

## Supporting Information

# A Redox-Active Cobalt(II/III) Metal-Organic Framework for Selective Oxidation of Cyclohexene

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## 1. Experimental Section

### General consideration:

All chemicals were purchased from commercial sources and used as received. The *tert*-butyl hydroperoxide (TBHP) is ca. 6 M in *n*-decane. All the experiments were handled in air unless specific mention. The tpt ligand was synthesized according to previous report.<sup>1</sup> Powder X-ray diffractometry spectroscopy (PXRD) data were collected on a Rigaku Smartlab X-ray diffractometer with CuK $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). XPS measurements were recorded on powder sample using Kratos AXIS ULTRABLD analyzer. Thermogravimetric Analysis (TGA) was conducted on Mettler-Toledo TGA/DSC 1 analyzer in the temperature range of 25 °C to 800 °C under the flowing N<sub>2</sub>. The temperature is increasing at 10 °C/min. Infrared spectra were collected on a Thermo Fisher Nicolet 6700 FT-IR spectrometer using ATR (Attenuated Total Reflectance) method. GC-MS were taken at Thermo Trace 1300 gas chromatograph mass spectrometer and a TR-5MS column (0.25 mm  $\times$  30 m, Film: 0.25  $\mu$ m). Gas adsorption measurement was conducted by using Micromeritics ASAP 2020 Plus HD88 at Instrument Analysis Center of Xi'an Jiaotong University. Cyclic voltammetry (CV) experiments were performed in a three-electrode system at an electrochemical station (CHI 660D). Elemental analyses (C, H and N) were performed on a Vario MICRO cube elemental analyzer.

### Magnetic Measurements

Dc susceptibility measurements were collected in the temperature range 2–300 K. Dc magnetization measurements were obtained in the temperature range 2–5 K under dc fields up to 7 T. Diamagnetic corrections were calculated from Pascal constants and applied to all the constituent atoms and sample holder.

### X-ray Structure Determination.

Crystal data was collected on a Bruker Apex CCD area-detector diffractometer using MoK $\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) radiation. The structures were solved using direct methods and refined with a full-matrix

least-squares technique using OLEX2 program package.<sup>2</sup> Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The hydrogen atoms were generated geometrically. The guest molecules are not well defined. CCDC-1559010 **1** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

### Synthesis of **1**

In a 15 mL Teflon-lined stainless steel reactor,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (125 mg, 0.50 mmol), bdc (benzene-1,4-dicarboxylate) (120 mg, 0.50 mmol) and tpt (2,4,6-tri(4-pyridinyl)-1,3,5-triazine, 100 mg, 0.32 mmol) were dissolved in 11 mL DMF/EtOH (1:1 in v/v), then the tube was capped and heated at 130 °C for 48 hours. After cooling down to room temperature in 12 hours, reddish orange block crystals suitable for single-crystal analysis were obtained. (95 mg, 57.0 % based on Co). Anal. Calcd (%) for **1**: C, 48.26; H, 4.35; N, 10.42. Found: C, 50.01; H, 4.63; N, 10.61.

### Activation

The as-synthesized **1** was soaking in acetone for 24 hours and subsequently treating at 130 °C for 12 hours.

### Oxidation of cyclic alkene

To a mixture of cyclic alkene (18 mmol), TBHP (3 mL) and 1,2,4-trichlorobenzene (18 mmol), catalyst **1** (0.05 mmol, based on  $\text{Co}_3$  SBU) was added. The reaction was stirred at 70 °C and small amount of sample (ca. 50  $\mu\text{L}$  each time) was taken out at certain time, which was further filtered with 0.22  $\mu\text{m}$  nylon filter and diluted with 1 mL AcOEt. The sample was recognized by GC-MS and quantified by GC.

To investigate the stability of the catalyst, the catalyst was filtered from the reaction mixture, washed with AcOEt and air dried before reuse. After 4 runs of catalysing, the catalyst was collected and tested by PXRD to confirm the structural completeness.

The oxidation of cyclohexene using O<sub>2</sub> as oxidant was carried out with an oxygen ballon (1 bar O<sub>2</sub>). To make a fair comparison, the mixture of cyclohexene (18 mmol), catalyst **1** (0.05 mmol, based on Co<sub>3</sub> SBU) and 1,2,4-trichlorobenzene (18 mmol) was also stirred at 70 °C for 24 hours. The analysis of cyclohexenyl hydroperoxide was conducted by iodometric titration: after reaction, the mixture was filtered and weighed. Then the mixture reacted with excess amount of KI in the present of acetic acid. A colour change from colourless to brown was observed. Then the mixture was titrated by 0.1 mol/L NaS<sub>2</sub>O<sub>4</sub> using starch as indicator. Other products were quantified by GC.

### Cyclic voltammetry (CV) measurement

A three-electrode system was used to invest the electrochemical property of **1**. The reference electrode was Ag/AgCl in saturated KCl, and the counter electrode was platinum wire. The catalyst **1** (5 mg) was dispersed in the mixture of 1 mL of CH<sub>3</sub>CH<sub>2</sub>OH and 50 µL Nafion and subsequently loaded on the carbon cloth and dried under the infrared light source, which was used as the working electrode. The CV measurement was conducted in 0.1 M NBu<sub>4</sub>PF<sub>6</sub> in degassed CH<sub>3</sub>CN with indicated scan rate.

## 2. X-Ray Crystallography Structure and Data

**Table S1.** Crystal data and structure refinement for **1**.

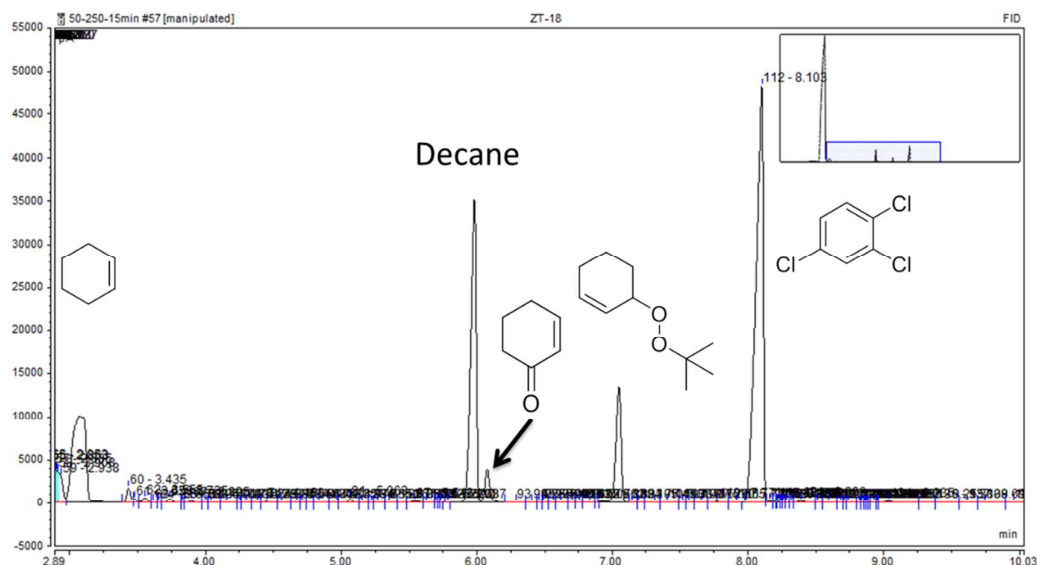
<b>1</b>	
formula	C <sub>42</sub> H <sub>24</sub> Co <sub>3</sub> N <sub>6</sub> O <sub>13</sub>
<i>M</i> /g mol <sup>-1</sup>	997.46
crystal system	Hexagonal
space group	<i>P6<sub>3</sub>/mmc</i>
<i>a</i> , Å	16.929(4)
<i>b</i> , Å	16.929(4)
<i>c</i> , Å	15.306(4)
<i>α</i> , deg	90.00
<i>β</i> , deg	90.00
<i>γ</i> , deg	120.00
<i>V</i> , Å <sup>3</sup>	3799(2)
<i>Z</i>	2
<i>d</i> <sub>cal</sub> /g cm <sup>-3</sup>	0.872
temperature, K	296(2)

$2\theta$ range	2.778 to 49.996
completeness	0.998
residual map, e $\text{\AA}^{-3}$	0.43 and -0.33
Goodness-of-fit <sup>[a]</sup>	1.100
final indices $[I > 2\sigma(I)]$ <sup>[b]</sup>	$R_1 = 0.0299$ , $wR_2 = 0.0799$
$R$ indices (all data)	$R_1 = 0.0386$ , $wR_2 = 0.0855$

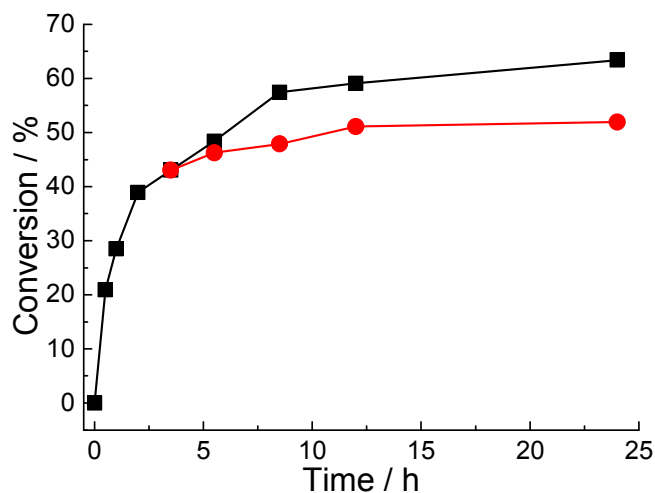
<sup>[a]</sup>  $GOF = [\sum w(F_o^2 - F_c^2)^2 / (n_{obs} - n_{param})]^{1/2}$ .

<sup>[b]</sup>  $R_1 = ||F_o| - |F_c|| / \sum |F_o|$ ,  $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$ .

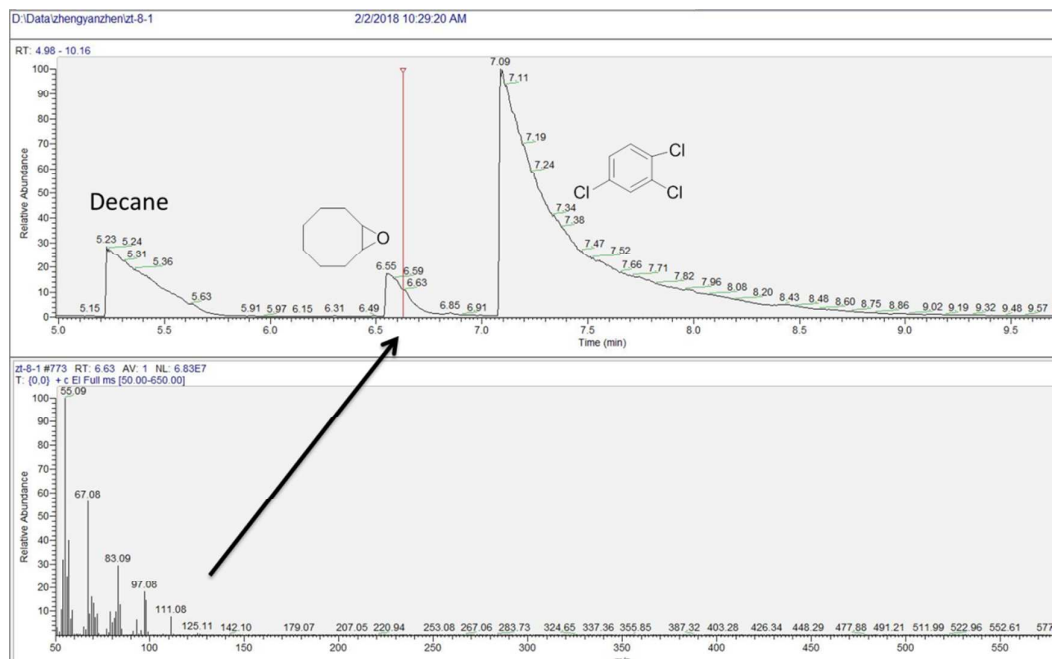
### 3. Catalytic Property



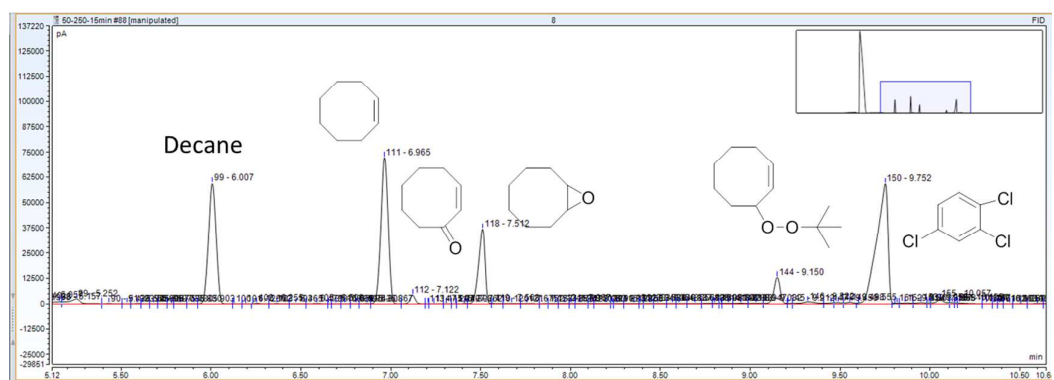
**Figure S1.** The GC spectrum for the first run using TBHP as oxidant.



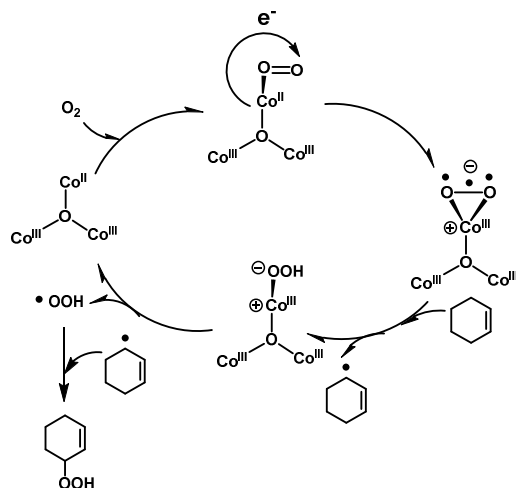
**Figure S2.** The hot filtration test for **1** using TBHP as oxidant.



**Figure S3.** The GCMS spectrum for the oxidation of cyclooctene using TBHP as oxidant, noting the formation of epoxide.

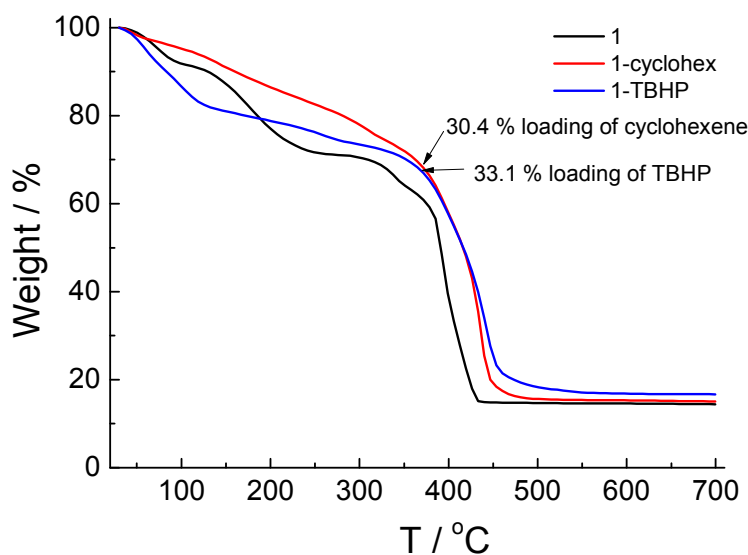


**Figure S4.** The GC spectrum for the oxidation of cyclooctene using TBHP as oxidant.



**Scheme S1** The mechanism of oxidation of cyclohexene catalyzed by **1** using O<sub>2</sub> as oxidant.

#### 4. Thermogravimetric Analysis (TGA)



**Figure S5.** TGA for **1**, **1-cyclohex** and **1-TBHP** (TBHP = *tert*-butyl hydroperoxide).

**Loading of reactant:** the evacuated phase of **1** was soaking into the cyclohexene and TBHP for 24 hours and subsequently tested by TGA. The TGA curves show 30.4 % loading of cyclohexene and 33.1 % loading of TBHP, respectively, confirming the free diffusion of reactant into the pore of **1**. Furthermore, element analyses together with TGA indicate the capacities of **1** towards cyclohexene and TBHP are 5.2 and 5.5 per formula. Anal. Calcd (%) for **1-cyclohex**: C, 61.71; H, 5.37; N, 5.90. Found: C, 62.03; H, 5.51; N, 5.83. Calcd (%) for **1-TBHP**: C, 51.48; H, 5.33; N, 5.62. Found: C, 52.83; H, 5.23; N, 5.77.



## 5. Powder X-ray Diffraction

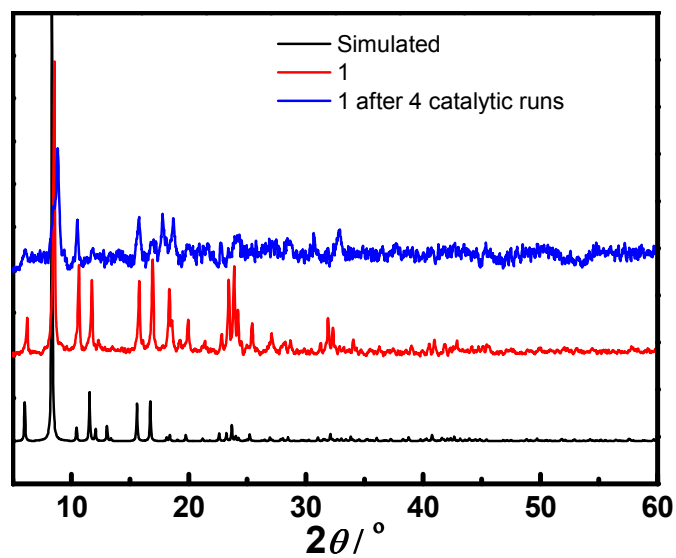


Figure S6. PXRD pattern of **1** and **1** after 4 catalytic runs.

## 6. FT-IR Spectra

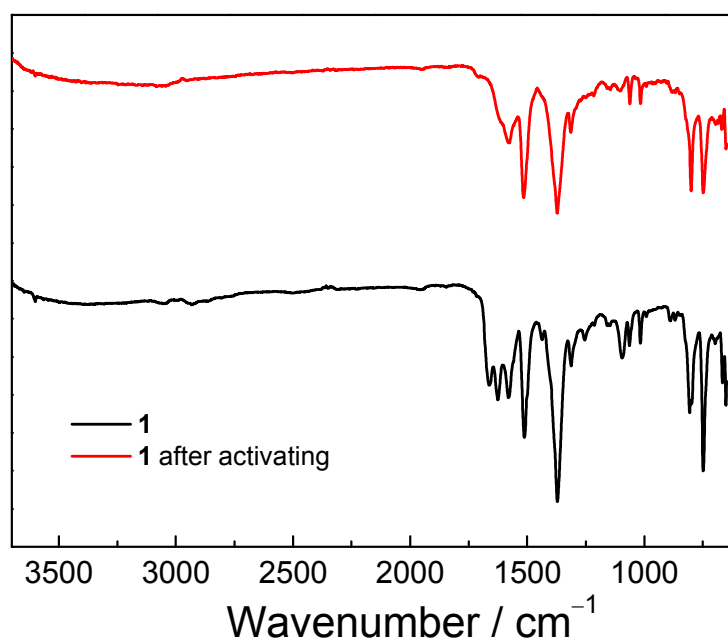
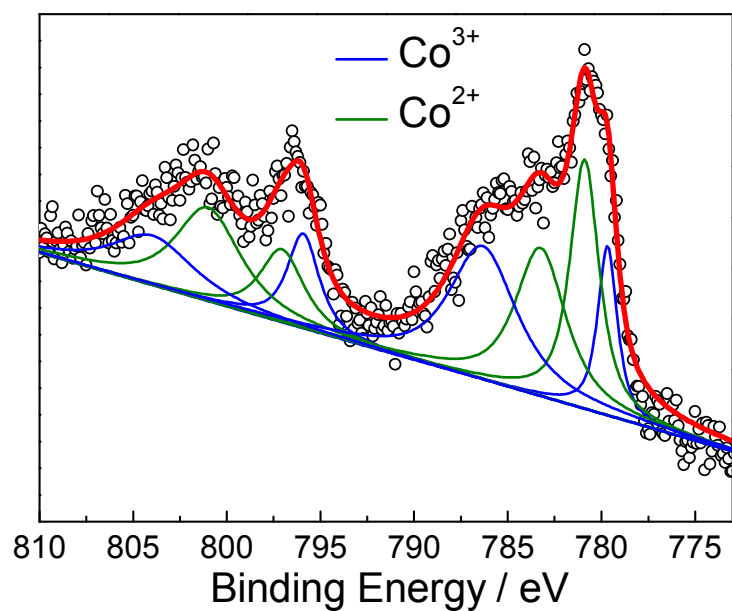
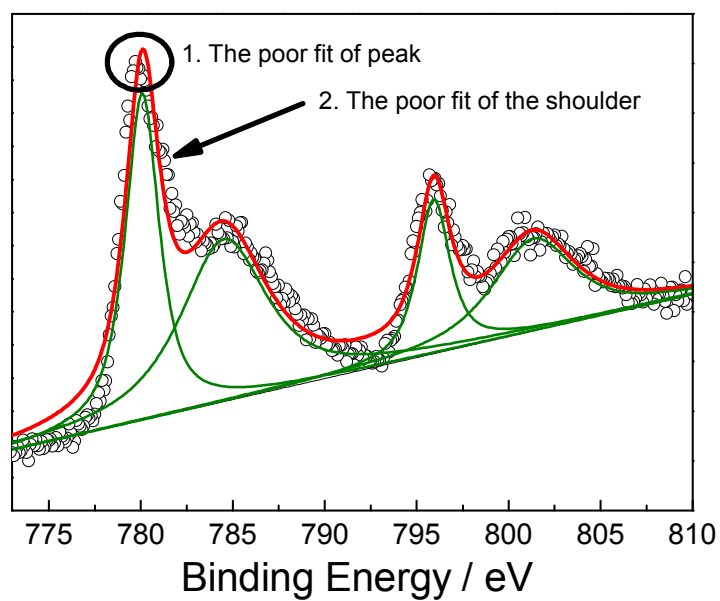


Figure S7. IR spectra of indicated compounds.

## 7. XPS



**Figure S8.** XPS spectrum of **1** after catalyzing.

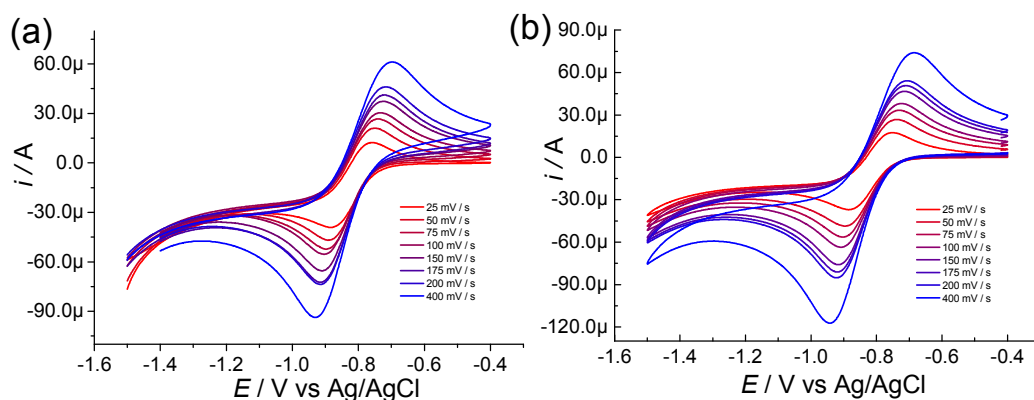


**Figure S9.** The poorly fitted XPS spectrum of **1** with consideration of  $\text{Co}^{\text{II}}$  only.

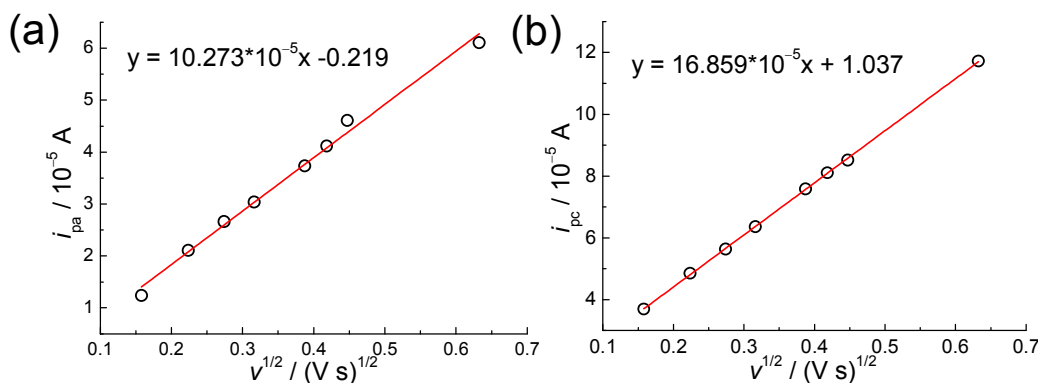
Firstly, we carefully re-analysed the XPS data. According to the comment, we tried to simulate the data with  $\text{Co}^{\text{II}}$  only, as shown in Figure S9, which gave peaks at 780.1 and 795.9 eV for  $2p_{3/2}$  and  $2p_{1/2}$  electrons of the  $\text{Co}^{\text{II}}$  ions, and 784.7 and 801.4 for the  $\text{Co}^{\text{II}}$  satellites. All the peaks are in agree with the reported result and the result seems resonable. However, a carefully review of the data rised some questions: 1. The peak at 780.1 eV was not totally fitted, the real binding energy is smaller than the fitted result. 2. The shoulder of the peak was poorly fitted. The discrepancies in detail may suggest there would be something wrong during the analysis.

Secondly, we simulated the data with the consideration of  $\text{Co}^{\text{II}}$  and  $\text{Co}^{\text{III}}$ , as shown in Figure 2a, the fitting is better than the previous one. 1. The peak at 779.6 was totally fitted with the contribution of  $\text{Co}^{\text{III}} 2p_{3/2}$ , also the shoulder was fitted perfectly owing to the overlap of  $\text{Co}^{\text{III}}$  and  $\text{Co}^{\text{II}} 2p_{3/2}$ . Thus, the sumilation with the conderation of  $\text{Co}^{\text{II}}$  and  $\text{Co}^{\text{III}}$  gave a more reasonable result than  $\text{Co}^{\text{II}}$  only. The addittional disscusion was added to the Supporting Information and highlight.

## 8. CV Measurements



**Figure S10.** Cyclic voltammogram of **1** in 0.1 M  $\text{NBu}_4\text{PF}_6$  in degassed  $\text{CH}_3\text{CN}$  with different scan rates: (a) started from -1.5 V; (b) started from 0.4 V.



**Figure S11.** Extracted (a)  $i_{pa}$  and (b)  $i_{pc}$  vs  $v^{1/2}$  plots and linear fits (red lines) of the data.

Detailed electrochemical measurements were performed to confirm the presence of mixed-valence  $\text{Co}^{\text{II}}\text{Co}^{\text{III}}$  SBUs. The scan range of cyclic voltammogram (CV) measurements was from -1.5 to 0.4 V. When we started from -1.5 V, during the first circle, the  $\text{Co}^{\text{II}}$  in  $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}_2(\mu_3\text{-O})]$  was oxidized to  $\text{Co}^{\text{III}}$  and generated  $[\text{Co}^{\text{III}}_3(\mu_3\text{-O})]$  at -0.4 V, and in the following circles, the trimer was no more mixed-valence. In a similar way, when we started from -0.4 V, during the first circle, the  $\text{Co}^{\text{III}}$  ions in the  $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}_2(\mu_3\text{-O})]$  were reduced to  $\text{Co}^{\text{II}}$  ions to generate  $[\text{Co}^{\text{II}}_3(\mu_3\text{-O})]$  at -1.5 V, from which point the SBUs were no longer mixed-valence and normal redox processes happened. Since the first circle is critical for the chemical evolutions for the mixed-valence SBUs, a detailed discussion based on the first circle was conducted.

As shown in Figure S10, with the scan rates increase, the peak currents of anode and cathode  $i_{pa}$  and  $i_{pc}$  increase. As described by the Randles-Sevcik equation (eq S1):

$$i_p = (2.69 \times 10^5)n^{3/2}AD_0^{1/2}C_0v^{1/2} \quad \text{eq S1}$$

where  $n$  is number of electrons transferred in the redox event,  $A$  is electrode area,  $D$  is diffusion coefficient,  $C$  is concentration of the substance and  $v$  is scan rate, the  $i_p$  increases linearly with  $v^{1/2}$ . Thus we extracted the  $i_{pa}$  and  $i_{pc}$  from Figure S11a and S11b respectively (Figure S11), which stands for the processes of oxidation of  $\text{Co}^{\text{II}}$  and reduction of  $\text{Co}^{\text{III}}$  ions, as discussed above. Considering that during the experiment, the parameters  $n$ ,  $A$  and  $D$  are the same, the molar ratio of  $\text{Co}^{\text{II}}$  and  $\text{Co}^{\text{III}}$  can be obtained from the slope value. Thus,  $C_{\text{Co}(\text{II})}/C_{\text{Co}(\text{III})} = 10.273 / 16.860 = 1.7$ , which is in agreement with the formula  $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}_2(\mu_3\text{-O})]$ .

## 9. Reference

1. Li, M. X.; Miao, Z. X.; Shao, M.; Liang, S. W.; Zhu, S. R. Metal-Organic Frameworks Constructed from 2,4,6-Tris(4-pyridyl)-1,3,5-triazine. *Inorg. Chem.* **2008**, *47*, 4481–4489.
2. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339–341.