Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Electronic Supplementary Information (ESI)

Self-assembly generation, structural features, and oxidation catalytic properties of new aqua-soluble copper(II)-aminoalcohol derivatives

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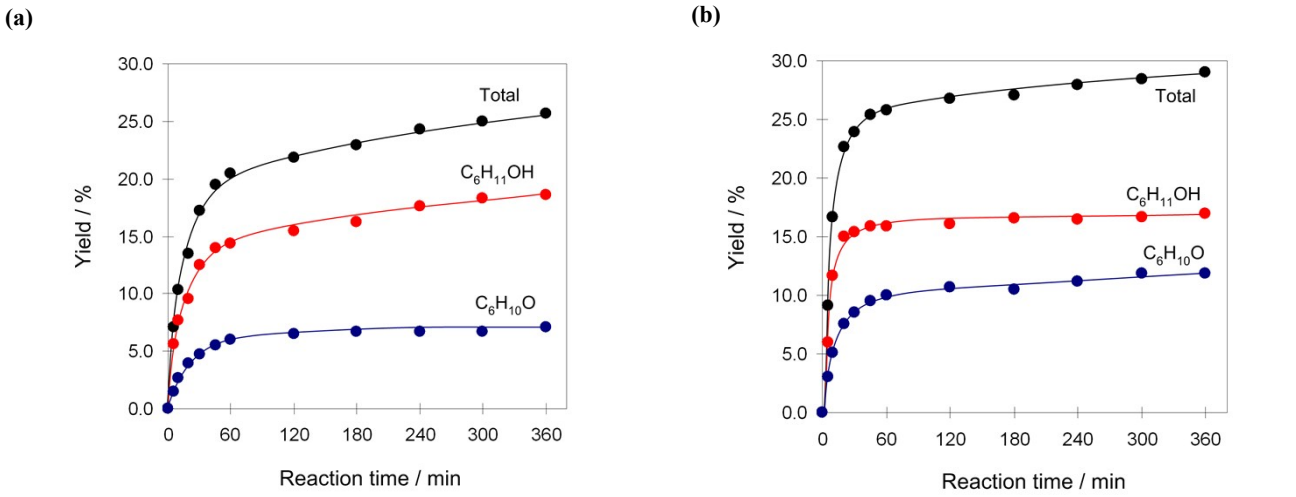


Figure S1. Accumulation of products (cyclohexanol and cyclohexanone) with time in the oxidation of cyclohexane by H_2O_2 catalyzed by **1** (a) and **2** (b). Reaction conditions: C_6H_{12} (2 mmol), catalyst (5-10 μmol), H_2O_2 (10 mmol; added in one portion), 50 °C, CH_3CN (up to 3 mL total volume).

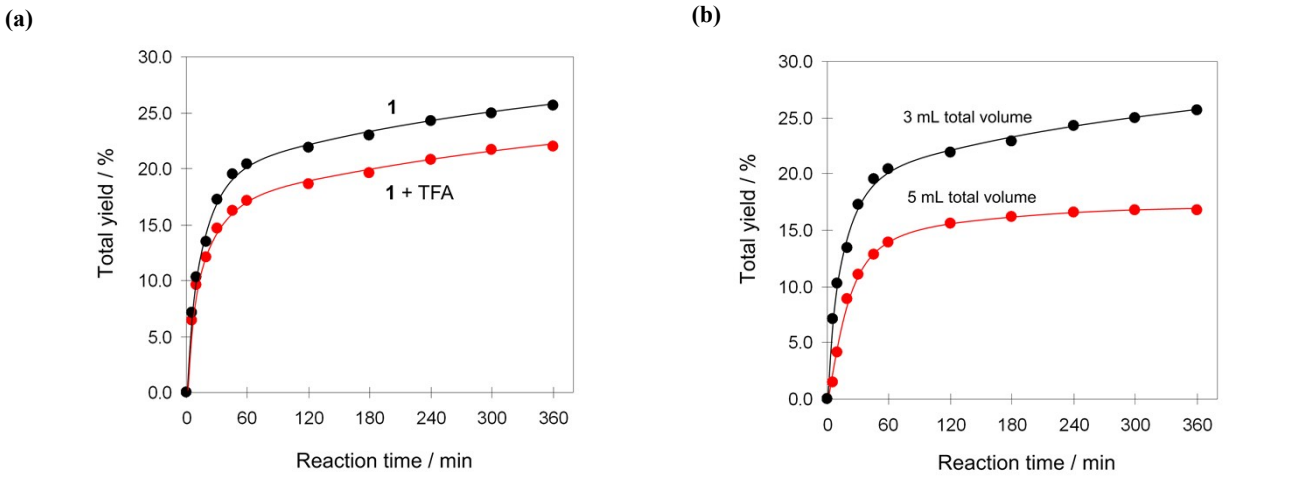


Figure S2. (a) Effect of the trifluoroacetic acid (TFA) addition and (b) effect of total reaction volume (CH_3CN solvent amount) on the total yield of cyclohexanol and cyclohexanone in the oxidation of cyclohexane by H_2O_2 catalyzed by **1**. Reaction conditions: C_6H_{12} (2 mmol), catalyst (5 μmol), TFA (0.05 mmol, added only in (a)), H_2O_2 (10 mmol; added in one portion), 50 °C, CH_3CN (up to 3 mL total volume in (a) and 3 or 5 mL total volume in (b)).

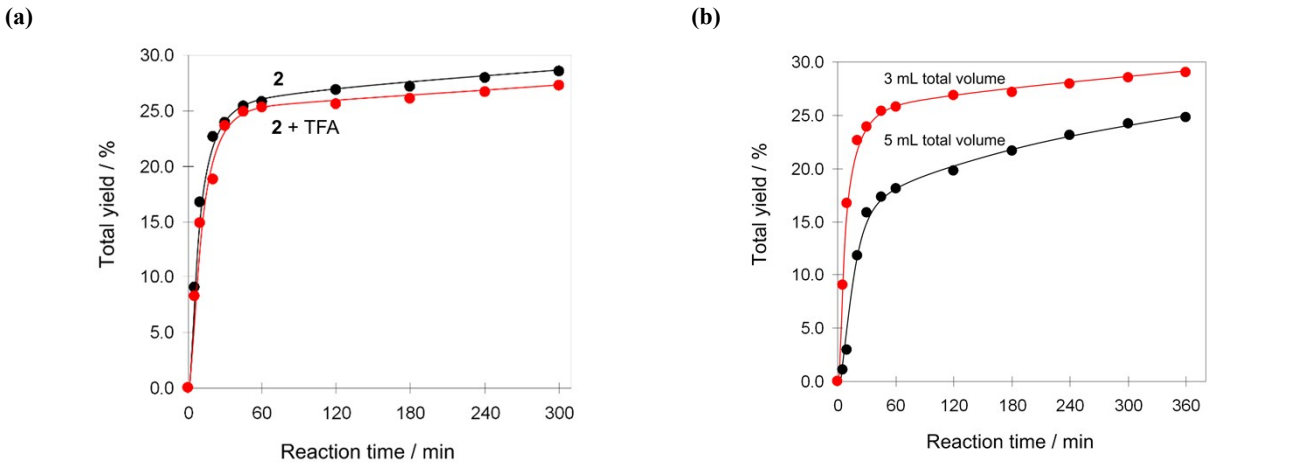


Figure S3. (a) Effect of the trifluoroacetic acid (TFA) addition and (b) effect of total reaction volume (CH_3CN solvent amount) on the total yield of cyclohexanol and cyclohexanone in the oxidation of cyclohexane by H_2O_2 catalyzed by **2**. Reaction conditions: C_6H_{12} (2 mmol), catalyst (10 μmol), TFA (0.05 mmol, added only in (a)), H_2O_2 (10 mmol; added in one portion), 50 °C, CH_3CN (up to 3 mL total volume in (a) and 3 or 5 mL total volume in (b)).

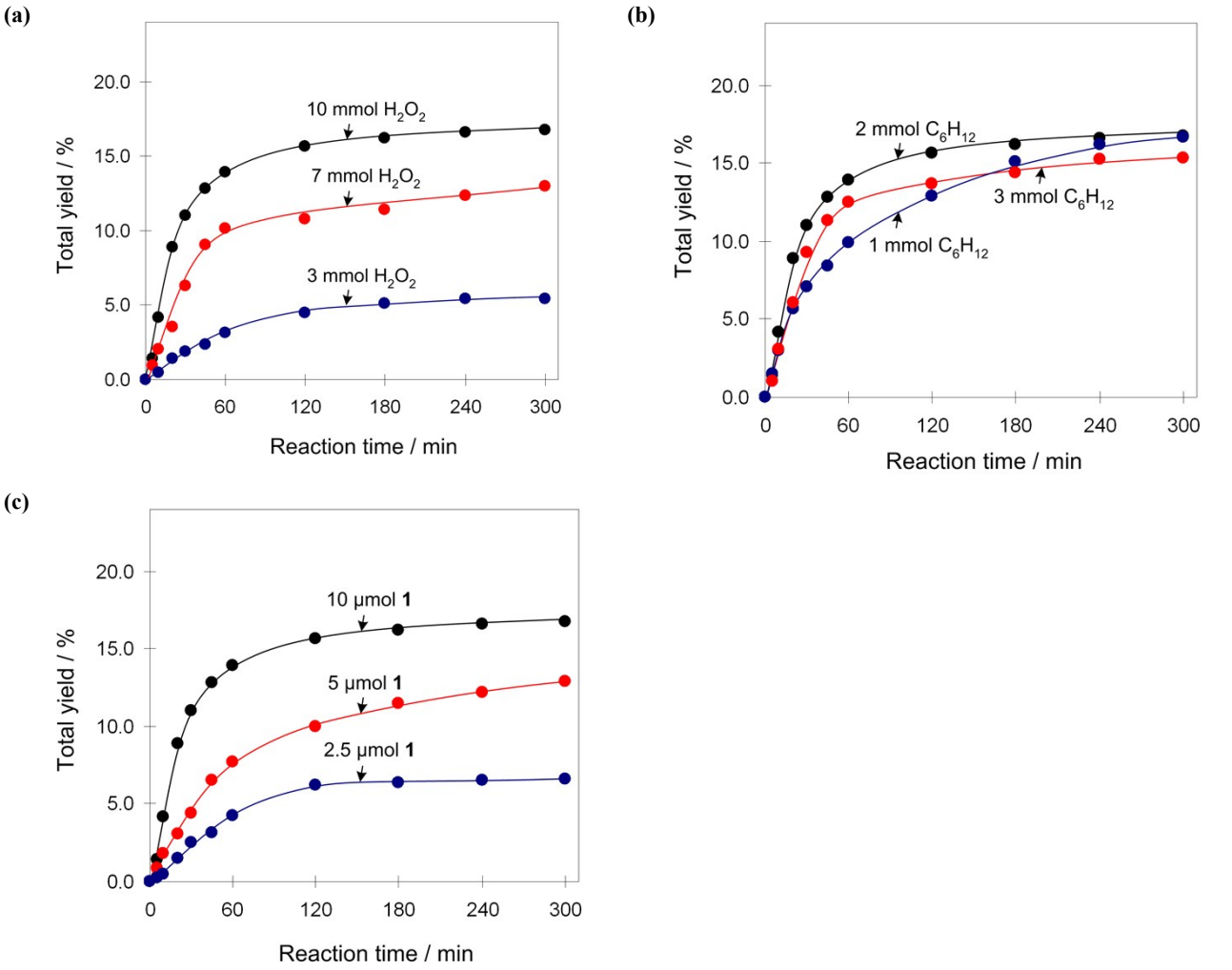


Figure S4. Effect of H_2O_2 (a), C_6H_{12} (b), and catalyst (c) amount on the total yield of cyclohexanol and cyclohexanone in the oxidation of cyclohexane by H_2O_2 catalyzed by **1**. Reaction conditions: C_6H_{12} (2 mmol in (a, c); 1-3 mmol in (b)), catalyst (5 μmol in (a,b), 2.5–10 μmol in (c)), H_2O_2 (added in one portion: 3.0–10 mmol in (a), 10 mmol in (b,c)), 50 °C, CH_3CN (up to 5 mL total volume).

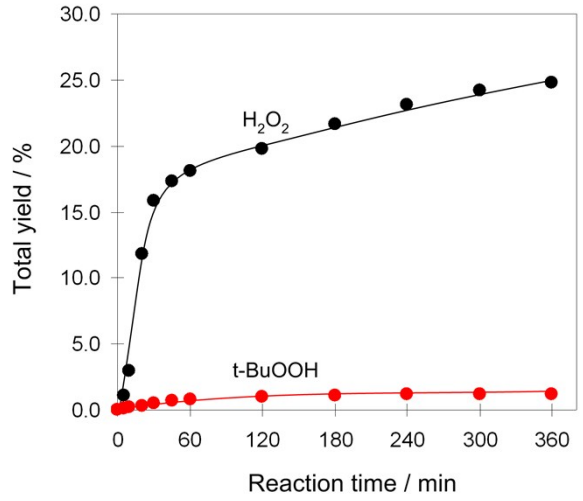


Figure S5. Effect of the oxidant type on the total yield of cyclohexanol and cyclohexanone in the oxidation of cyclohexane catalyzed by **2**. Reaction conditions: C_6H_{12} (2 mmol), catalyst (10 μmol), H_2O_2 or *t*-BuOOH (10 mmol; added in one portion), 50 °C, CH_3CN (up to 5 mL total volume).

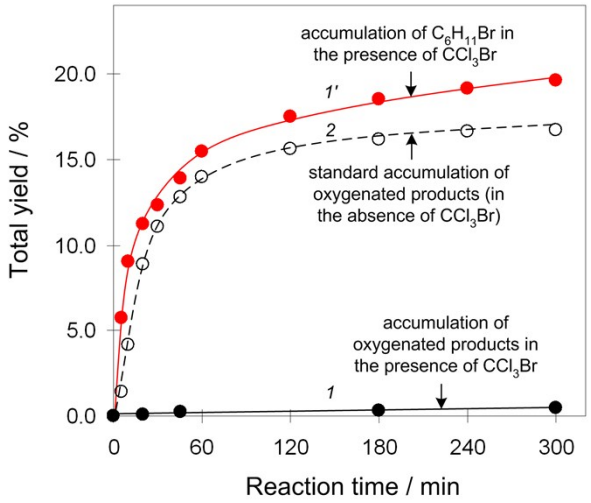
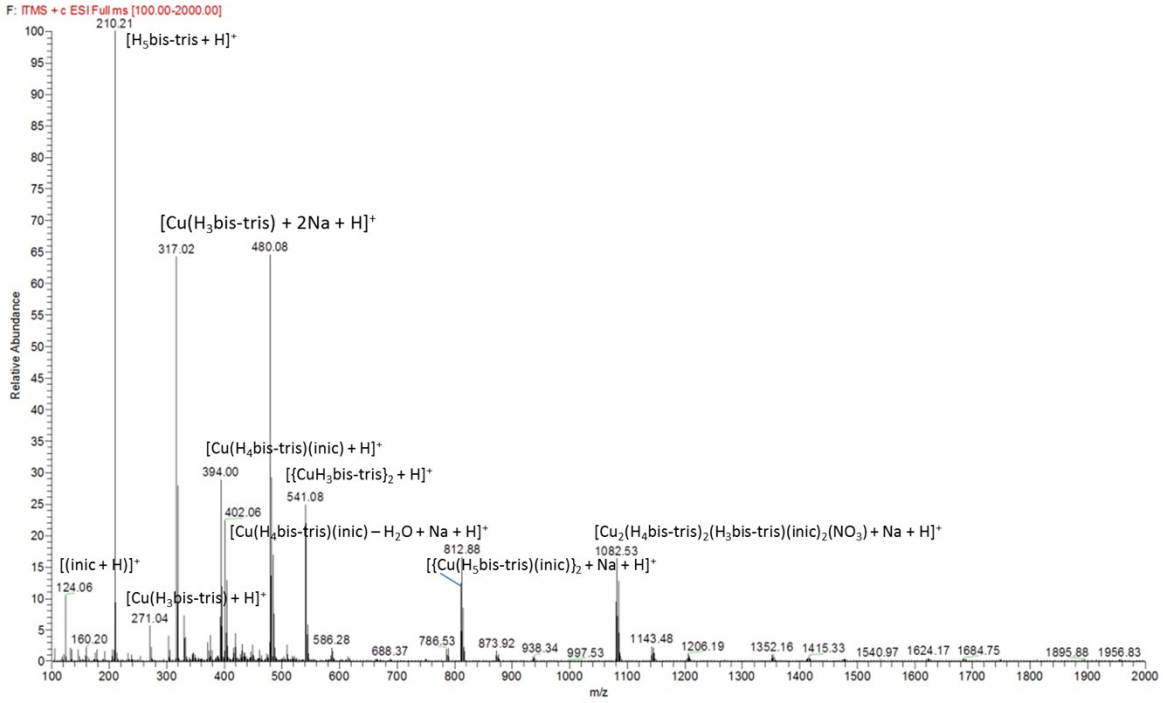


Figure S6. Effect of the CCl_3Br addition on the total yield of cyclohexanol and cyclohexanone (curve *1*) and formation of cyclohexylbromide (curve *1´*) in the oxidation of cyclohexane by H_2O_2 catalyzed by **1**. Reaction conditions: C_6H_{12} (2 mmol), CCl_3Br (2 mmol), catalyst (5 μmol), H_2O_2 (10 mmol; added in one portion), 50 ºC, CH_3CN (up to 5 mL total volume). Curve *2*: reaction in the absence of CCl_3Br under the same conditions.

a)



b)

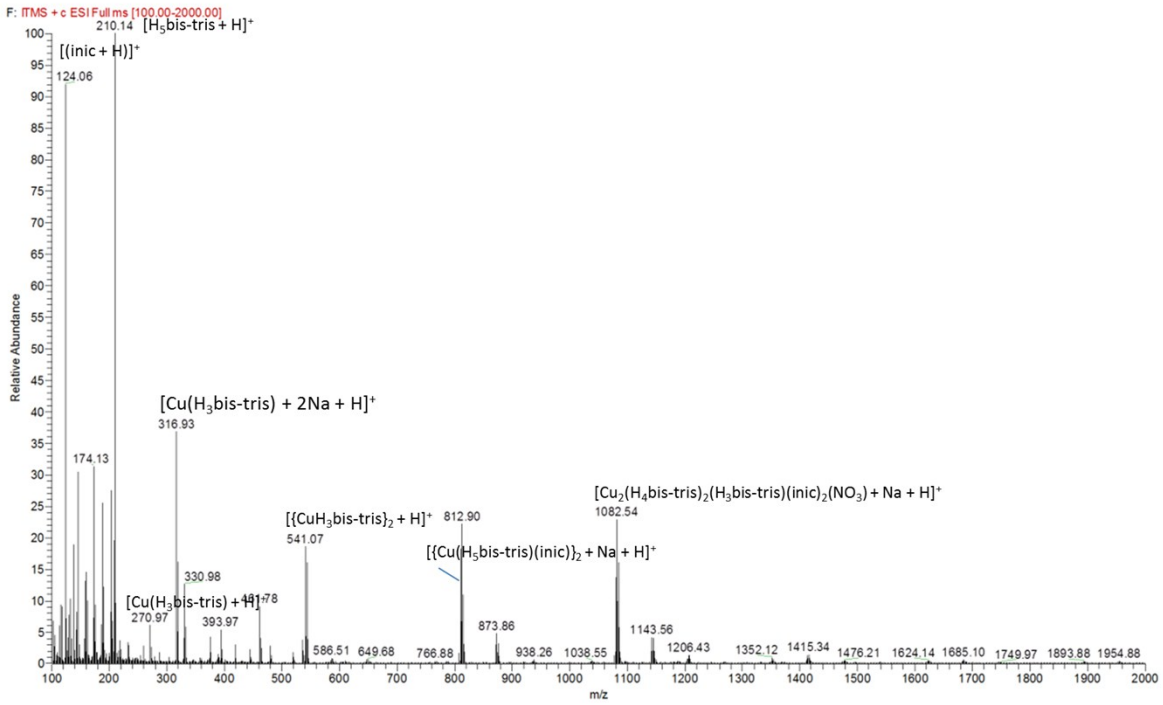


Figure S5. ESI-MS(+) plot of **1** before (a) and after (b) addition of H_2O_2.

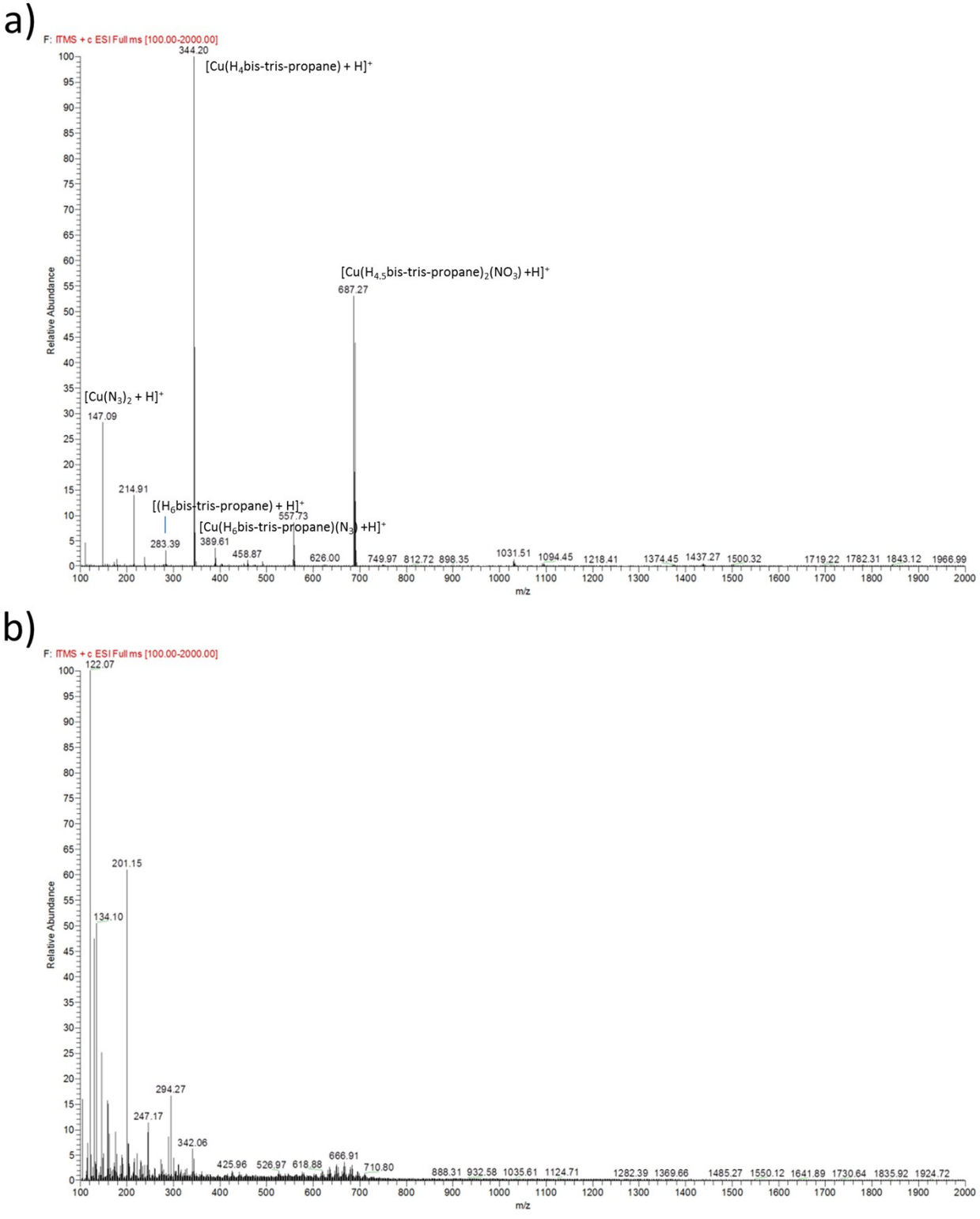


Figure S6. ESI-MS(+) plot of **2** before (a) and after (b) addition of H_2O_2.

Table S1. Fragments detected in the ESI-MS(±)(H_2O) studies of compound **1**.

Proposed ions	Experimental (*m/z*)	Calculated (*m/z*)
$[Cu_3(H_4bis\text{-}tris)_2(H_3bis\text{-}tris)(inic)_2 + Na]^+$	1082.53	1082.21
$[\{Cu(H_4bis\text{-}tris)(inic)\}_2 + Na]^+$	810.85	810.16
$[\{Cu(H_3bis\text{-}tris)\}_2 + H]^+$	541.08	541.11
$[Cu(H_4bis\text{-}tris)_2 + H]^+$	480.08	480.18
$[Cu(H_4bis\text{-}tris)(Hinic) - H_2O + Na]^+$	402.06	402.09
$[Cu(H_4bis\text{-}tris)(inic) + H]^+$	394.00	394.09
$[Cu(H_3bis\text{-}tris) + 2Na + H]^+$	317.02	317.04
$[Cu(H_3bis\text{-}tris) + H]^+$	271.04	271.06
$[H_5bis\text{-}tris + H]^+$	210.21	210.13
$[Hinic + H]^+$	124.06	124.04
$[\{Cu(H_4bis\text{-}tris)(inic)\}_2](NO_3)]^-$	848.50	848.15
$[Cu(H_4bis\text{-}tris)(inic)_2]^-$	514.81	515.11
$[Cu(H_4bis\text{-}tris)(inic)(NO_3)]^-$	454.80	455.07
$[Cu(H_2bis\text{-}tris)(NO_3)]^-$	331.13	331.03
$[H_4bis\text{-}tris]^-$	208.46	208.12
$[(inic)]^-$	122.62	122.02

Table S2. Selected MS^2 fragmentation of compound **1**.

(*m/z*) Proposed ions		(*m/z*) MS^2 fragmentation
1083* **$[Cu_3(H_4bis\text{-}tris)_2(H_3bis\text{-}tris)(inic)_2 + Na]^+$**	>	872 $[Cu_2(H_4bis\text{-}tris)_2(inic)_2(NO_3) + Na + H]^+$ (- $H_4bis\text{-}tris$)
811 **$[\{Cu(H_4bis\text{-}tris)(inic)\}_2 + Na]^+$**	>	604 $[Cu_2(H_5bis\text{-}tris)(inic)_2 + Na + H]^+$
541 **$[\{CuH_3bis\text{-}tris\}_2 + H]^+$**	>	511 $[(Cu_2H_3bis\text{-}tris) - CH_2O + H]^+$, 334 $[(Cu_2H_3bis\text{-}tris) + H]^+$
480 **$[Cu(H_4bis\text{-}tris)_2 + H]^+$**	>	272 $[Cu(H_4bis\text{-}tris) + H]^+$
394 **$[Cu(H_4bis\text{-}tris)(inic) + H]^+$**	>	271, 241, 223, 193

*MS^3 872 > 665 $[Cu(H_5bis\text{-}tris)(H_4bis\text{-}tris)(inic)(NO_3) + H]^+$ (-417 $[Cu(H_4bis\text{-}tris)(inic) + Na]$)

Table S3. Fragments detected in the ESI-MS(±) (H_2O) studies of compound **2**.

Proposed ions	Experimental (*m/z*)	Calculated (*m/z*)
$[Cu_2(H_4$bis-tris-propane$)_2 + H]^+$	687.27	687.21
$[Cu(H_6$bis-tris-propane$)(N_3) + H]^+$	389.61	388.13
$[Cu(H_4$bis-tris-propane$) + H]^+$	344.20	344.11
$[(H_6$bis-tris-propane$) + H]^+$	283.39	283.19
$[Cu(N_3)_2 + H]^+$	147.09	147.97
$[Cu_2(H_5$bis-tris-propane$)_2(N_3)_3 + Na]^-$	837.54	837.24
$[Cu_2(H_4$bis-tris-propane$)_2(N_3)_2 + Na]^-$	793.52	793.21
$[Cu(H_6$bis-tris-propane$)(N_3)]^-$	387.92	387.13
$[Cu(H_4$bis-tris-propane$)]^-$	344.03	343.10
$[Cu(H_5$bis-tris-propane$) – OH]^-$	327.04	327.11

Table S4. Selected MS^2 fragmentation of compound **2**.

(*m/z*) Proposed ions		(*m/z*) MS^2 fragmentation
687 $[Cu_2(H_4$bis-tris-propane$)_2 + H]^+$	>	656, 626, 407, 345 $[Cu(H_5$bis-tris-propane$) + H]^+$, 313
389 $[Cu(H_6$bis-tris-propane$)(N_3) + H]^+$	>	344 $[Cu(H_4$bis-tris-propane$) + H]^+$, 297, 214
344 $[Cu(H_4$bis-tris-propane$) + H]^+$	>	295, 247, 229
283 $[(H_6$bis-tris-propane$) + H]^+$	>	263, 233, 162