New tricopper(II) cores self-assembled from aminoalcohol biobuffers and homophthalic acid: synthesis, structural and topological features, magnetic properties and mild catalytic oxidation of cyclic and linear C_5–C_8 alkanes†

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†Electronic supplementary information (ESI)

Electronic supplementary information (ESI) available: TG–DTA plots (Figures S1, S2), additional topological representations (Figures S3, S4), EPR spectra (Figure S5), UV-vis spectra (Figures S6, S7), hydrogen bonding (Table S1) and catalytic (Tables S2–S4, Figure S8) details for **1** and **2**; CCDC 1014687 and 1014688.

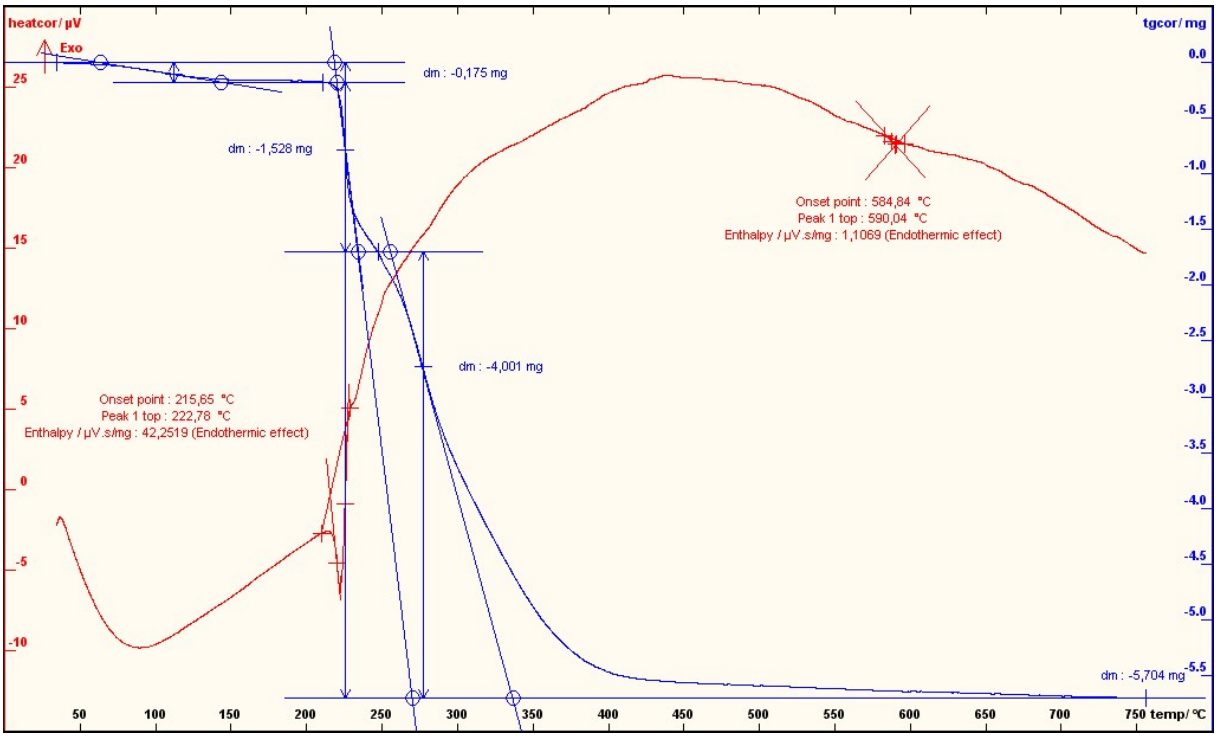


Figure S1. TG–DTA plot of **1** (30−750 °C, 10 °C/min, N_2 atmosphere, 8.430 mg sample). Colour codes: TG curve (blue), DTA curve (red).

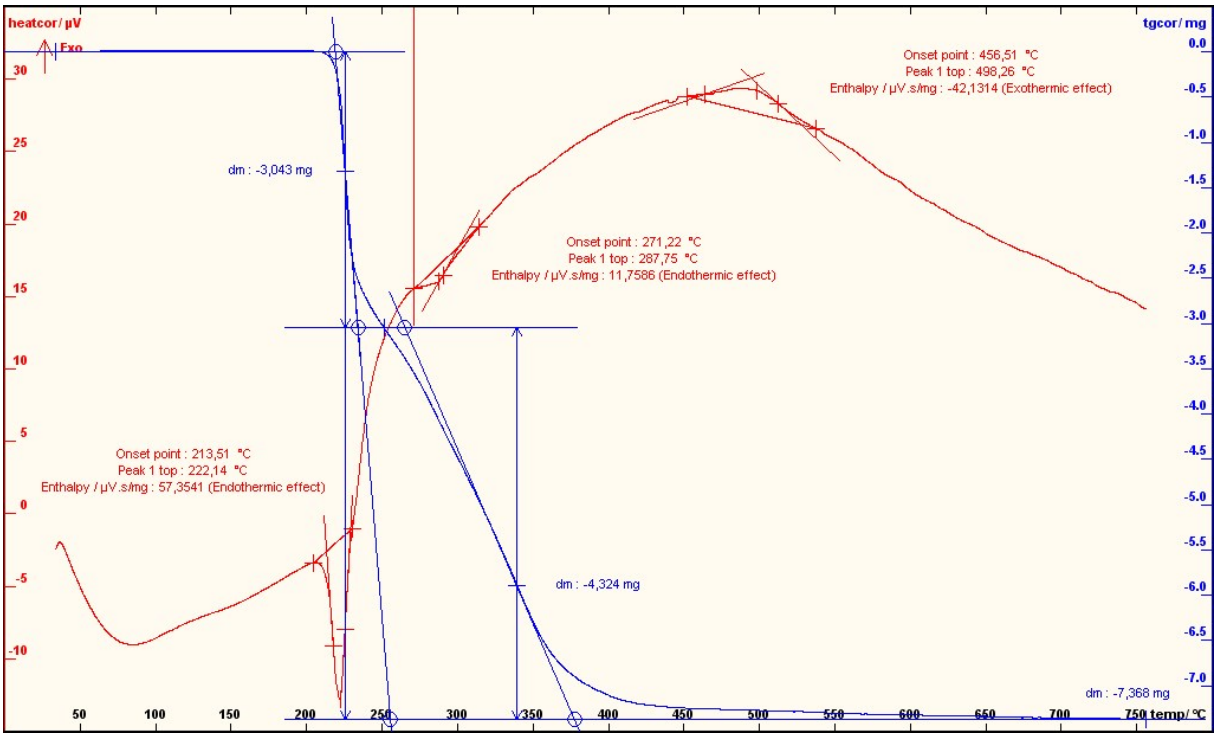


Figure S2. TG–DTA plot of **2** (30−750 °C, 10 °C/min, N_2 atmosphere, 10.318 mg sample). Colour codes: TG curve (blue), DTA curve (red).

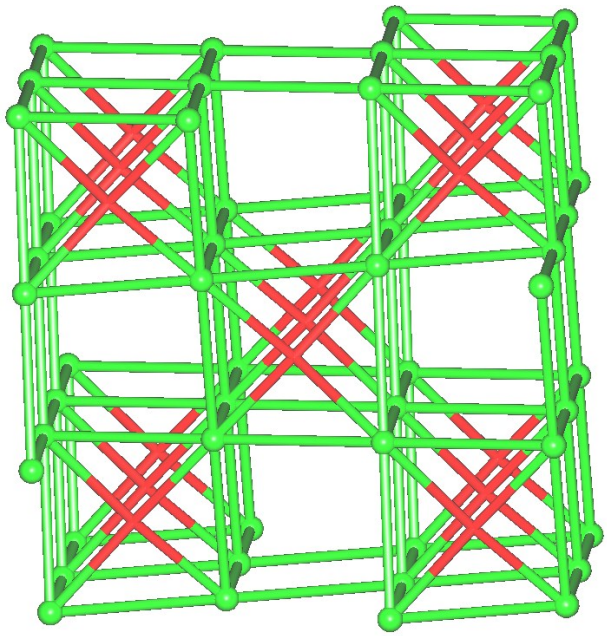


Figure S3. Topological representation of the underlying (first simplification) 3D H-bonded network in **1** showing a binodal 4,8-connected net with the unique topology defined by the point symbol of $(3^4.4^{10}.5^6.6^7.7)_2(3^4.4^2)$. Centroids of 8-connected $[Cu_3(\mu_2\text{-}H_3bis\text{-}tris)_2(\mu_2\text{-}Hhpa)_2]$ molecular nodes (green balls), centroids of 4-connected H_2O (O1w) nodes (red); view along the *c* axis.

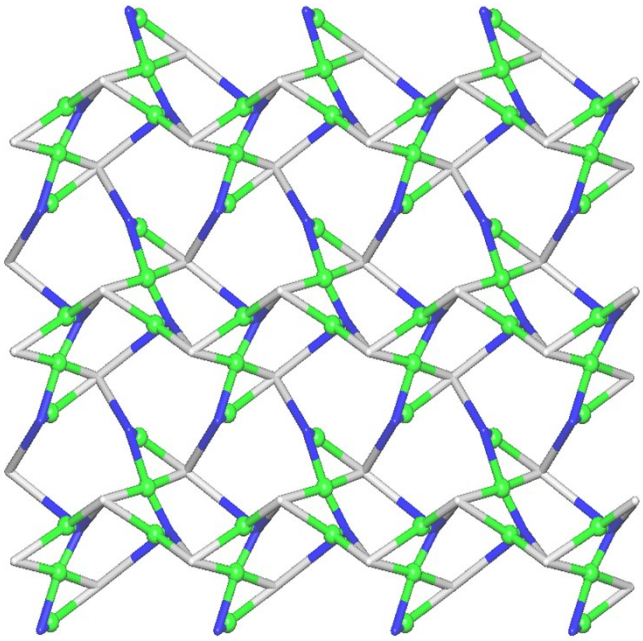


Figure S4. Topological representation of the underlying (first simplification) 2D H-bonded network in **2** showing a very complex hexanodal 3,3,4,4,4,4-c net with the unique topology defined by the point symbol of $(3.4.5.6^2.7)(3.4.5)(3.4.6.7^3)(3.4.6^2.7^2)(3.6.7^3.8)(3.7^2)$. Copper nodes (3-connected Cu1, 4-connected Cu2) and linkers (2-connected Cu3) (green balls), centroids of 3- and 4-connected H_2tea nodes (blue), centroids of 4-connected hpa nodes (grey); view along the *a* axis.

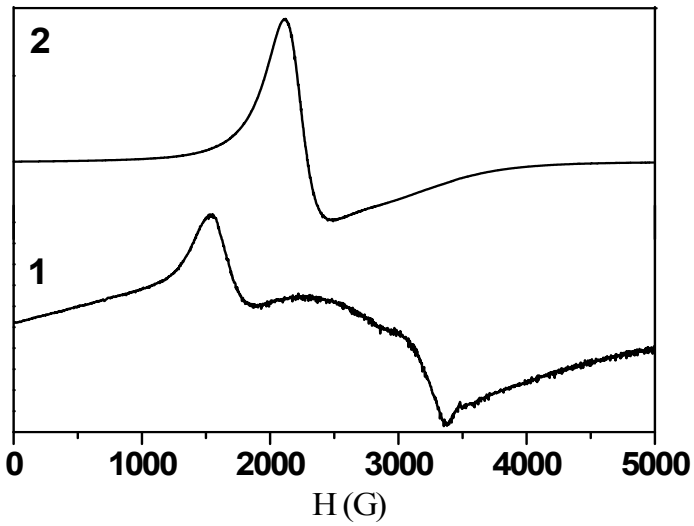


Figure S5. EPR (X-band) spectra of powdered samples **1** and **2** at 77 K.

Table S1. Hydrogen bonding details for compounds **1** and **2**.

	Sym. Op.	D–H···A	*d*(D–H) (Å)	*d*(H···A) (Å)	*d*(D···A) (Å)	D$\hat{H}$A (°)
1	¼+y, 5/4-x, ¼+z	O_3–H_3···O_7	0.84	2.20	2.615(11)	110
	¼+y, 5/4-x, ¼+z	O_3–H_3···O_8	0.84	2.57	3.266(13)	141
	5/4-y,-1/4+x, -1/4+z	O_8–H_{888}···O_4	0.91	2.16	2.629(12)	111
	x, y, z	O_9–H_{9a}···O_{1w}	0.84	2.0	2.710(13)	142
2	x, 3/2-y, -½+z	O_1–H_{003}···O_{11}	0.77(3)	2.01(3)	2.733(2)	158(3)
	x, 3/2-y, ½+z	O_3–H_{004}···O_7	0.82(3)	1.82(3)	2.648(2)	178(4)
	x, 5/2-y, -½+z	O_{12}–H_{001}···O_{11}	0.77(3)	1.80(3)	2.556(3)	172(3)
	x, 5/2-y, -½+z	O_{13}–H_{002}···O_{10}	0.84(3)	1.77(3)	2.602(3)	171(4)

Table S2. Mild oxidation of different C_5–C_8 alkanes by the $Cu(NO_3)_2$/TFA/H_2O_2 system.[a]

Alkane	Yield, %[b]		
	Alcohol(s)[c]	Ketone(s)[c]	Total
Cyclopentane	1.8	1.0	2.8
Cyclohexane	1.7 (1.7)[d]	1.4 (1.3)[d]	3.1 (3.0)[d]
Cycloheptane	2.3	1.8	4.1
Cyclooctane	2.1	2.7	4.8
n-Pentane	1.0	1.1	2.1
n-Hexane	1.6 (1.7)[d]	2.1 (2.0)[d]	3.7 (3.7)[d]
n-Heptane	1.4	1.4	2.8
n-Octane	2.2	1.3	3.5

[a]Reaction conditions: $Cu(NO_3)_2$ (0.01 mmol), TFA (0.1 mmol), alkane (1.0 mmol), H_2O_2 (50% aq., 5.0 mmol), MeCN (up to 5 mL total volume), 50 °C, 3 h. [b]Based on alkane substrate, calculated from GC analysis after treatment of the reaction mixture with PPh_3. [c]In the case of *n*-alkanes, the indicated total product yields correspond to the sum of yields of various isomeric alcohols and ketones (aldehydes), see Table S3 for details. [d]Values in brackets correspond to the oxidations by the $Cu(NO_3)_2$/H_2O_2 system without added TFA.

Table S3. Isomeric product distribution in the mild oxidation of linear C_5–C_8 alkanes by the **1**/TFA/H_2O_2 and $Cu(NO_3)_2$/TFA/H_2O_2 systems.[a]

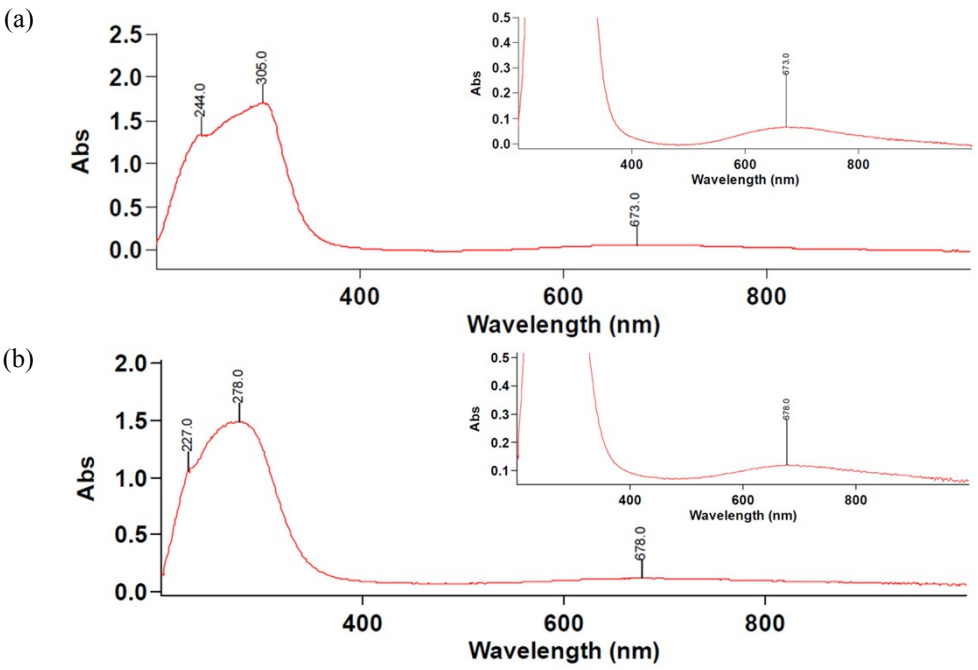
Alkane	Yield, %[b]		
	Alcohols C(1), C(2), C(3), C(4)	Ketones/Aldehyde C(1) C(1), C(2), C(3), C(4)	Total
	1/TFA/H_2O_2		
n-Pentane	0.6, 4.0, 1.9	0.2, 1.8, 1.0	9.5
n-Hexane	0.6, 2.8, 3.5	0.2, 1.6, 1.3	10.0
n-Heptane	0.8, 3.6, 3.4, 1.8	0.3, 1.7, 1.7, 0.7	14.0
n-Octane	0.8, 3.5, 3.3, 2.7	0.2, 1.4, 1.5, 1.4	14.8
	$Cu(NO_3)_2$/TFA/H_2O_2		
n-Pentane	0.1, 0.6, 0.3	traces, 0.7, 0.4	2.1
n-Hexane	0.2, 0.7, 0.7	0.1, 1.0, 1.0	3.7
n-Heptane	0.1, 0.5, 0.5, 0.3	traces, 0.6, 0.6, 0.2	2.8
n-Octane	0.2, 0.6, 0.7, 0.7	traces, 0.5, 0.4, 0.4	3.5

[a]Reaction conditions: pre-catalyst **1** or $Cu(NO_3)_2$ (0.01 mmol), TFA (0.1 mmol), alkane (1.0 mmol), H_2O_2 (50% aq., 5.0 mmol), MeCN (up to 5 mL total volume), 50 °C, 3 h. [b]Based on alkane substrate, calculated from GC analysis after treatment of the reaction mixture with PPh_3.

Table S4. Mild oxidation of cyclohexane by H_2O_2 with pre-catalysts **1**, **2**, $Cu(NO_3)_2$ and various model or control systems.[a]

System	Yield, %[b]		
	Cyclohexanol	Cyclohexanone	Total
H_2O_2 (no Cu)	0.1	0.0	0.1
TFA/H_2O_2 (no Cu)	0.2	0.0	0.2
$Cu(NO_3)_2/H_2O_2$	1.7	1.3	3.0
$Cu(NO_3)_2$/TFA/H_2O_2	1.7	1.4	3.1
$Cu(NO_3)_2/H_5$bis-tris/H_2hpa/H_2O_2	7.3	4.8	12.1
$Cu(NO_3)_2/H_3$tea/H_2hpa/H_2O_2	8.4	5.9	14.3
$Cu(NO_3)_2/H_5$bis-tris/H_2hpa/TFA/H_2O_2	8.5 (5.1)[c]	4.9 (2.8)[c]	13.4 (7.9)[c]
$Cu(NO_3)_2/H_3$tea/H_2hpa/TFA/H_2O_2	9.2 (6.9)[c]	6.4 (4.1)[c]	15.6 (10.5)[c]
1/H_2O_2	0.8	0.4	1.2
2/H_2O_2	0.8	0.3	1.1
1/TFA/H_2O_2	15.9 (15.1)[d]	4.0 (3.6)[d]	19.9 (18.7)[d]
2/TFA/H_2O_2	16.0 (15.2)[d]	4.2 (3.7)[d]	20.2 (18.9)[d]

[a] Reaction conditions (unless stated otherwise): pre-catalyst **1** or **2** (0.01 mmol) or $Cu(NO_3)_2$ (0.01 mmol), TFA (0.1 mmol), aminoalcohol and H_2hpa (0.05 mmol; Cu:aminoalcohol:H_2hpa molar ratio 1:5:5), cyclohexane (1.0 mmol), H_2O_2 (50% aq., 5.0 mmol), MeCN (up to 5 mL total volume), 50 °C, 3 h. [b]Based on cyclohexane, calculated from GC analysis after treatment of the reaction mixture with PPh_3. [c]Cu:aminoalcohol:H_2hpa molar ratio 1.5:1:1. [d]Pre-catalyst **1** or **2** (0.0033 mmol), TFA (0.033 mmol).



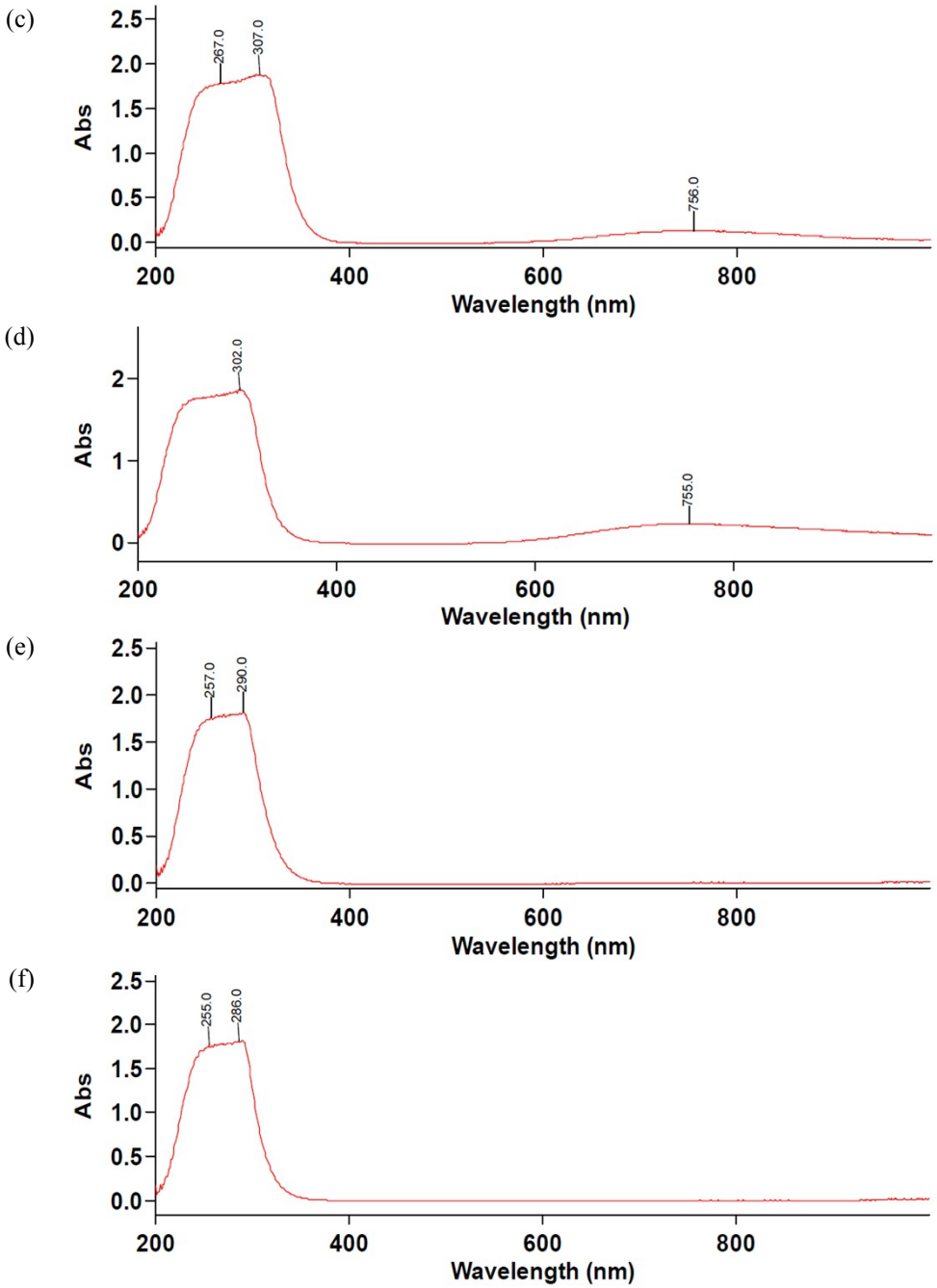
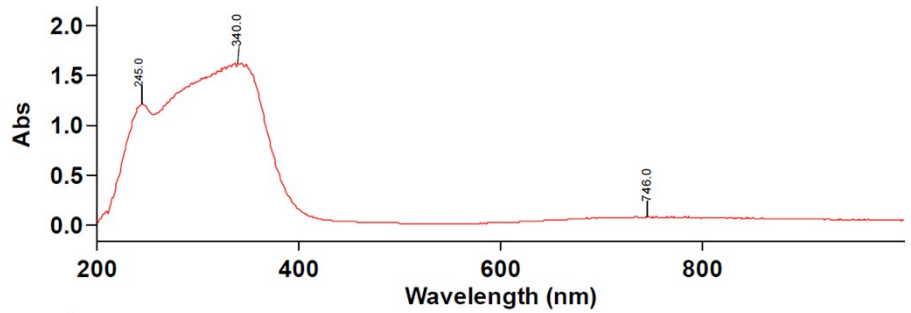


Figure S6. Solution UV-vis spectra: (a) **1**, (b) **2**, (c) **1**+TFA, (d) **2**+TFA, (e) **1**+TFA+H_2O_2 (f) **2**+TFA+H_2O_2. Further details: conditions are similar to those of alkane oxidation experiments (Table 2): pre-catalyst **1** or **2** (0.01 mmol), TFA (0.1 mmol), H_2O_2 (50% aq., 5.0 mmol), MeCN (up to 5 mL total volume); (a, b) spectra of **1** (a) and **2** (b) were measured after additional dilution with MeCN/H_2O (1:1 v/v, up to 20 mL total volume) to allow their complete solubilisation, insets provide a closer view of 670–680 nm bands.

(a)


Abs
Wavelength (nm)
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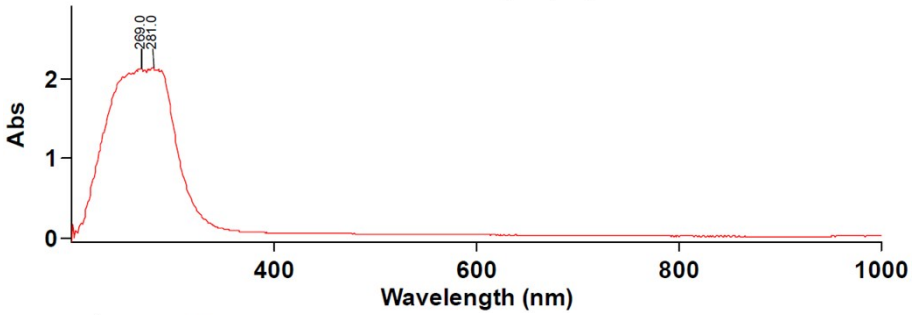
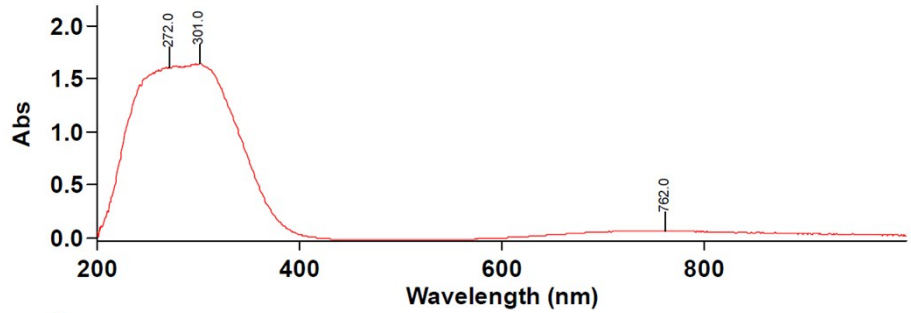
340.0
746.0

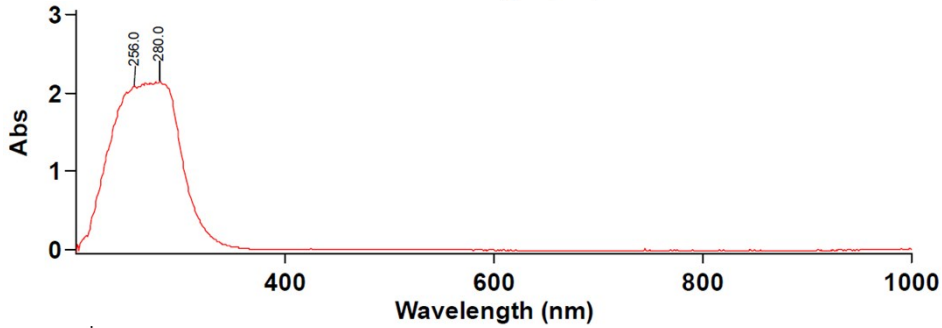
(b)


Abs
Wavelength (nm)
269.0
281.0

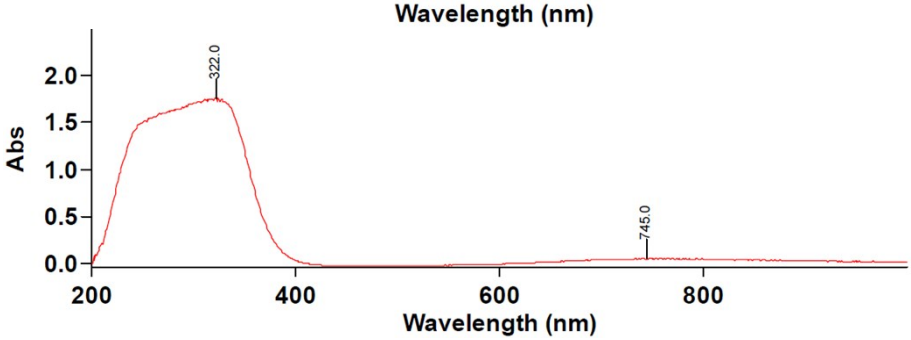
(c)


Abs
Wavelength (nm)
272.0
301.0
762.0

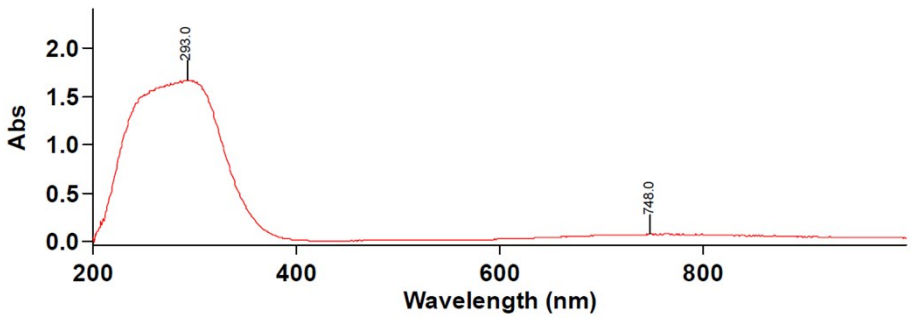
(d)


Abs
Wavelength (nm)
256.0
280.0

(e)


Abs
Wavelength (nm)
322.0
745.0

(f)


Abs
Wavelength (nm)
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748.0

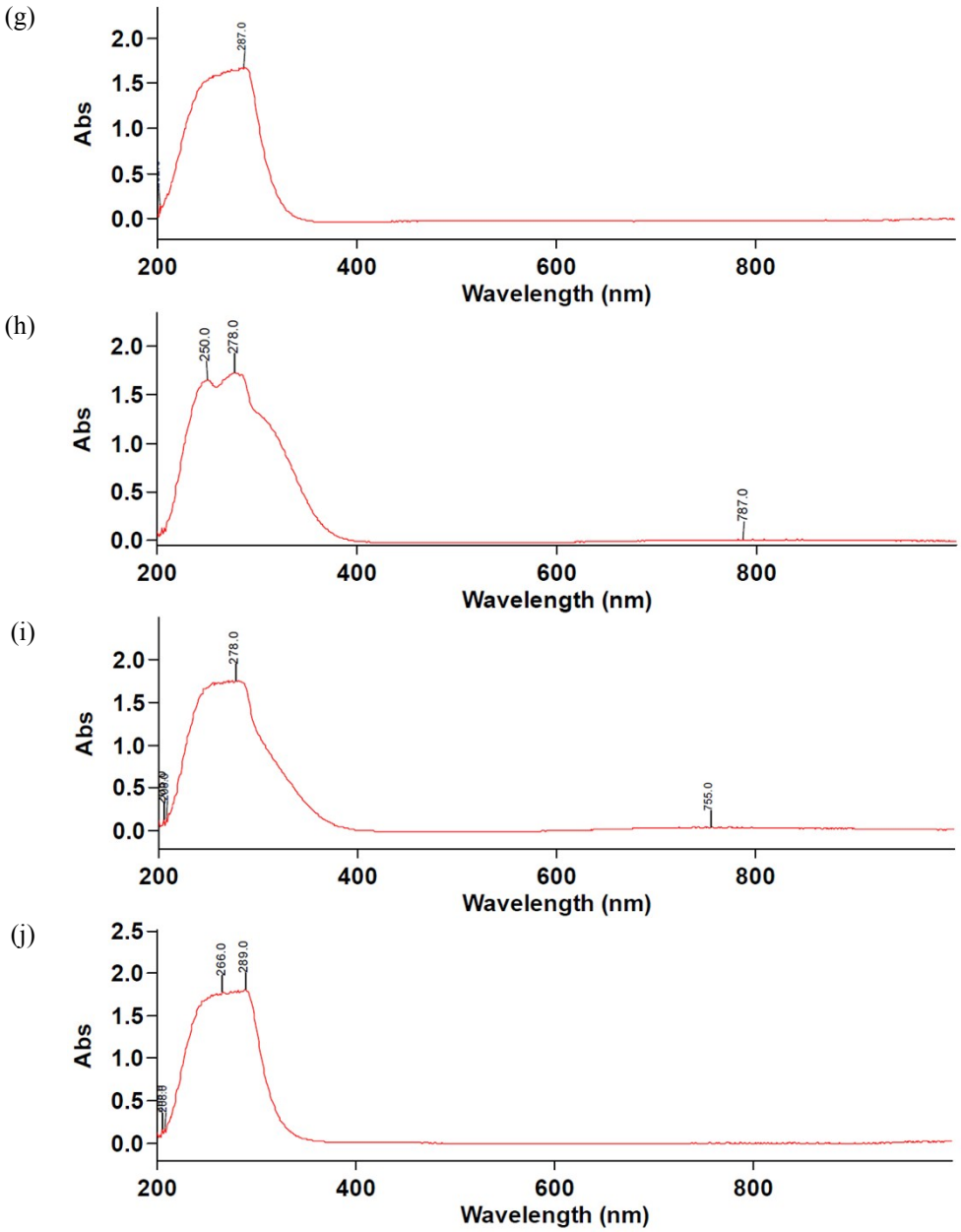

Figure S7. UV-vis spectra of $Cu(NO_3)_2$ and various model solutions: (a) $Cu(NO_3)_2$, (b) $Cu(NO_3)_2$+H_2O_2, (c) $Cu(NO_3)_2$+TFA, (d) $Cu(NO_3)_2$+TFA+H_2O_2, (e) $Cu(NO_3)_2$+H_5bis-tris+H_2hpa, (f) $Cu(NO_3)_2$+H_5bis-tris+H_2hpa+TFA, (g) $Cu(NO_3)_2$+H_5bis-tris+H_2hpa+TFA+H_2O_2, (h) $Cu(NO_3)_2$+H_3tea+H_2hpa, (i) $Cu(NO_3)_2$+H_3tea+H_2hpa+TFA, (j) $Cu(NO_3)_2$+H_3tea+H_2hpa+TFA+H_2O_2. Further details: conditions are similar to those of alkane oxidation experiments (Table 2): $Cu(NO_3)_2$ (0.01 mmol), TFA (0.1 mmol), H_2O_2 (50% aq., 5.0 mmol), H_5bis-tris or H_3tea (0.007 mmol), H_2hpa (0.007 mmol), MeCN (up to 5 mL total volume).

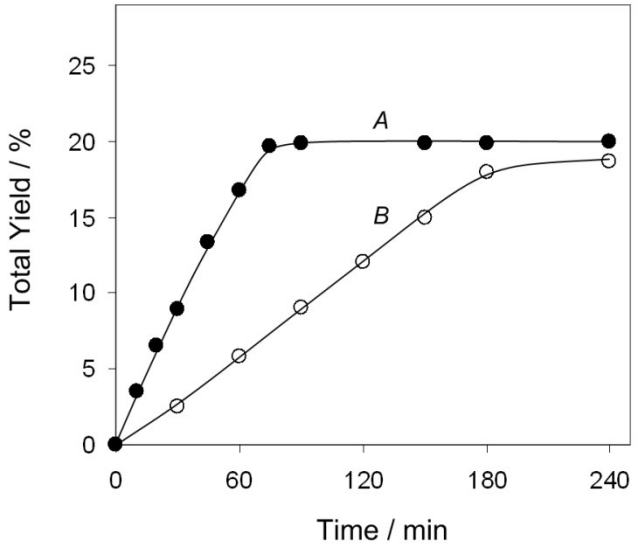

Figure S8. Oxidation of cyclohexane to cyclohexanol and cyclohexanone by H_2O_2 showing the evolution of the total product yield with time at different loadings of pre-catalyst **1** and TFA co-catalyst: curve A (0.01 mmol of **1**, 0.1 mmol of TFA), curve B (0.0033 mmol of **1**, 0.033 mmol of TFA). General conditions: C_6H_{12} (1 mmol), H_2O_2 (50% aq., 5 mmol), 50 ºC, MeCN (up to 5 mL).