Supporting Information for:

Mononuclear copper(II)-hydroperoxo complex derived from reaction of copper(I) complex with dioxygen as a model of DβM and PHM

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Table S1. Crystallographic data and refinement parameters for $[Cu^{I}(H_2bppa)]ClO_4 \cdot 0.5EtOH$

Complex	$[Cu^{I}(H_2bppa)]ClO_4 \cdot 0.5EtOH$
Empieical Formula	$C_{29}H_{36}ClCuN_6O_{6.5}$
Formula Weight	671.64
Crystal Color	red, block
Crystal Dimensions / mm	0.20×0.20×0.10
Crystal System	triclinic
Space Group	P-1 (#2)
a / Å	9.973(5)
b / Å	12.38(3)
c / Å	14.08(3)
α / deg	112.72(13)
β / deg	91.375(9)
γ / deg	98.20(4)
Cell Volume / Å^3	1581(5)
Z value	2
Dcalc / gcm^{-3}	1.413
F(000)	702.00
Radiation	Mo K_α (λ =0.71070 Å)
Detectometer	Rigaku/MSC mercury CCD
T/℃	-100.0
2θ max /deg	55.0
No.of Reflections Measured	Total:12632
No.of Observations	5318
No.of Variables	427
Reflection/Parameter Ratio	12.45
R / *Rw*	0.0597/0.1775
G.O.F	1.001
Max Shift/Error	0.000

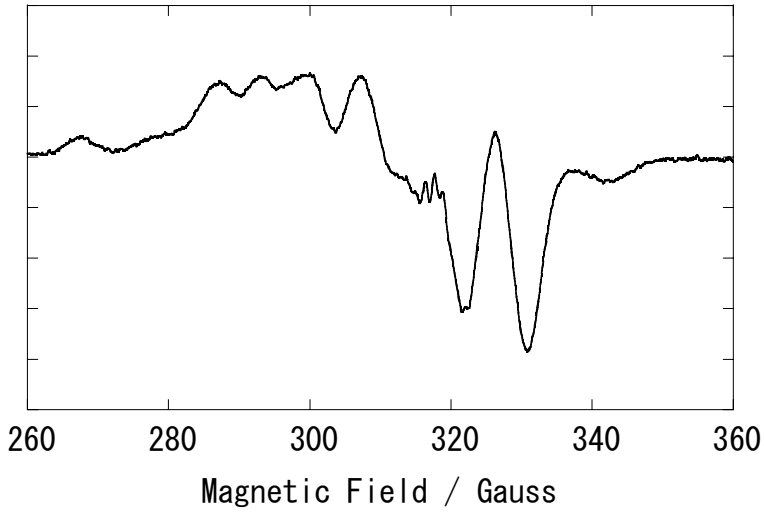


Figure S1. ESR spectrum of the reaction solution of **1** with O_2 in MeOH.

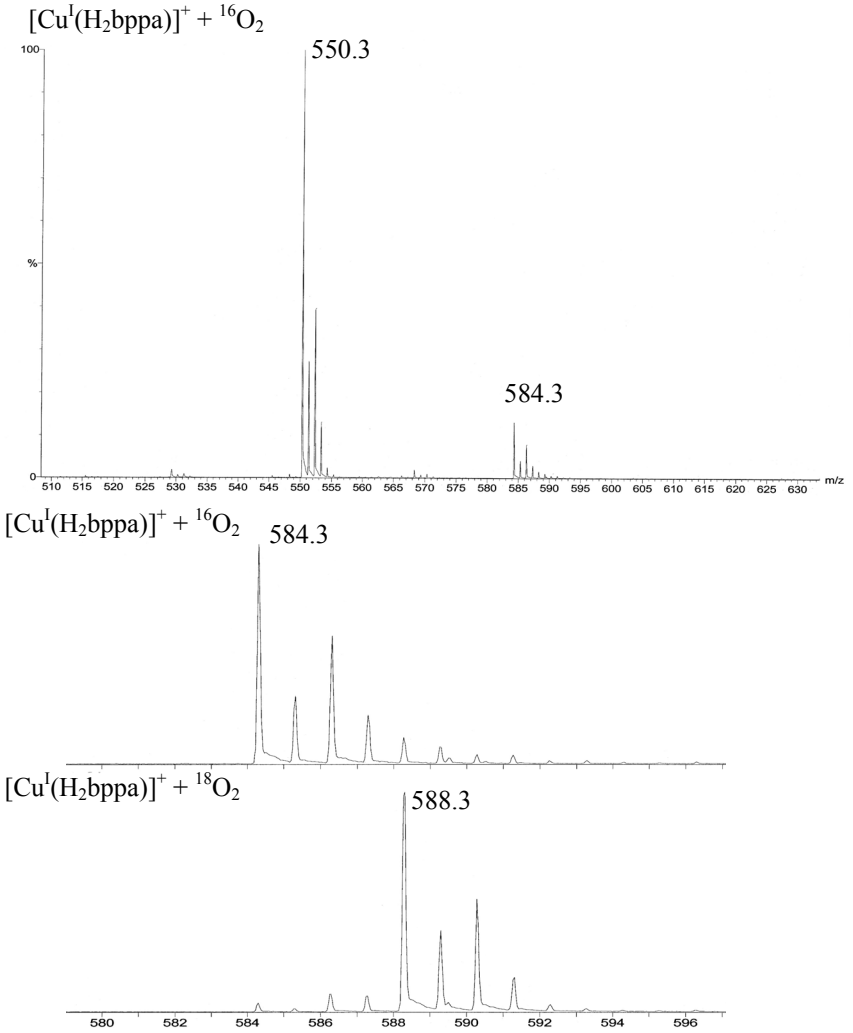
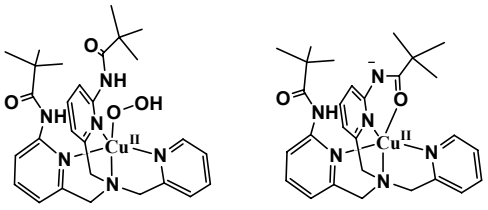


Figure S2. ESI-mass spectra of the reaction solution of **1** with O_2 in acetone.
(top) reaction of **1** with $^{16}O_2$
m/z = 550.3 : $[Cu^{II}(Hbppa)]^+$, m/z = 584.3 : $[Cu^{II}(H_2bppa)(^{16}O^{16}OH)]^+$
(bottom) isotope shift of the reaction of **1** with $^{18}O_2$
m/z = 588.3 : $[Cu^{II}(H_2bppa)(^{18}O^{18}OH)]^+$



$[Cu^{II}(H_2bppa)(OOH)]^+$ $[Cu^{II}(Hbppa)]^+$

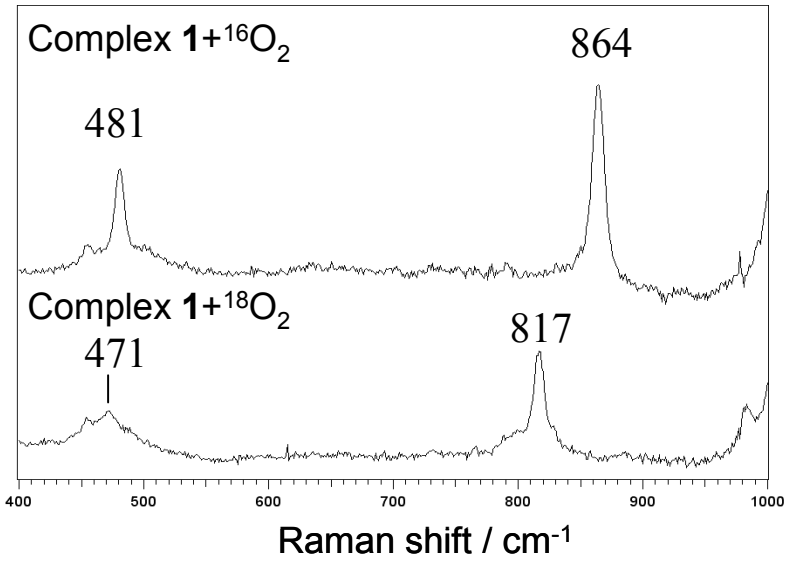


Figure S3. Resonance Raman spectra of the reaction solution of **1** with O_2 in MeOH.
(top) reaction of **1** with $^{16}O_2$
$\nu(Cu\text{-}^{16}O) = 481\ cm^{-1}$, $\nu(^{16}O\text{-}^{16}O) = 861\ cm^{-1}$
(bottom) reaction of **1** with $^{18}O_2$
$\nu(Cu\text{-}^{18}O) = 471\ cm^{-1}$, $\nu(^{18}O\text{-}^{18}O) = 817\ cm^{-1}$

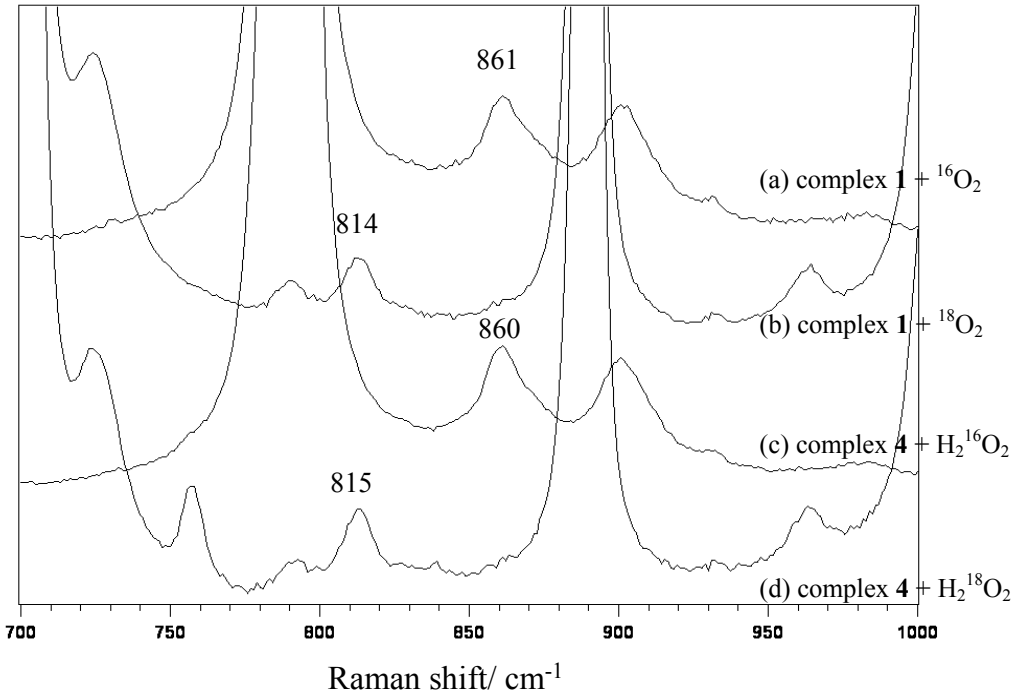


Figure S4. Comparison of resonance Ramam spectra of the reaction of (**1** + O_2) system with that of ($[Cu^{II}(Hbppa)]^+ + H_2O_2$) system.

(a) $[Cu^{I}(H_2bppa)]ClO_4$ (**1**) + $^{16}O_2$ / acetone
$\nu(^{16}O\text{-}^{16}O) = 861\ cm^{-1}$

(b) $[Cu^{I}(H_2bppa)]ClO_4$ (**1**) + $^{18}O_2$ / acetone-d_6
$\nu(^{18}O\text{-}^{18}O) = 814\ cm^{-1}$ ($\Delta\nu = 47\ cm^{-1}$)

(c) $[Cu^{II}(Hbppa)]ClO_4$ (**4**) + $H_2{}^{16}O_2$ / acetone
$\nu(^{16}O\text{-}^{16}O) = 860\ cm^{-1}$

(d) $[Cu^{II}(Hbppa)]ClO_4$ (**4**) + $H_2{}^{18}O_2$ / acetone-d_6
$\nu(^{18}O\text{-}^{18}O) = 815\ cm^{-1}$ ($\Delta\nu = 45\ cm^{-1}$)

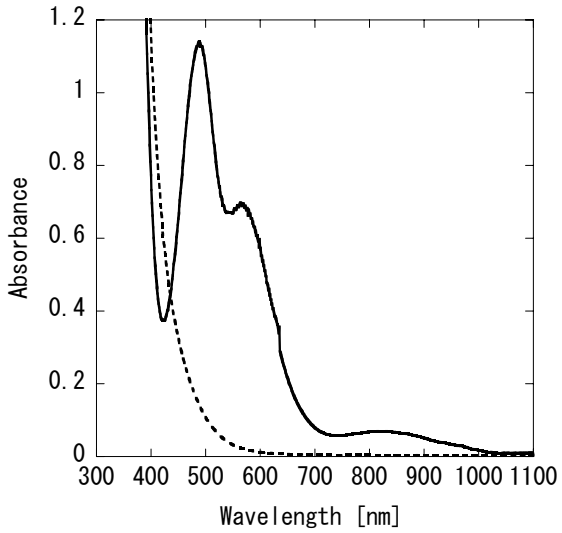


Figure S5. UV-vis spectral change in the reaction of **1** with O_2 in the presence of a large amount of DMPO.

(dotted line) **1** (1 mM) + DMPO (40 mM) / MeOH
(solid line) O_2 bubbling at -78 °C

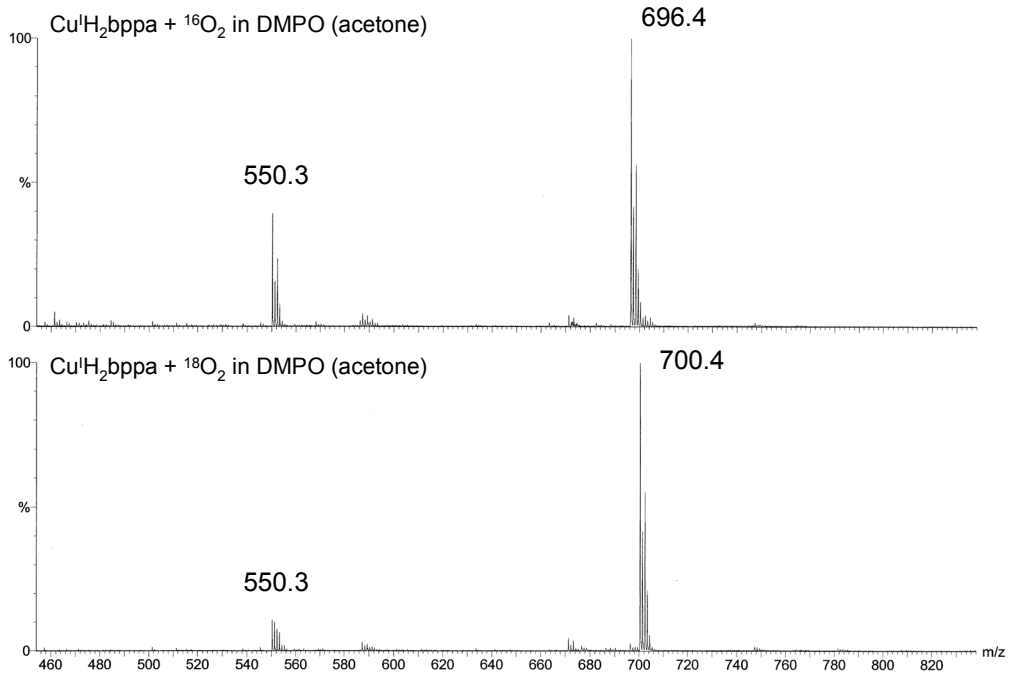


Figure S6(a). ESI-mass spectra of the reaction solution of **1** with O_2 in the presence of a large amount of DMPO.

(top) reaction of **1** + $^{16}O_2$
m/z = 550.3 : $[Cu^{II}(Hbppa)]^+$, 696.4 : $[Cu^{II}(H_2bppa)(^{16}O_2^-)(DMPO)]^+$
(bottom) reaction of **1** + $^{18}O_2$
m/z = 550.3 : $[Cu^{II}(Hbppa)]^+$, 700.4 : $[Cu^{II}(H_2bppa)(^{18}O_2^-)(DMPO)]^+$

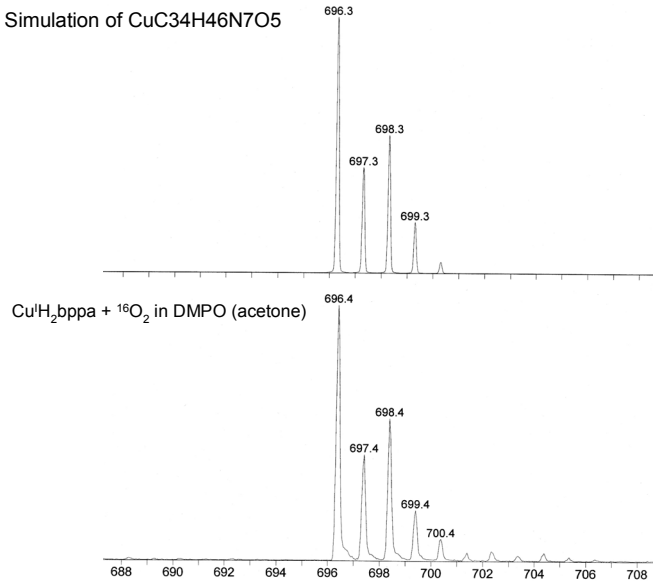


Figure S6(b). Comparison of the ESI-mass spectra of **1** + $^{16}O_2$ and isotope simulation.

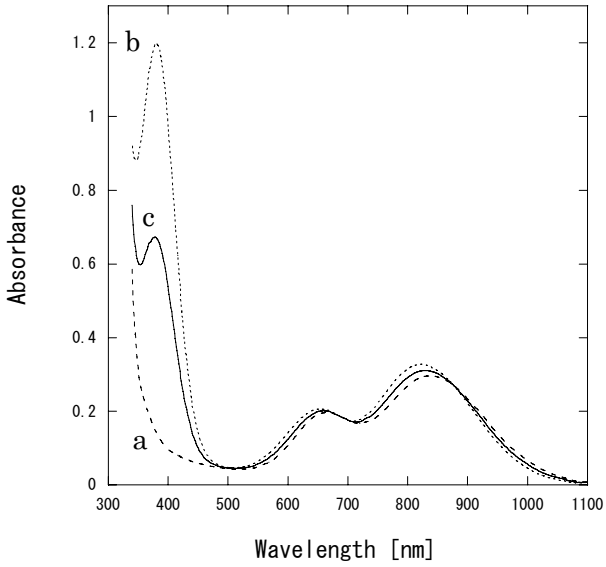


Figure S7. Simulation of spectrum of the reaction mixture after reaction of **1** with O_2.
Spectrum **c** is the sum of the spectra **3** (spectrum **b**) and **4** (spectrum **a**) which is good agreement with the spectrum after reaction of **1** with O_2.
It makes reasonable to consider that the mass balance is about 1:1 (complex **3** : complex **4**) after reaction of **1** with O_2.