Electronic Supplementary Information for Dalton Transactions

Supporting Information for:

H-atom abstraction reaction for organic substrates *via* mononuclear copper(II)-superoxo species as a model of DβM and PHM

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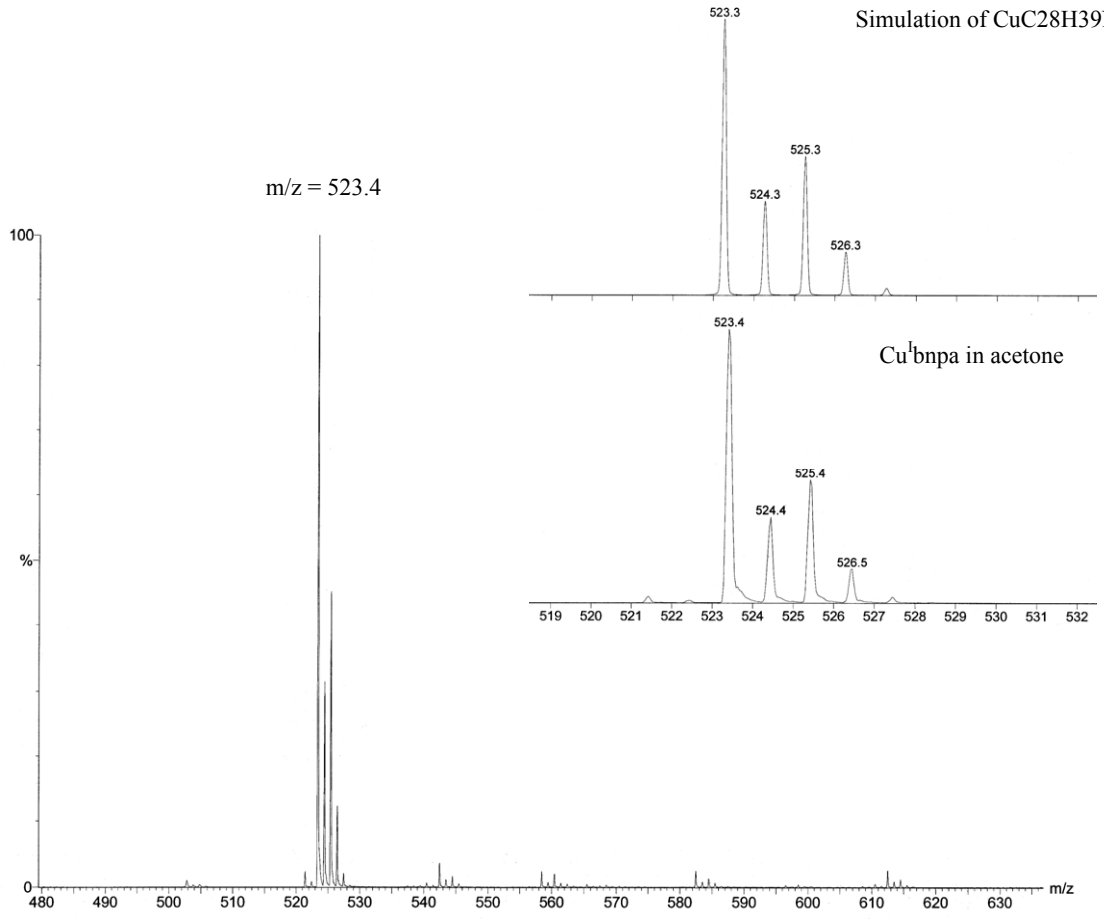
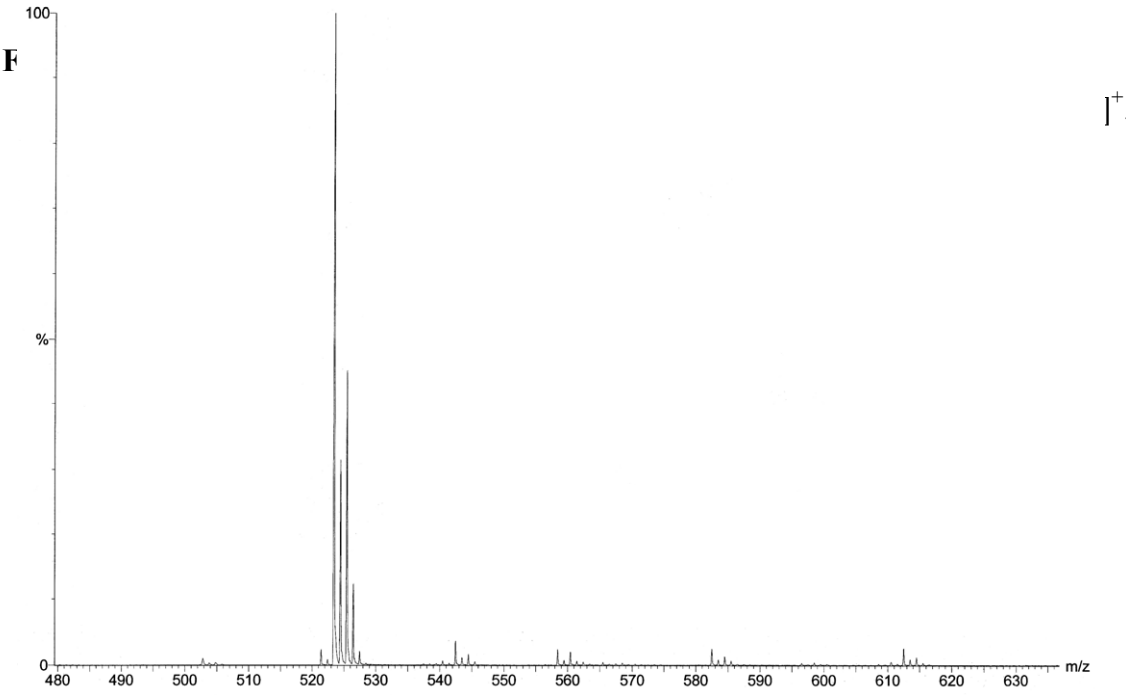
Contents:

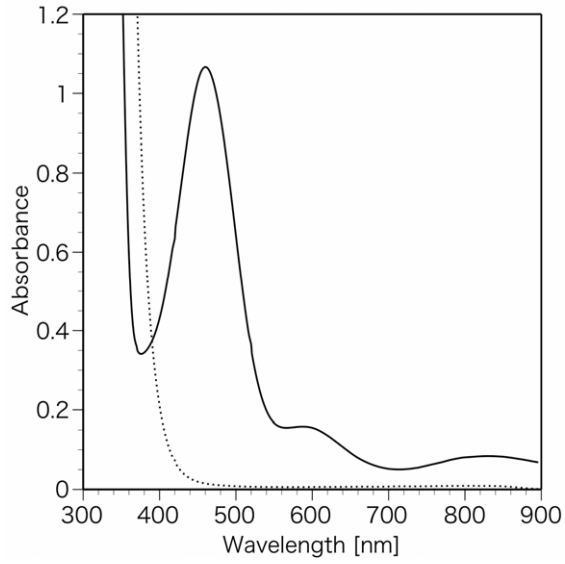

Simulation of CuC28H39N6
523.3
525.3
524.3
526.3
m/z = 523.4
100
%
0
Cu^Ibnpa in acetone
523.4
525.4
524.4
526.5
519 520 521 522 523 524 525 526 527 528 529 530 531 532
480 490 500 510 520 530 540 550 560 570 580 590 600 610 620 630
m/z

F


100
%
0
480 490 500 510 520 530 540 550 560 570 580 590 600 610 620 630
m/z

$]^{+}$.

(a) MeOH solution



(b) THF solution

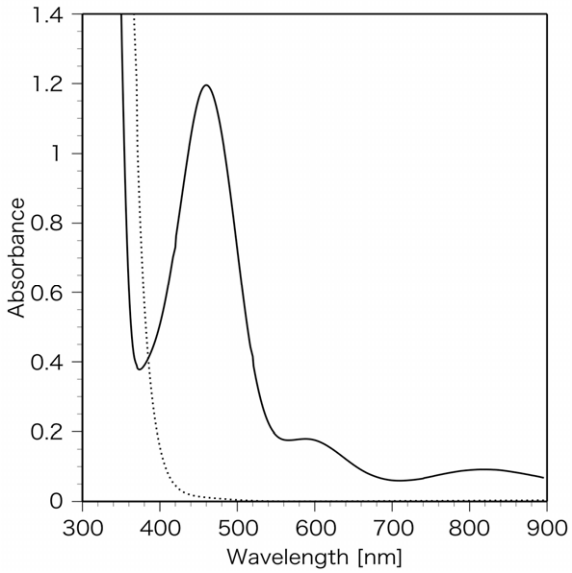


Fig.S2 UV-vis spectral change of the reaction of **1** (0.5 mM) with O_2 in MeOH and THF solutions at -80 ^{o}C.

List of the characteristic LMCT band after bubbling O_2

(a) 460 nm (ε = 4270 $M^{-1}cm^{-1}$), 580 nm (ε = 630 $M^{-1}cm^{-1}$)

(b) 460 nm (ε = 4780 $M^{-1}cm^{-1}$), 580 nm (ε = 720 $M^{-1}cm^{-1}$)

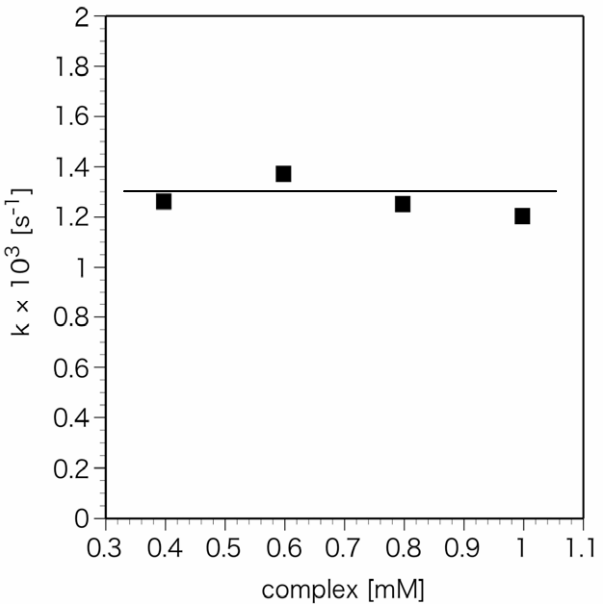


Fig.S3 Plots of decomposition rates (k) vs. concentrations of **1** in acetone at -20 ^{o}C. Decomposition process obeyed first-order kinetics.

$k_1 = 1.26\times10^{-3}$ s^{-1} : complex 0.4 mM

$k_2 = 1.37\times10^{-3}$ s^{-1} : complex 0.6 mM

$k_3 = 1.25\times10^{-3}$ s^{-1} : complex 0.8 mM

$k_4 = 1.20\times10^{-3}$ s^{-1} : complex 1.0 mM

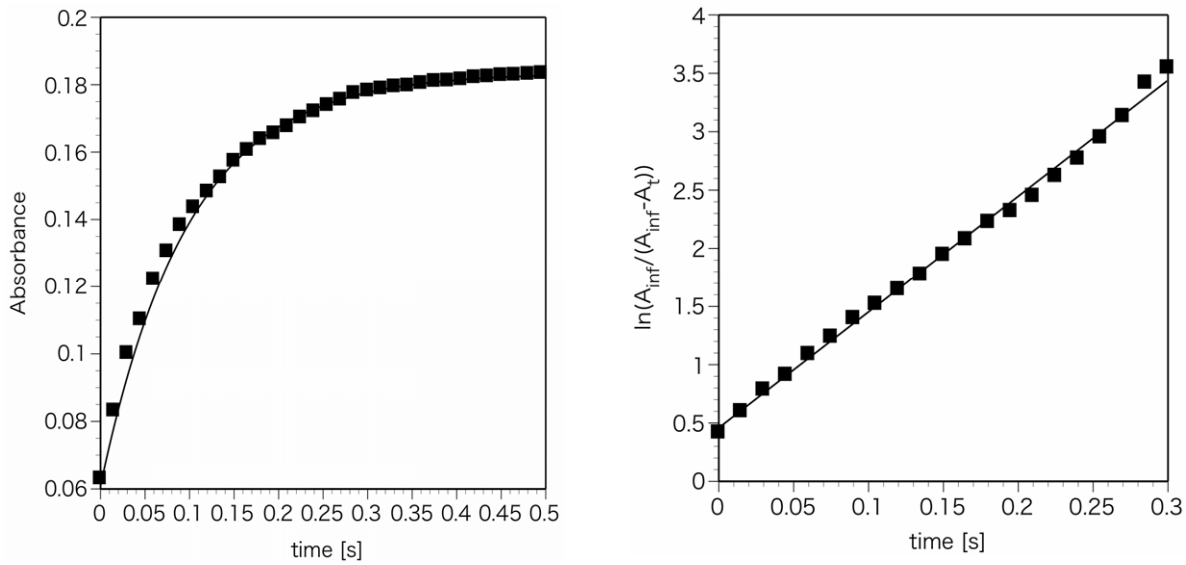


Fig.S4 Estimation of the generation rate for the $[Cu^{II}(bnpa)(O_2^{2-})]^{2+}$ (**2**) in acetone (0.25 mM) at 10 ^{o}C. Time course of the absorption change at 460 nm and it's first-order fitting.

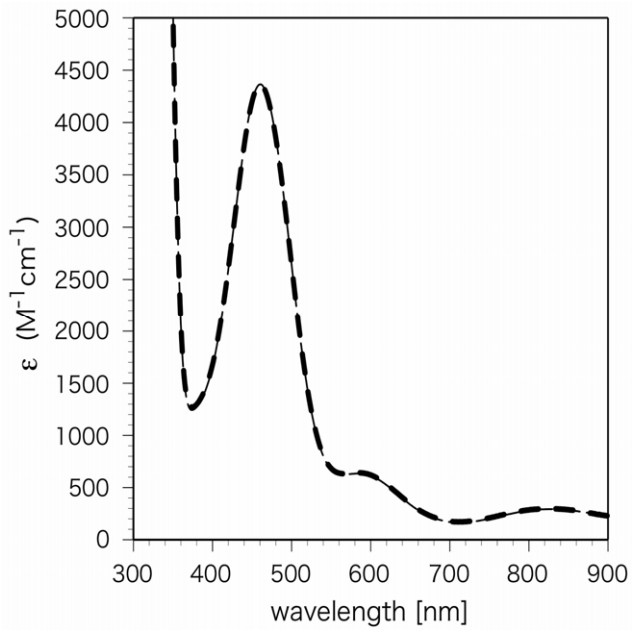


Fig.S5 UV-vis spectral change of the reaction of **2** (0.5 mM) with DMPO (50 mM) in acetone solution at -80 ^{o}C.

(a) solid line : Spectrum of the $[Cu^{II}(bnpa)(O_2^{2-})]^{2+}$ (**2**) after bubbling Ar gas.

(b) dotted line : Spectrum of the solution after adding DMPO.

* Reversibility was not observed by bubbling Ar gas in the solution of **2**.
* Spectral change was not observed by adding DMPO.

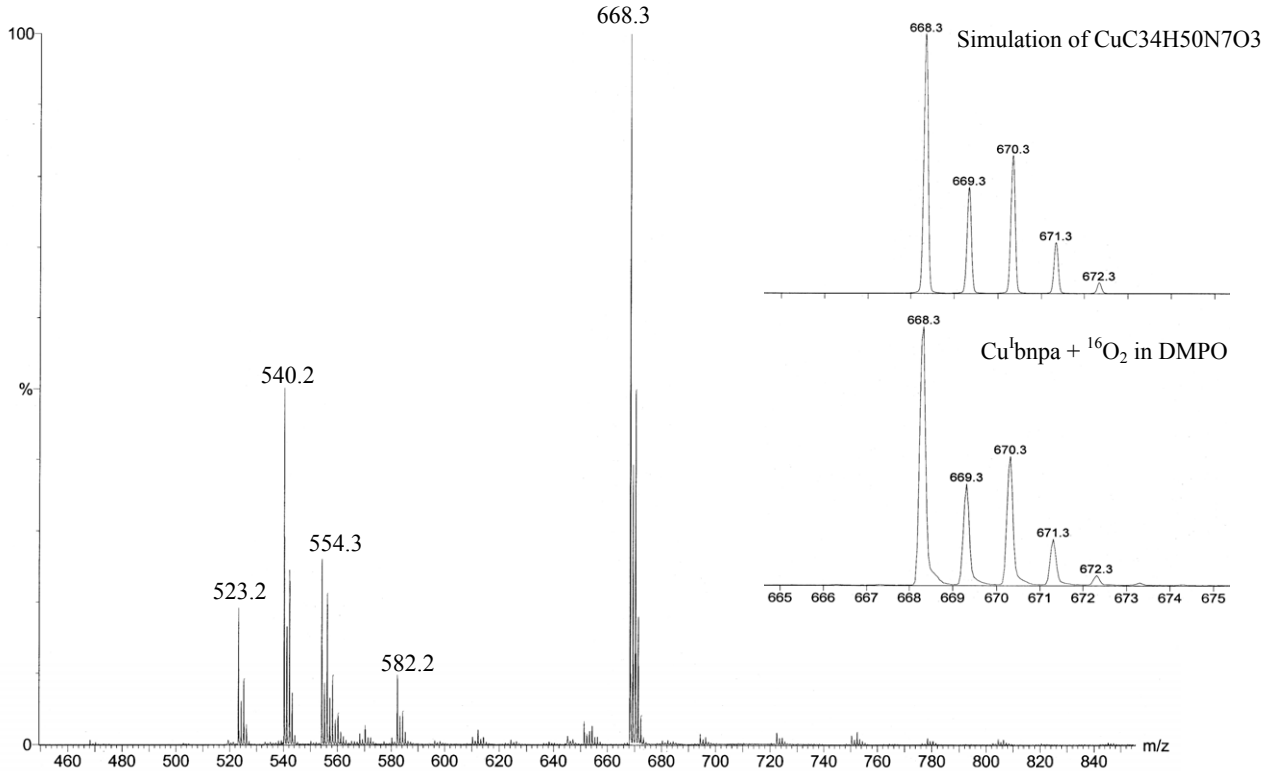


Fig.S6(a) ESI-mass spectra of the reaction solution of **1** with $^{16}O_2$ in the presence of a large excess amount of DMPO in acetone. (inset) Comparison of the parent peak and isotope simulation of $[Cu^{II}(bnpa)(^{16}O_2^{-})(DMPO)]^{+}$.

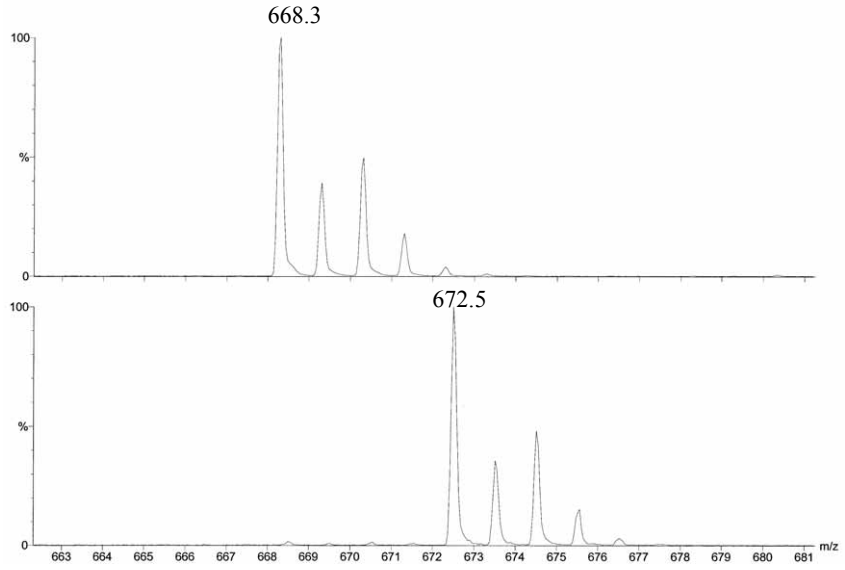


Fig.S6(b) Comparison of the ESI-mass spectra for the reaction solution of **1** with $^{16}O_2$ and $^{18}O_2$ in the presence of a large excess amount of DMPO in acetone. (top) **1** + $^{16}O_2$, (bottom) **1** + $^{18}O_2$

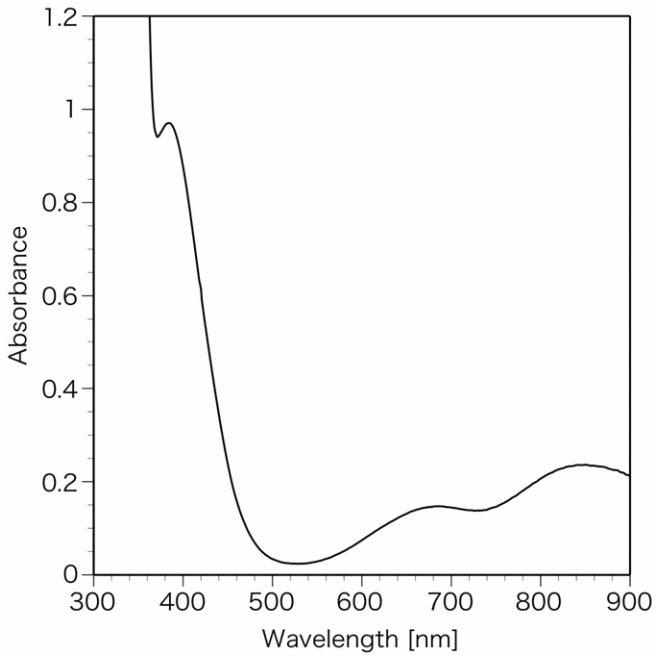


Fig.S7 UV-vis spectrum of $[Cu^{II}(bnpa)(OOH)]^{+}$ (1 mM) prepared by the reaction of $[Cu^{II}(bnpa)]^{+}$ with H_2O_2 (10eq) in acetone solution at -40 ^{o}C.

380 nm (ε = 970 $M^{-1}cm^{-1}$) : LMCT band ($^{-}OOH \rightarrow Cu^{II}$)

680 nm (ε = 147 $M^{-1}cm^{-1}$), 840 nm (ε = 235 $M^{-1}cm^{-1}$) : d-d band

* The formation of $[Cu^{II}(bnpa)(OOH)]^{+}$ was also confirmed from other spectroscopic measurements (ESI-mass, ESR, rRaman).[18]

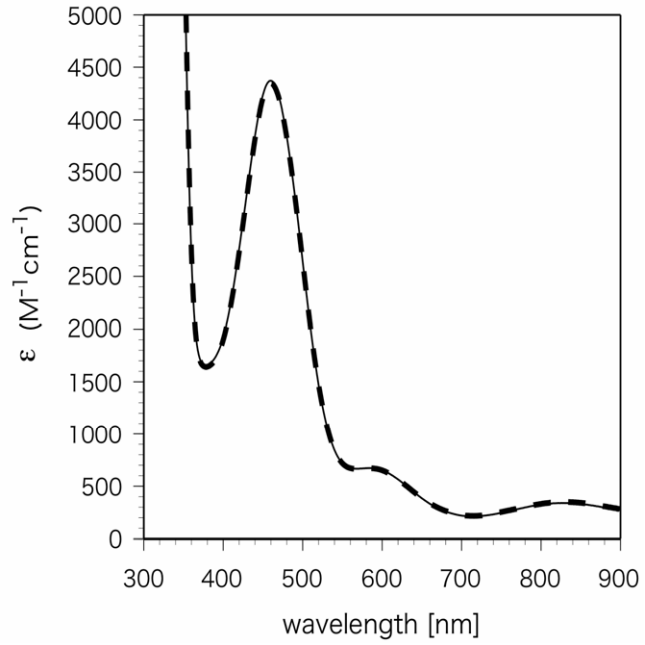


Fig.S8 UV-vis spectral change of the reaction of **2** (0.5 mM) with TEMPO-H (50 mM) in acetone solution at -80 ^{o}C.

(a) solid line : Spectrum of the $[Cu^{II}(bnpa)(O_2^{2-})]^{2+}$ (**2**) after bubbling Ar gas.

(b) dotted line : Spectrum of the solution after adding TEMPO-H.

＊ Spectral change was not observed by adding TEMPO-H.

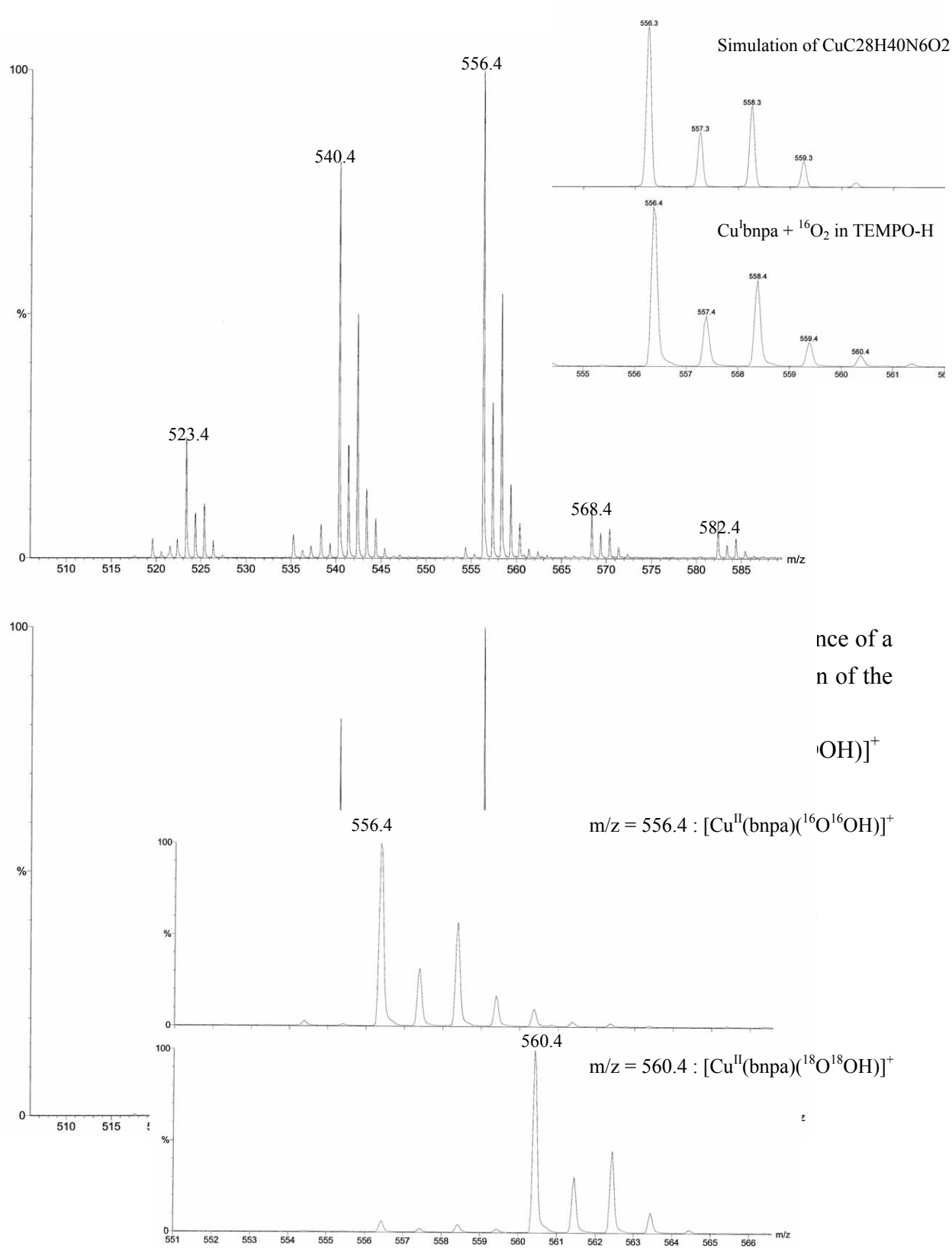


Fig.S9(b) Comparison of the ESI-mass spectra for the reaction solution of **1** with $^{16}O_2$ and $^{18}O_2$ in the presence of a large excess amount of TEMPO-H in acetone. (top) **1** + $^{16}O_2$, (bottom) **1** + $^{18}O_2$

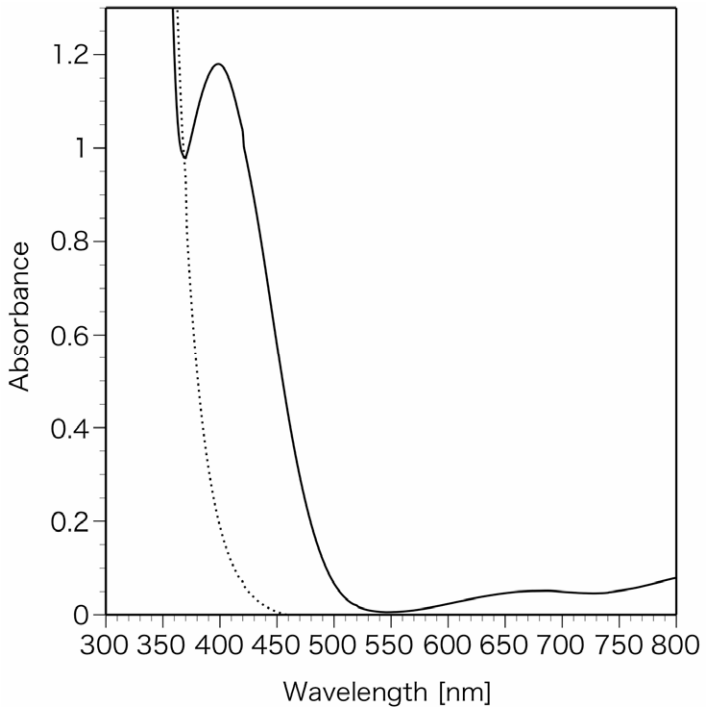


Fig.S10 UV-vis spectral change in the reaction of **1** with O_2 in the presence of a large excess amount of phenylhydrazine in acetone at -80 ^{o}C.
(dotted line) complex **1** (0.5 mM) + phenylhydrazine (100 eq)
(solid line) after O_2 bubbling

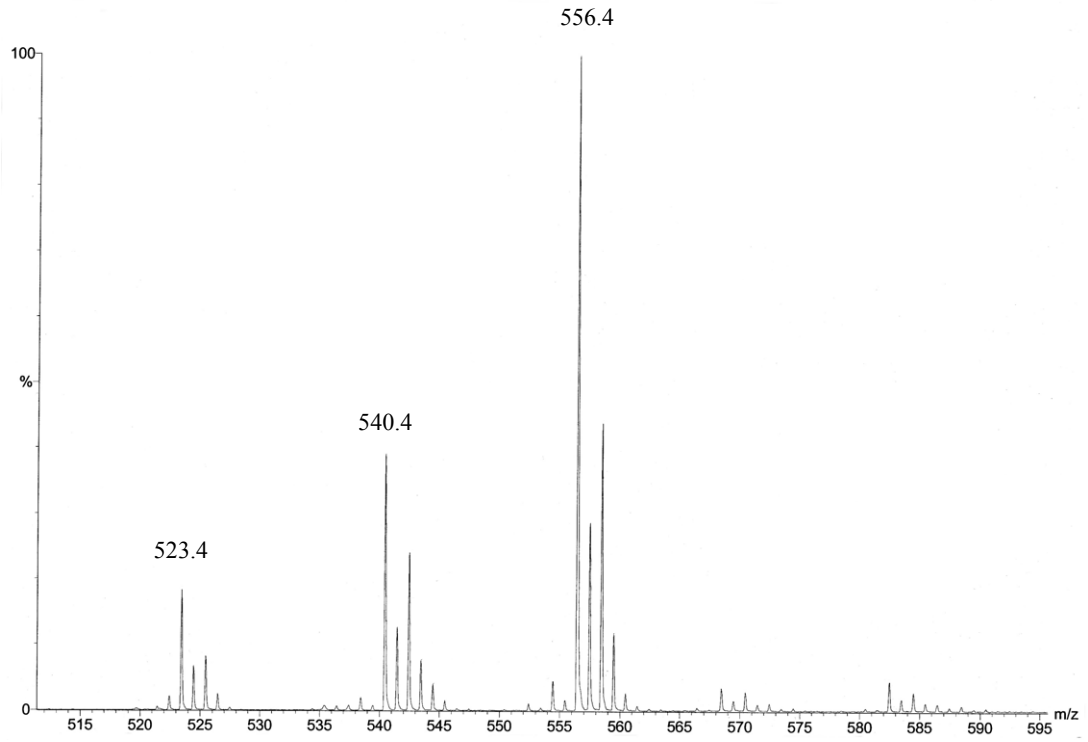


Fig.S11(a) ESI-mass spectra of the reaction solution of **1** with $^{16}O_2$ in the presence of a large amount of phenylhydrazine in acetone.
m/z = 523.4 : $[Cu^{I}(bnpa)]^{+}$, 540.4 : $[Cu^{II}(bnpa)(OH)]^{+}$, 556.4 : $[Cu^{II}(bnpa)(^{16}O^{16}OH)]^{+}$

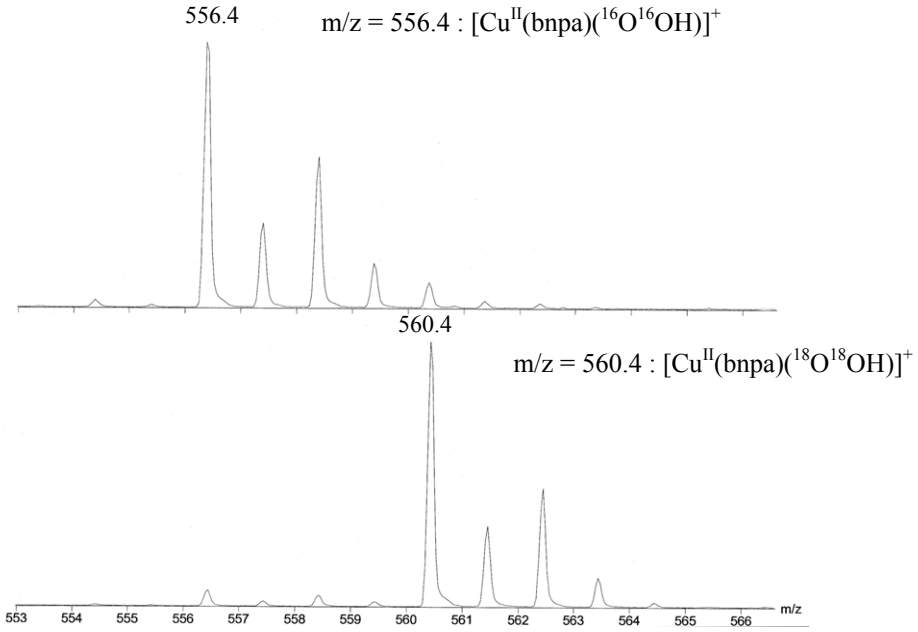


Fig.S11(b) Comparison of the ESI-mass spectra for the reaction solution of **1** with $^{16}O_2$ and $^{18}O_2$ in the presence of a large amount of Phenylhydrazine in acetone. (top) **1** + $^{16}O_2$, (bottom) **1** + $^{18}O_2$