Ar at 273 K, showed a characteristic peak at 1271 cm<sup>-1</sup> for Co<sup>II</sup>-bound nitrite. However, the peak for Co<sup>II</sup>-bound <sup>14</sup>NO<sub>2</sub><sup>-</sup> in complex **3** was shifted to 1245 cm<sup>-1</sup>, when isolated in the reaction of <sup>15</sup>N-labeled [(12TMC)Co<sup>III</sup>(<sup>15</sup>NO)](BF<sub>4</sub>)<sub>2</sub> (25 mg, 0.05 mmol) with Bu<sub>4</sub>NOH (13 mg, 0.05 mmol). The change in the IR stretching frequency of Co<sup>II</sup>-bound NO<sub>2</sub><sup>-</sup> (Δ = 26 cm<sup>-1</sup>) confirmed

evidently that an increase in the reduced mass of nitrogen atom (from  $^{14}\text{N}$  to  $^{15}\text{N}$ ) is responsible for the decrease in the IR stretching frequency of  $\text{NO}_2^-$  functional group.

**NOM Reaction and  $^{15}\text{N}$ -labeling Experiments by ESI-Mass Spectrometry.** Furthermore, to establish the source of nitrogen, complex **1** with  $^{14}\text{N}$ -labeled and  $^{15}\text{N}$ -labeled NO ligand,  $[(12\text{TMC})\text{Co}^{\text{III}}(^{14}\text{NO})](\text{BF}_4)_2$  and  $[(12\text{TMC})\text{Co}^{\text{III}}(^{15}\text{NO})](\text{BF}_4)_2$ , were reacted with one fold  $\text{Bu}_4\text{NOH}$  in  $\text{CH}_3\text{CN}$  under Ar at 273 K. For the above experiment, a cuvette (4 mL) containing a solution of complex **1** (0.5 mM / 2.5 mL), having different isotopic NO ligands, in  $\text{CH}_3\text{CN}$  sealed with a rubber septum under an Ar atmosphere was reacted with one fold  $\text{Bu}_4\text{NOH}$  (25 mM / 50  $\mu\text{L}$ ), and the reactions were monitored by UV-vis spectroscopy. After the completion of the reactions, the ESI mass spectra of the reaction mixtures were recorded for both the reaction mixtures in two different experiments. The ESI-MS spectrum of **3**, formed in the reaction of  $([(12\text{TMC})\text{Co}^{\text{III}}(^{14}\text{NO})]^+ + \text{Bu}_4\text{NOH})$ , showed a prominent peak at  $m/z$  333.2, whose mass value and isotopic distribution pattern corresponds to  $[(12\text{TMC})\text{Co}^{\text{II}}(^{14}\text{NO}_2^-)]^+$  (calcd  $m/z$  333.2). However, the ESI-MS spectrum of **3**, formed in the reaction of  $([(12\text{TMC})\text{Co}^{\text{III}}(^{15}\text{NO})]^+ + \text{Bu}_4\text{NOH})$ , showed a prominent peak at 334.2, whose mass value and isotopic distribution pattern corresponded to  $[(12\text{TMC})\text{Co}^{\text{II}}(^{15}\text{NO}_2^-)]^+$  (calcd  $m/z$  334.2). These reactions indicate clearly that  $\text{NO}_2^-$  in **3** is derived from NO moiety of complex **1**.

**NOM Reaction and  $^{18}\text{O}$ -labeling Experiments by ESI-Mass Spectrometry.** To establish the source of oxygen, complex **1**,  $[(12\text{TMC})\text{Co}^{\text{III}}(\text{NO})](\text{BF}_4)_2$  were reacted with one fold  $\text{Na}^{18}\text{OH}$  in double distilled  $\text{CH}_3\text{CN}$  solvent system under Ar at 298 K. For the above experiment, a culture vial (5 mL) containing a solution of complex **1** (1 mM / 1 mL), in  $\text{CH}_3\text{CN}$  sealed with a rubber septum under an Ar atmosphere was reacted with one fold  $\text{Na}^{18}\text{OH}$  (50 mM / 20  $\mu\text{L}$ ), and the reaction was stirred for 30 minutes. After the completion of the reactions, the ESI mass spectra of the reaction mixtures were recorded. The ESI-MS spectrum of **3**,

formed in the reaction of  $[(12\text{TMC})\text{Co}^{\text{III}}(\text{NO})]^{2+} + \text{Na}^{18}\text{OH}$ , showed a prominent peak at  $m/z$  335.2 and its mass value and isotopic distribution pattern corresponds to  $[(12\text{TMC})\text{Co}^{\text{II}}(\text{NO}^{18}\text{O}^-)]^+$  (calcd  $m/z$  335.2). These reaction indicate clearly that other oxygen of  $\text{NO}_2^-$  in **3** is derived from  $\text{OH}^-$  moiety of the used base.

**Nitrite estimation by Griess reagent.** The amount of nitrite formed in two different NOM reactions of **1**, with one fold base ( $\text{Bu}_4\text{NOH}$ ) /or Oxo ( $\text{Na}_2\text{O}$  in the presence of 15-Crown-5) in  $\text{CH}_3\text{CN}$  at 298 K, were determined using Griess reagent titration curve. The color of the  $\text{CH}_3\text{CN}$  solution of **1** (0.5 mM, 2.0 mL) changed from dark pink to light pink upon reaction with reagents (*i.e.*,  $\text{OH}^-$  /or  $\text{O}^{2-}$ ) and the characteristic absorption band of **1** (370 nm) disappear within 2 minutes. The reaction mixtures were dried by rotary evaporator and then dissolved in water (2 mL). To these solutions, an aqueous solution of  $\text{Na}_2\text{S}$  (5.0 mM, 3.0 mL) was added to remove the Cobalt as  $\text{CoS}$  species. The black precipitates were filtered out, and the organic part was removed by the solvent extraction using  $\text{CHCl}_3$  in both cases. The aqueous layers were diluted up to 10 mL. 125  $\mu\text{L}$  of this stock solution was added to a sample vial containing 2.0 mL of fresh Griess reagent (naphthyl ethylenediamine dihydrochloride (0.20%) and sulphanilic acid (2.0%) in aqueous phosphoric acid (5.0%)) and then diluted to 2.5 mL by adding  $\text{H}_2\text{O}$ . We have observed the immediate color change from colorless to violate. We have compared the UV-vis spectra of this solution with a calibration curve prepared by employing authentic  $\text{NaNO}_2$  solutions (Figure. S6a). The yields of nitrite formed in the reaction of **1**, with one fold base ( $\text{OH}^-$ ) /or Oxo ( $\text{O}^{2-}$ ), were  $90 \pm 5\%$  and  $85 \pm 5\%$ , respectively.

We have prepared the calibration plot from the stock solutions of  $\text{NaNO}_2$  in various concentration (0, 0.10, 0.20, 0.30, 0.40, 0.50, 0.60, 0.70, 0.80, 0.90, 1.0 mM). Addition of 125  $\mu\text{L}$  of each stock solution to a sample vial containing 1.0 mL of fresh Griess reagent and then diluted to 2.5 mL by adding  $\text{H}_2\text{O}$ . UV-vis spectra for the standard solutions were recorded and



calibration curve between varying concentrations of nitrite (0, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0  $\mu\text{M}$ ) and corresponding absorbance at 547 nm were plotted (Figure. S6b).

#### **Hydrogen gas detection and D-labeling experiments by headspace Mass spectrometry.**

In order to authorize the source of  $\text{H}_2$ , complex **1** was reacted with NaOH, D-labeled OD (NaOD) and also with NaOH/NaOD (in 1:1 ratio) in  $\text{CH}_3\text{CN}$  under Ar atmosphere at 298 K, in three different experiments, and the gases formed in the reactions were determined by following the mass of particular gas. We had determined the different gases ( $\text{H}_2$ ,  $m/z = 2$ ; HD,  $m/z = 3$  and  $\text{D}_2$ ,  $m/z = 4$ ) formed in the reaction of **1** with base (NaOH, NaOD and the mixture of NaOH/NaOD in 1:1 ratio) using an on-line MS with an OmniStar<sup>TM</sup> Gas Analysis System GSD 320 (Pfeiffer) quadrupole mass spectrometer apparatus (Figure S13). To perform the experiments, we had taken a vial (5.0 mL), having a  $\text{CH}_3\text{CN}$  solution of **1** (5.0 mM, 2.0 mL), sealed with a rubber septum and attached to the capillary from mass spectrometer into the headspace of the sealed vial for real-time measurement. The solutions of NaOH or NaOD (100 mM) were prepared in other sample vials in  $\text{CH}_3\text{CN}$  under an Ar atmosphere. All the samples were prepared in an ultra-pure Ar (6 grade) atmosphere to avoid the interference by other gases. One equivalent amount of NaOH /or NaOD (0.1 mL, 100 mM) was added to the solution of **1** (in two different experiments) by using a gas-tight Hamilton syringe, piercing through the rubber septum. The reaction solution was kept for 10 minutes at 298 K before the analysis of gases ( $\text{H}_2$  /or  $\text{D}_2$ , respectively). Similarly, to verify that the  $\text{H}_2$  gas is forming via  $\text{H}\cdot$  atom coupling, we have performed the reaction of **1** (5.0 mM, 2.0 mL) with a mixture of NaOH (50.0  $\mu\text{L}$ , 100 mM) + NaOD (50.0  $\mu\text{L}$ , 100 mM) (in 1:1 ratio) and detected the gases formed in the reaction. We have observed the formation of a mixture of gases ( $\text{H}_2$ ,  $\text{D}_2$ , and HD) under similar reaction conditions (*vide supra*).

**Confirmation of O-H bond homolysis in Co<sup>II</sup>(NOOH) intermediate:** To confirm the O–H bond homolysis of N-bound nitrous acid intermediate (Co<sup>II</sup>(NOOH)), we have performed the experiment to trap the intermediate, Co<sup>II</sup>(NOOH) /or Co<sup>III</sup>-H, using 2,4-di-*tert*-butyl phenol (2,4-DTBP). For this reaction, we have reacted complex **1** (1.0 mM) with 2,4-DTBP (5.0 mM) in the presence of 1 fold Bu<sub>4</sub>NOH in CH<sub>3</sub>CN under an Ar atmosphere at 273 K. The reaction mixture was then analysed by GC-MS for the identification of different components of the mixture, and their amounts were quantified by liquid chromatography (LC) against the standard plots of all the compounds. In this experiment, we have observed the formation of only 2,4-DTBP-dimer (3,5-DTBP-D) (Figure S7a), suggesting the O–H bond homolysis to generates a Co<sup>III</sup>-H intermediate and hence indirectly proving the formation of N-bound Co<sup>II</sup>-NOOH intermediate (**2**) and the evolution of H<sub>2</sub> gas. The amount of 2,4-DTBP-D formed in the reaction was found to be ~ 67 % (~ 0.26 mM), accounting for ~ 67 % H-atom generation. In this reaction, H-atom (or Co<sup>II</sup>-NOOH or Co<sup>III</sup>-H) abstract one H-atom from 2,4-DTBP and hence generating 3,5-DTBP-D by the coupling of two 2,4-DTBP radicals, however; a specific amount of H-atoms forms H<sub>2</sub> gas due to its high reactivity. Furthermore, we had determined the H<sub>2</sub> gas formed in the reaction of **1** with base in the presence of 2,4-DTBP using the on-line MS Gas Analysis System.

**Single-Crystal XRD Studies:** Crystals were mounted on Hampton cryoloops. All geometric and intensity data for the crystals were collected using a Super-Nova (Mo) X-ray diffractometer equipped with a micro-focus sealed X-ray tube Mo-K $\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) X-ray source and HyPix3000 (CCD plate) detector of with increasing  $\omega$  (width of 0.3 per frame) at a scan speed of either 5 or 10 s/frame. The CrysAlisPro software was used for data acquisition and data extraction. Using Olex2<sup>S3</sup>, the structure was solved with the SIR2004<sup>S4</sup> structure solution program using Direct Methods and refined with the ShelXL<sup>S5</sup> refinement package using Least Squares minimization. All non-hydrogen atoms were refined with anisotropic

thermal parameters. The anion mainly  $\text{ClO}_4$  in  $\text{Ni-ClO}_4$  complex found to be highly disordered, and appropriate disordered model applied including two O-atoms refined with isotropically. Detail crystallographic data and structural refinement parameters are summarized in Table T1 – T2. CCDC-1974616 (**Co-BF<sub>4</sub>**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

**Nitric Oxide Preparation and Purification.** Nitric oxide (NO) was prepared and purified by following a detailed procedure, as shown in Figure. S12. First, NO gas was prepared by the reaction of  $\text{NaNO}_2$  with  $\text{H}_2\text{SO}_4$  under an Argon (Ar) atmosphere and then passed through two different types of columns. First, pass through a column filled with NaOH beads to remove higher nitrogen oxides impurities. After that, the gas pass through a set of two columns filled with NaOH beads molecular sieves to remove the minor amount of remaining higher nitrogen oxides and moisture impurities. The highly purified NO gas was then collected in a vacuum Schlenk flask fitted with a rubber septum (free from oxygen; after several cycles of vacuum and Ar purging). High pressure NO gas (with pressure  $>1$  atmosphere; the septum bulges outward due to high pressures) then passed through an Ar saturated (oxygen-free) and dry  $\text{CH}_3\text{CN}$  solution for 15 minutes. The concentration of NO in the NO saturated  $\text{CH}_3\text{CN}$  solution is  $\sim 14$  mM.<sup>S6</sup>

**Magnetic moment calculation and determination of number of unpaired electrons in complex 3:** Evans' method of <sup>1</sup>H-NMR was performed to determine the number of unpaired electrons (spin state) in complex **3** at room temperature<sup>S7-S9</sup>. A WILMAD® coaxial insert (with a sealed capillary) tube containing the only CD<sub>3</sub>CN solvent (with 1.0% TMS) was inserted into the normal NMR tubes containing the complex **3** (4.0 mM, with 0.1% TMS). We have calculated the chemical shift value of the TMS peak in the presence of the complex **1** with respect to that of the TMS peak in the outer NMR tube. The magnetic moment was calculated using the given equation,

$$\mu_{eff} = 0.0618(\Delta\nu T / 2fM)^{1/2}$$

$$\mu_{eff} = 0.0618 * (60 * 298 / 2 * 400 * 0.004)^{1/2}$$

$$\mu_{eff} = 4.62 \text{ BM}$$

Where f = oscillator frequency (MHz) of the superconducting spectrometer, T = absolute temperature, M = molar concentration of the complex **1**, and  $\nu$  = difference in frequency (Hz) between the two TMS signals<sup>S9</sup>. The calculated magnetic moment of complex **3** was determined to be 4.62 BM in CD<sub>3</sub>CN at RT, suggesting 3 unpaired electrons in Co<sup>2+</sup> centre of complex **3**.

## References

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**Table T1** Crystallographic data for **3**.

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Chemical formula	C <sub>12</sub> H <sub>28</sub> BCoF <sub>4</sub> N <sub>5</sub> O <sub>2</sub>
Formula weight	420.13
Wavelength /Å	0.71073
Crystal system	orthorhombic
Space group	Pbca
<i>T</i> , K	293
<i>a</i> , Å	13.0883(2)
<i>b</i> , Å	14.8329(3)
<i>c</i> , Å	19.5325(3)
$\alpha$ , °	90
$\beta$ , °	90
$\gamma$ , °	90
<i>V</i> / Å <sup>3</sup>	3791.99(11)
<i>Z</i>	8
Calculated density, g/cm <sup>3</sup>	1.472
Abs. Coeff. /mm <sup>-1</sup>	0.958
Reflections collected	4208
Unique reflections	3007
Refinement method	Least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	3007/72/302
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.129
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> =0623, <i>WR</i> <sub>2</sub> =1908
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> =0792, <i>WR</i> <sub>2</sub> =2051

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**Table T2** Selected bond lengths (Å) and bond angles (°) for **3**.

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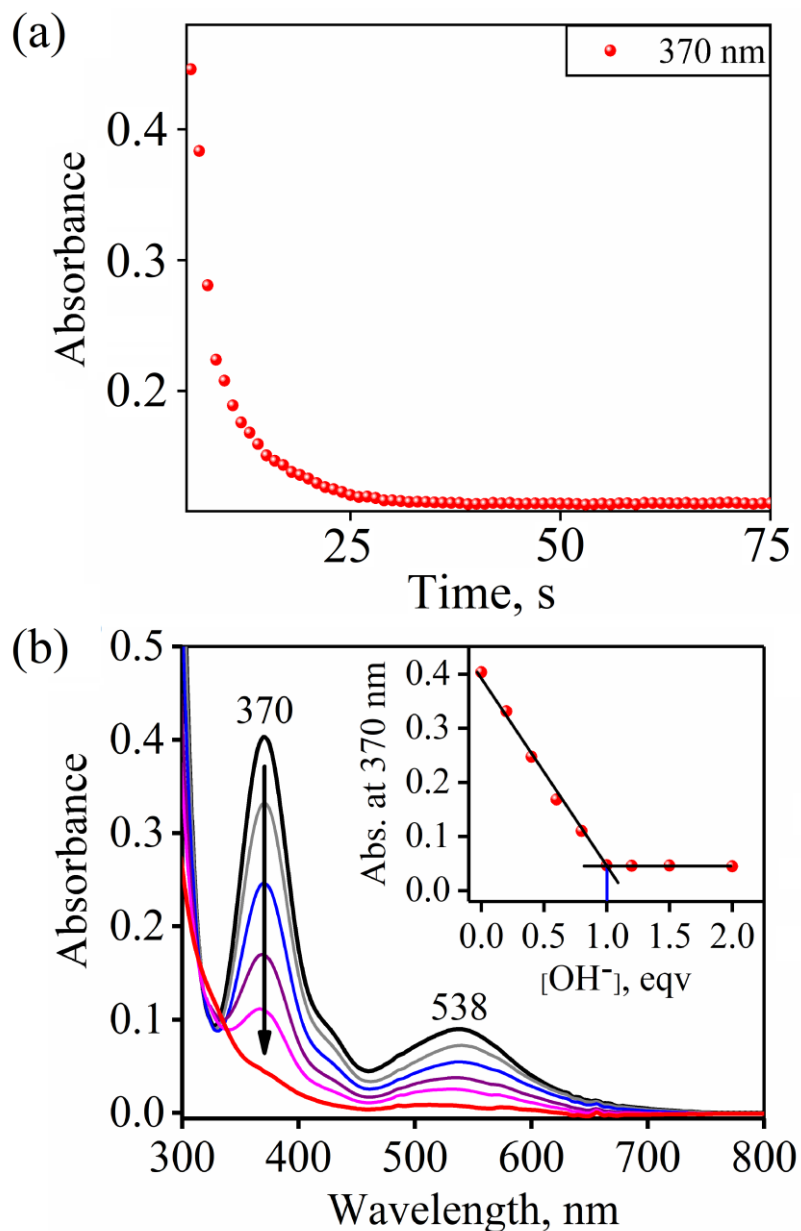
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Co1 N3	2.164(3)
Co1 N2	2.183(4)
Co1 N4	2.164(4)
Co1 N1	2.150(4)
Co1 O1	2.198(5)
Co1 O2	2.113(4)

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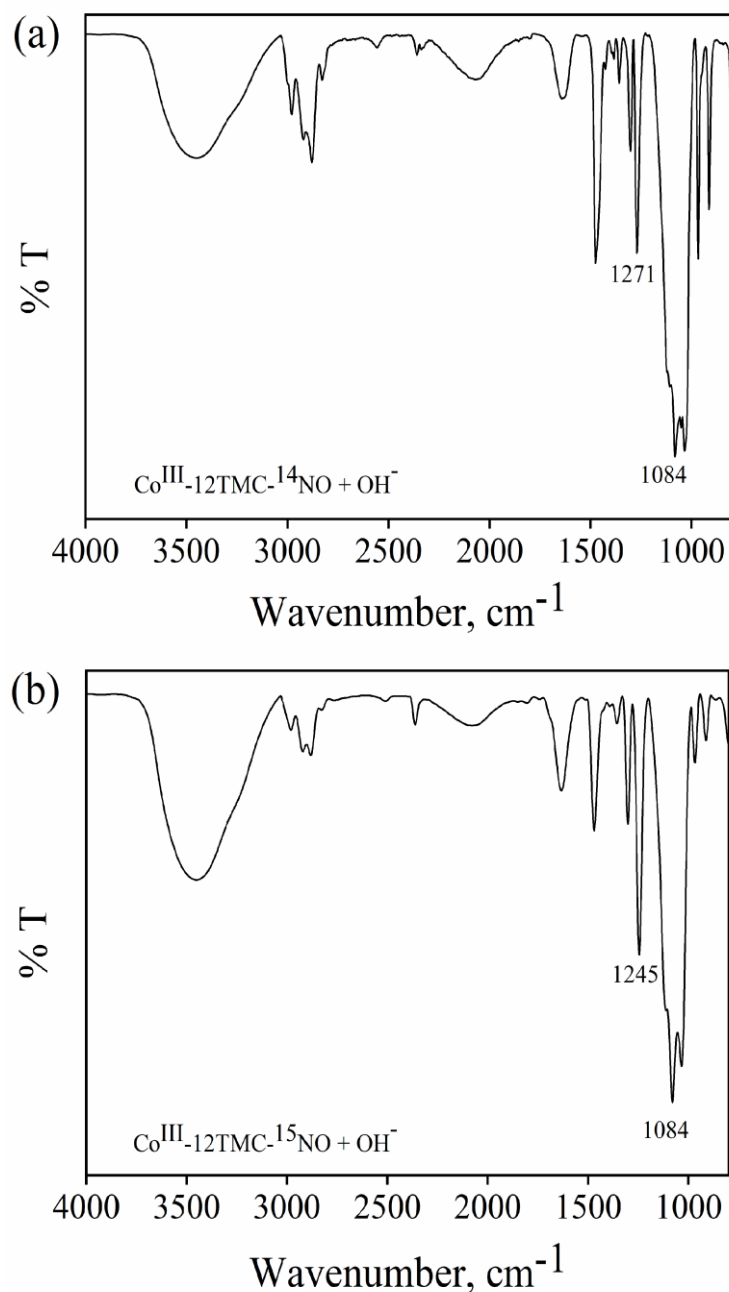
N3 Co1 N2	81.06(15)
N3 Co1 N4	80.84(15)
N3 Co1 O1	132.01(18)
N2 Co1 O1	129.48(17)
N4 Co1 N2	135.17(15)
N4 Co1 O1	92.27(16)
O2 Co1 N3	94.05(17)
O2 Co1 N2	93.58(18)
N1 Co1 N3	132.86(14)
N1 Co1 N2	80.94(15)
N1 Co1 N4	82.08(15)
N1 Co1 O1	92.17(18)
O2 Co1 N4	128.33(18)
O2 Co1 N1	130.24(18)
O2 Co1 O1	54.16(17)

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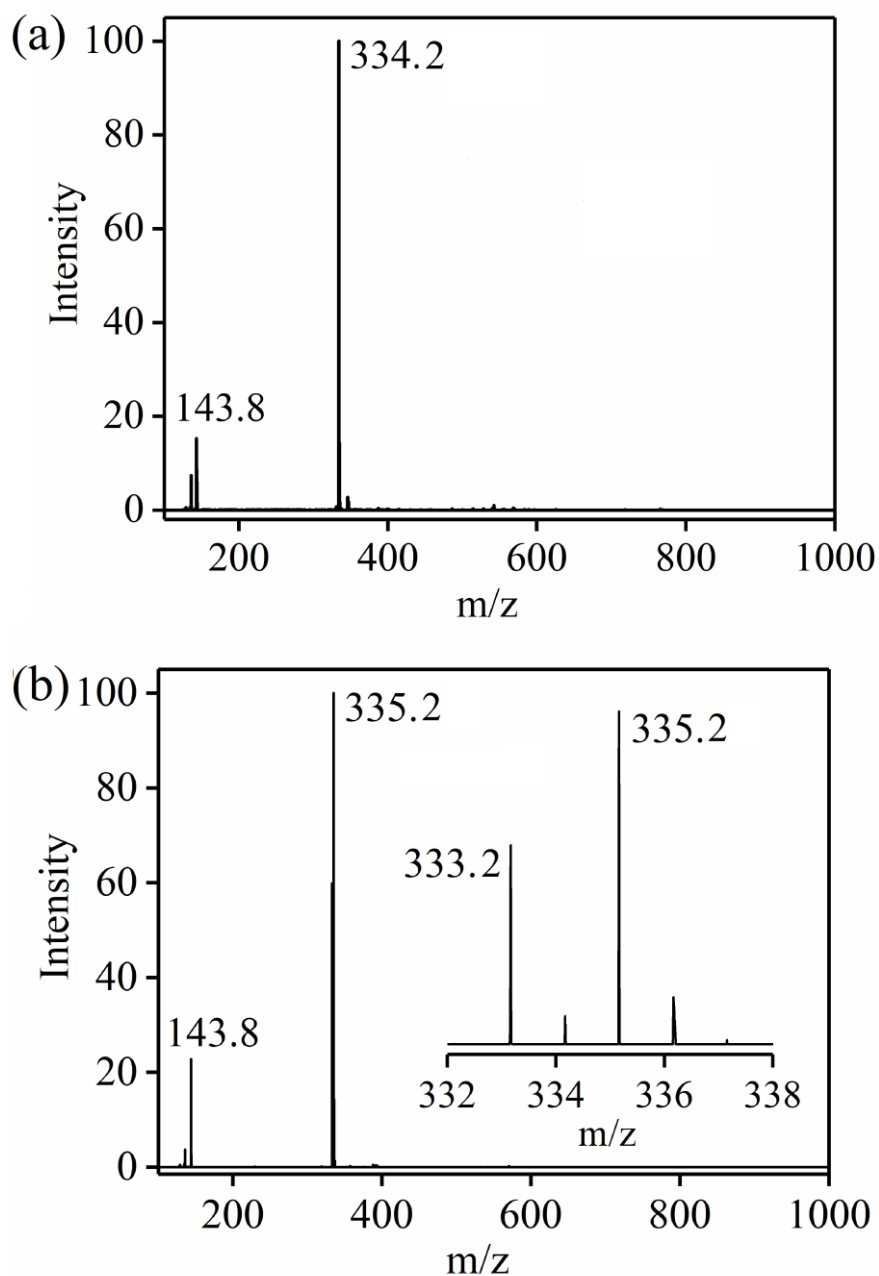


**Figure. S1.** (a) Time course of the decay of **1** (red circles) monitored at 370 nm upon addition Bu<sub>4</sub>NOH (1 equiv.) to a solution of **1** (0.5 mM) in CH<sub>3</sub>CN at 273 K. (b) UV-vis spectral changes observed in the reaction **1** with OH<sup>-</sup> (in the increments of 0, 0.20, 0.40, 0.60, 0.8, 1.0, 1.2, 1.5, 2.0 equiv) in CH<sub>3</sub>CN under Ar at 298 K.

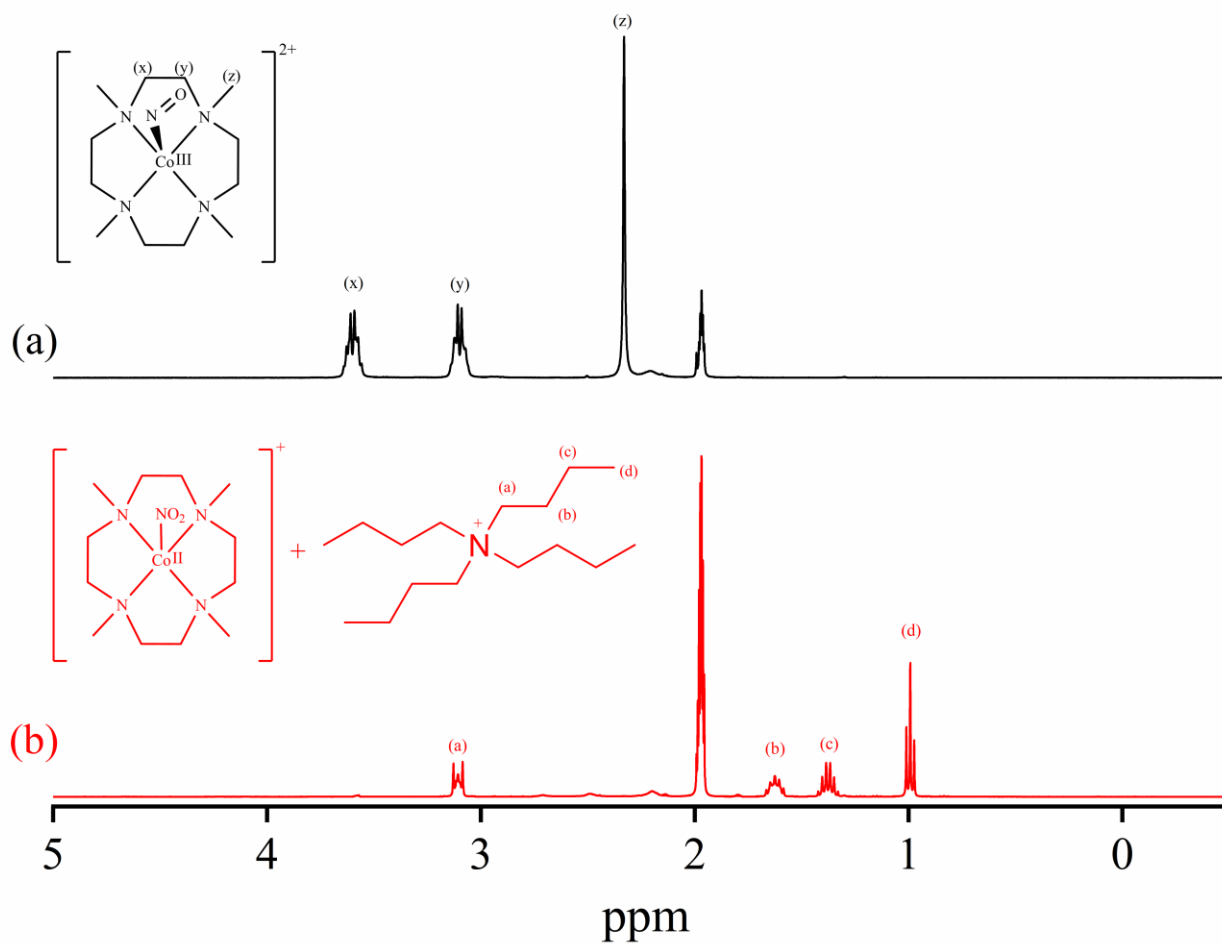




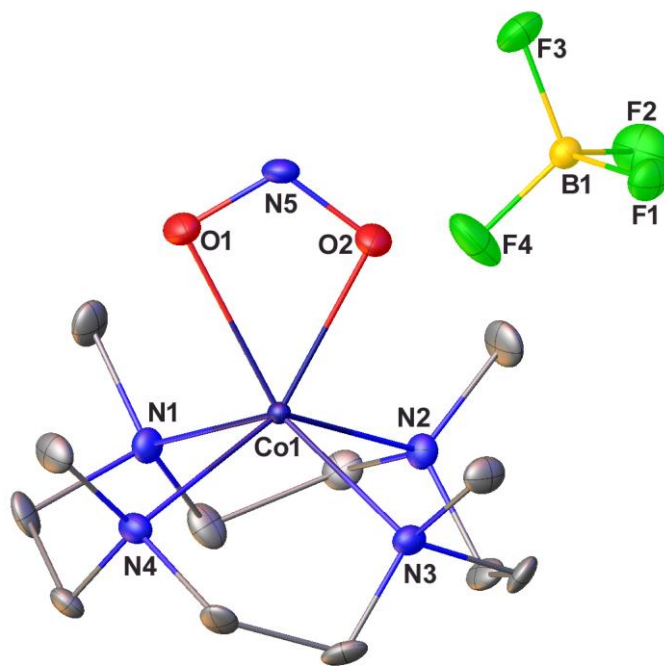
**Figure. S2.** FT-IR spectrum of (a) isolated product, obtained in the reaction of [(12TMC)Co<sup>III</sup>(<sup>14</sup>NO)]<sup>2+</sup> (40 mM) + Bu<sub>4</sub>NOH (40 mM), recorded in KBr pellet at 298 K. The spectrum showed the peaks for aliphatic chain (2925 cm<sup>-1</sup>), [Co-<sup>14</sup>NO<sub>2</sub>] (1271 cm<sup>-1</sup>), and addition peak for BF<sub>4</sub><sup>-</sup> (1084 cm<sup>-1</sup>). (b) Isolated product of obtained in the reaction of [(12TMC)Co<sup>III</sup>(<sup>15</sup>NO)]<sup>2+</sup> (40 mM) + Bu<sub>4</sub>NOH (40 mM), recorded in KBr pellet at 298 K. The spectrum showed the peaks [Co-<sup>15</sup>NO<sub>2</sub>] (1245 cm<sup>-1</sup>) and an addition peak for BF<sub>4</sub><sup>-</sup> (1084 cm<sup>-1</sup>).



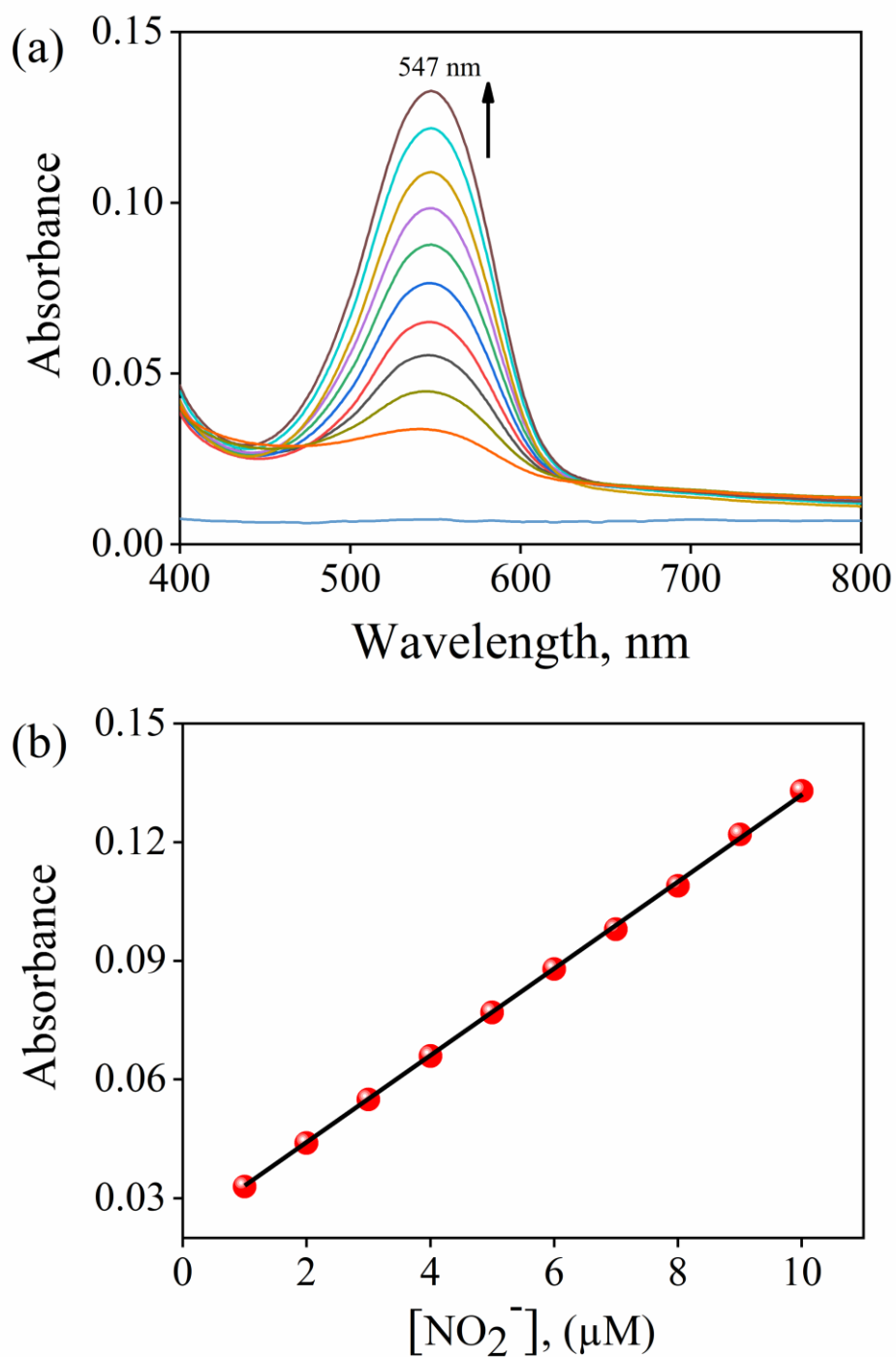
**Figure S3.** (a) ESI-MS spectrum of  $3\text{-}^{15}\text{NO}_2$ , formed in the reaction of  $([(12\text{TMC})\text{Co}^{\text{III}}(^{15}\text{NO})])^+ + \text{Bu}_4\text{NOH}$ ), recorded in  $\text{CH}_3\text{CN}$ . The peaks at  $m/z$  334.2 and 143.8 are assigned to be  $[(12\text{TMC})\text{Co}^{\text{II}}(^{15}\text{N}^{16}\text{O}_2)]^+$  (calcd:  $m/z$  334.2) and  $[(12\text{TMC})\text{Co}^{\text{II}}]^{2+}$  (calcd:  $m/z$  143.6). (b) ESI-MS spectrum of  $3\text{-}^{18}\text{ONO}$ , formed in the reaction of  $([(12\text{TMC})\text{Co}^{\text{III}}(\text{NO})]^{2+} + \text{Na}^{18}\text{OH}$ ), recorded in  $\text{CH}_3\text{CN}$ . The peaks at  $m/z$  335.2 and 143.8 are assigned to be  $[(12\text{TMC})\text{Co}^{\text{II}}(^{18}\text{O}\text{N}^{16}\text{O})]^+$  (calcd:  $m/z$  335.2) and  $[(12\text{TMC})\text{Co}^{\text{II}}]^{2+}$  (calcd:  $m/z$  143.6).



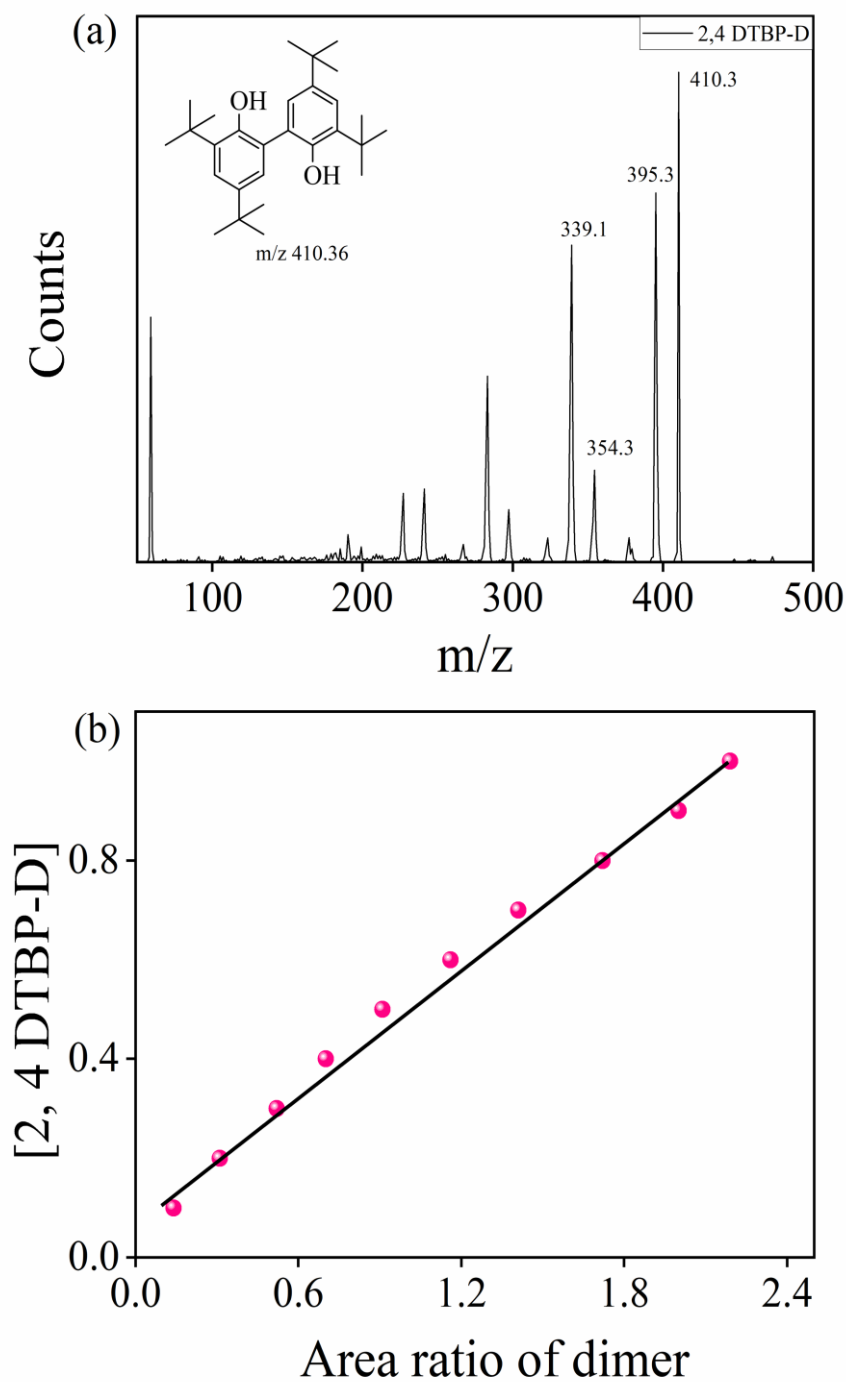
**Figure. S4.**  $^1\text{H-NMR}$  (400 MHz) spectra of (a) complex **1** (20 mM) and (b) reaction mixture (**1**, 20 mM +  $\text{Bu}_4\text{NOH}$ , 20 mM) in  $\text{CD}_3\text{CN}$  at RT.



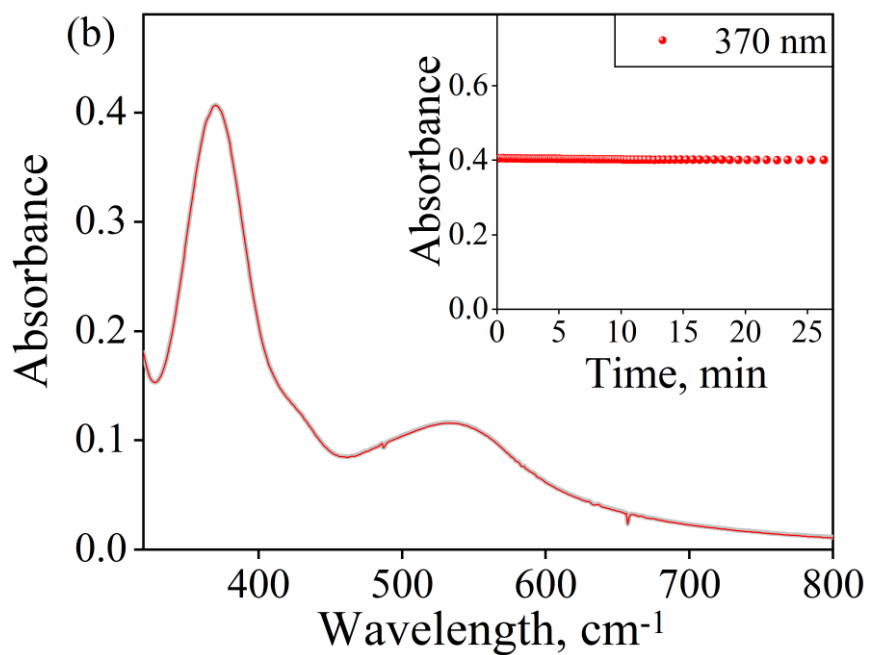
**Figure. S5:** Displacement ellipsoid plots of **3** with 20 % probability. Disordered C-atoms in the TMC ring and the H atoms have been removed for clarity



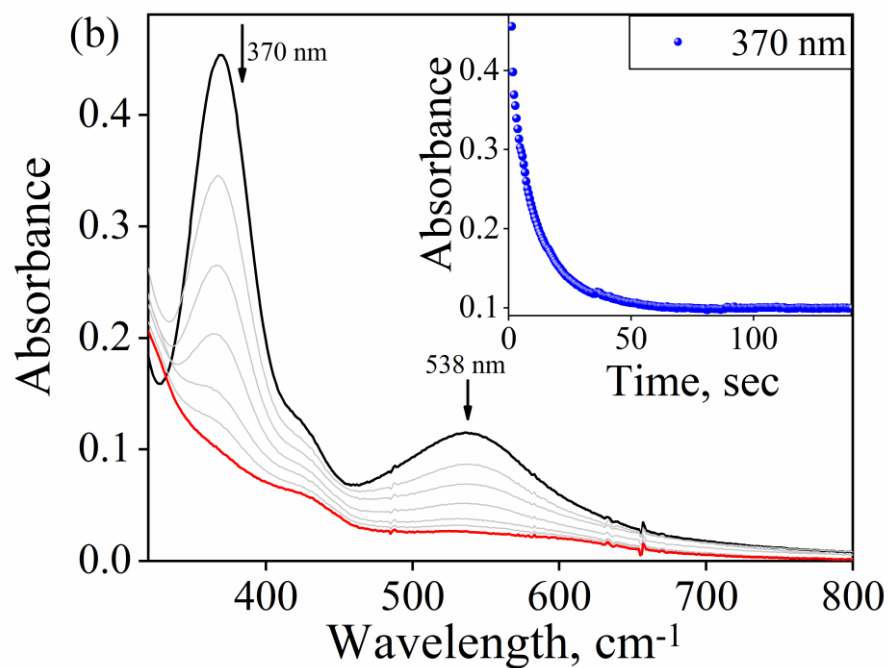
**Figure. S6.** a) UV-vis spectral changes showing the increase in the absorbance at 547 nm (due to the formation of azo dye) upon addition of NaNO<sub>2</sub> solutions in various concentrations (1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10 μM ) to Griess reagent at 25 °C. (b) Spectral calibration curve for the formation of peak at 547 nm as a function of concentration of NaNO<sub>2</sub> (μM) in increments of 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.



**Figure. S7.** GC-MS characterisation of (a) 2,4-DTBP-dimer (2,4-DTBP-D); the peaks at  $m/z$  410.3, 395.3, 339.3 and 190.2 are assigned to be 2,4-DTBP-D, loss of  $\text{CH}_3$  from 2,4-DTBP-D, loss of  $\text{C}_4\text{H}_8$  and  $\text{CH}_3$  from 2,4-DTBP-D and loss of  $\text{CH}_3$  from monomer 2,4-DTBP (b) Calibration plot for 2,4-DTBP-D.

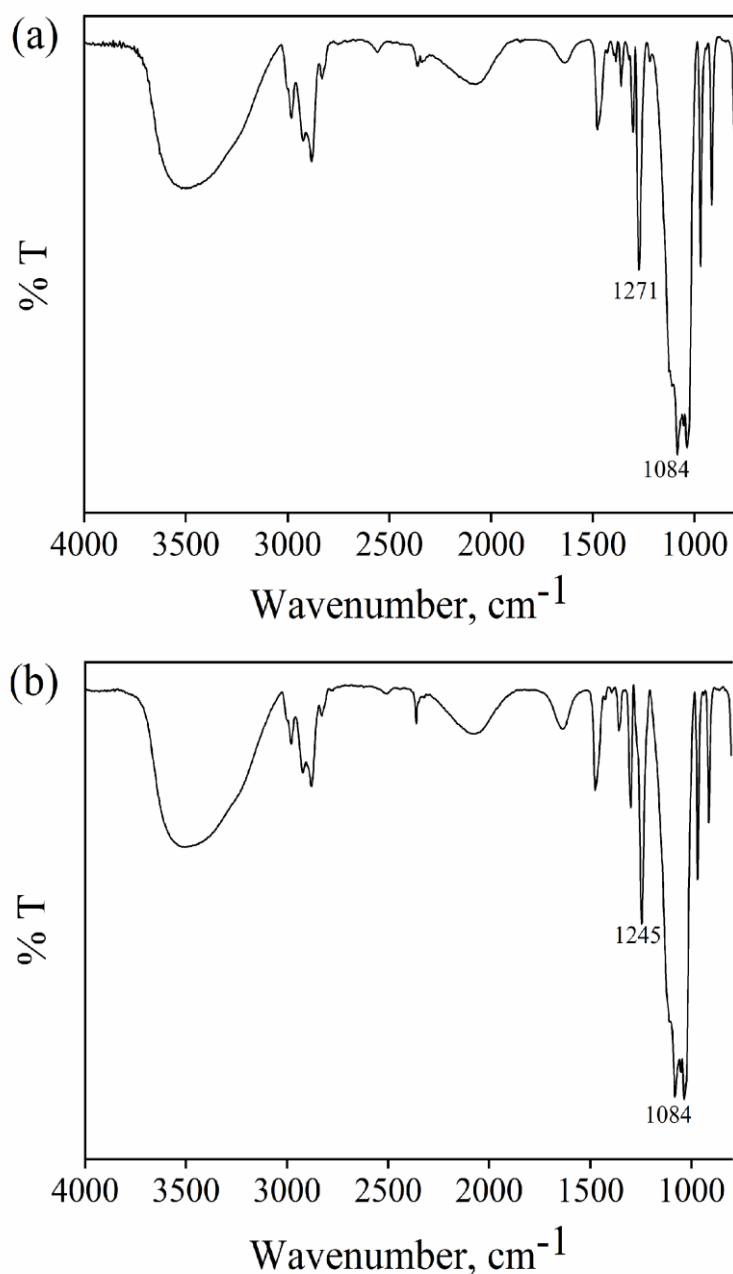


**Figure. S8.** UV-vis spectral changes of **1** (0.50 mM, Grayline) upon addition of 5 equiv. of H<sub>2</sub>O in CH<sub>3</sub>CN under Ar at 298 K( Redline). The Inset shows the time course of the decay of **1** (red circles) monitored at 370 nm upon addition H<sub>2</sub>O (5 equiv.) to a solution of **1** (0.5 mM) in CH<sub>3</sub>CN at 298 K.

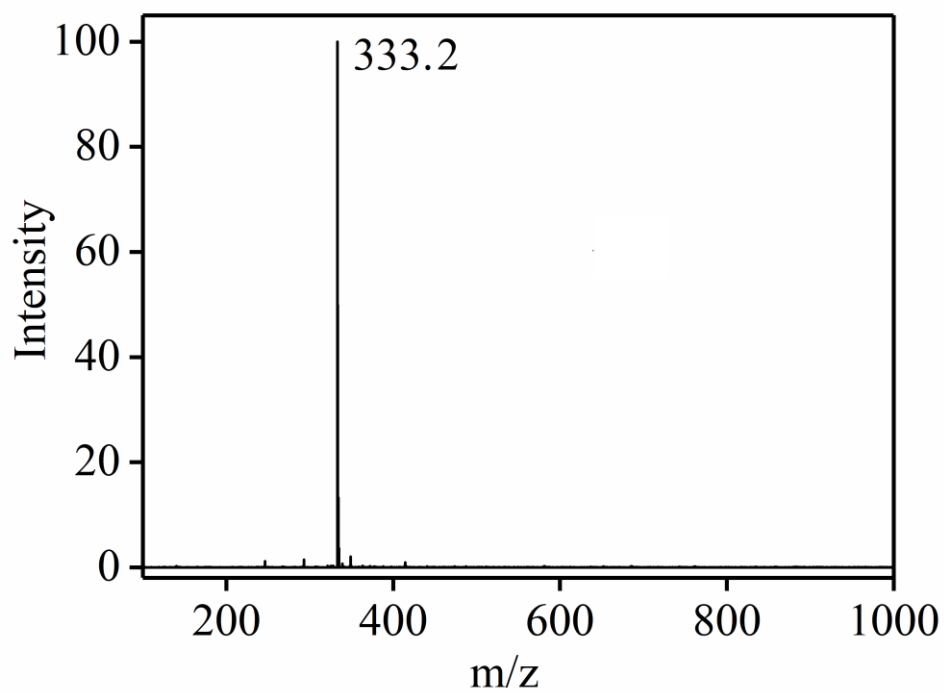


**Figure. S9.** UV-vis spectral changes of **1** (0.50 mM, black line) upon addition of 1 equiv. of O<sup>2-</sup> in CH<sub>3</sub>CN under Ar at 273 K. The Inset shows the time course of the decay of **1** (blue circles) monitored at 370 nm upon addition O<sup>2-</sup> (1 equiv.) to a solution of **1** (0.5 mM) in CH<sub>3</sub>CN at 273 K.

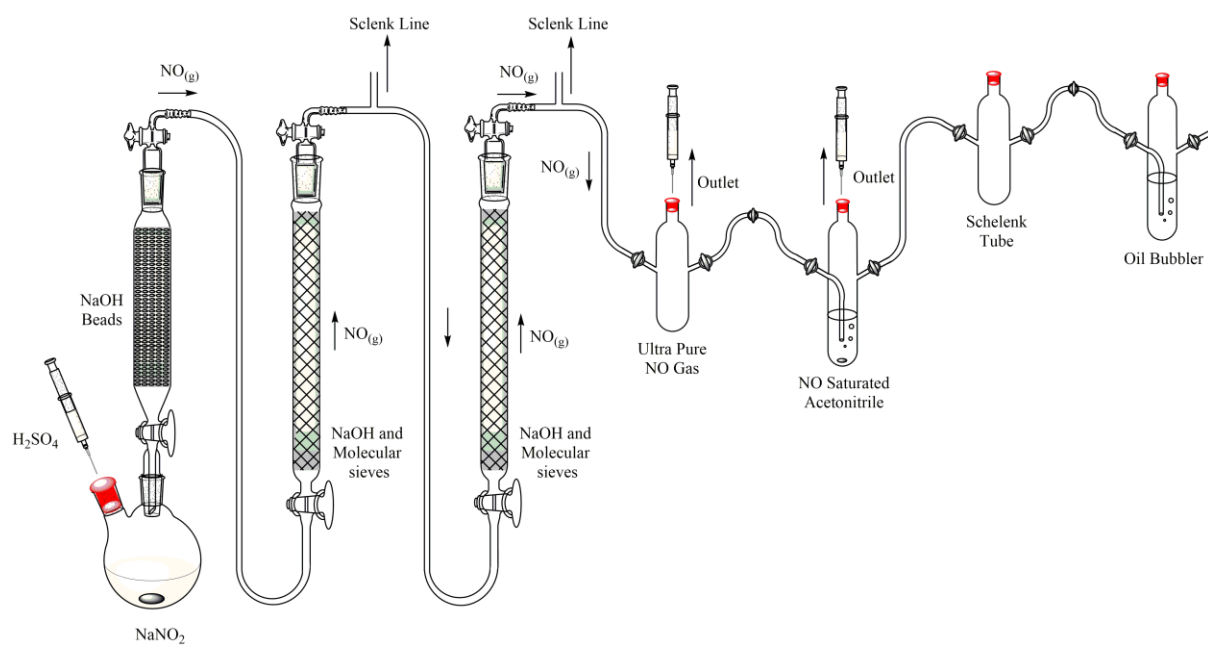




**Figure. S10.** FT-IR spectrum of (a) isolated product, obtained in the reaction of  $[(12\text{TMC})\text{Co}^{\text{III}}(^{14}\text{NO})]^{2+}$  (40 mM) +  $\text{O}^{2-}$  (40 mM), in KBr pellet at 298 K. The spectrum showed the peaks for  $[\text{Co}-^{14}\text{NO}_2]$  ( $1271\text{ cm}^{-1}$ ) and an addition peak for  $\text{BF}_4^-$  ( $1084\text{ cm}^{-1}$ ). (b) isolated product, obtained in the reaction of  $[(12\text{TMC})\text{Co}^{\text{III}}(^{15}\text{NO})]^{2+}$  (40 mM) +  $\text{O}^{2-}$  (40 mM), in KBr pellet at 298 K. The spectrum showed the peaks  $[\text{Co}-^{15}\text{NO}_2]$  ( $1245\text{ cm}^{-1}$ ) and an addition peak for  $\text{BF}_4^-$  ( $1084\text{ cm}^{-1}$ )



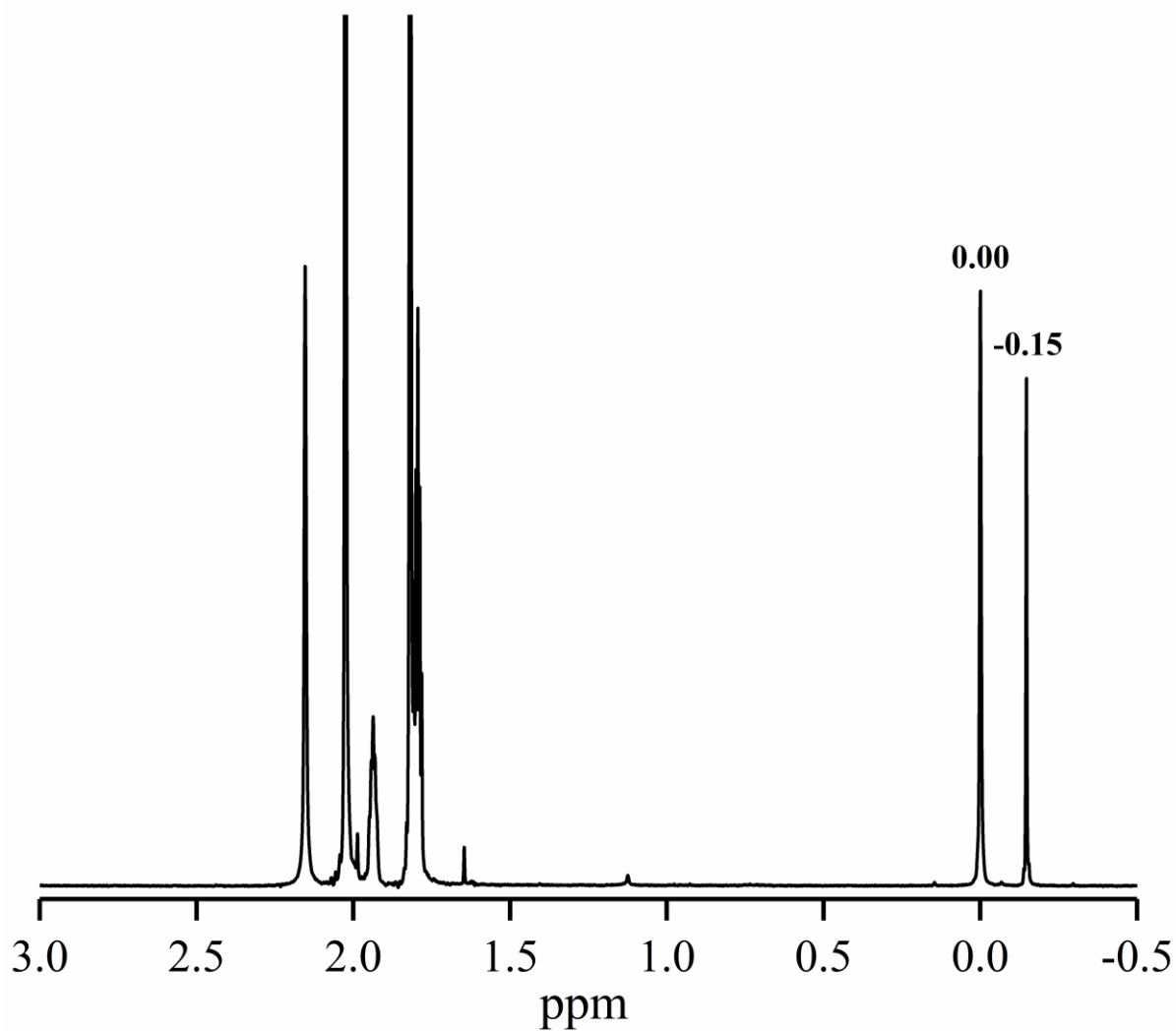
**Figure S11.** ESI-MS spectrum of **3**, formed in the reaction of  $[(12\text{TMC})\text{Co}^{\text{III}}(\text{NO})]^+ + \text{Na}_2\text{O}$  (with 5 equivalent crown ether), recorded in  $\text{CH}_3\text{CN}$ . The peak at  $m/z$  333.2 is assigned to be  $[(12\text{TMC})\text{Co}^{\text{II}}(\text{NO}_2)]^+$  (calcd:  $m/z$  333.2).



**Figure S12.** Schematic diagram showing the generation and purification setup for NO.



**Figure S13.** Photograph of OmniStar™ Gas Analysis System GSD 320 (Pfeiffer) quadrupole mass spectrometer apparatus used for the analysis of gases based on following their masses.



**Figure. S14.** <sup>1</sup>H-NMR (400 MHz) spectra of isolated complex **3** (4 mM) in CD<sub>3</sub>CN (0.1 % TMS), recorded in a coaxial NMR tube, with inside CD<sub>3</sub>CN (1.0 % TMS) at RT.