Electronic Supplementary Information (ESI)

Interplay between H-bonding and interpenetration in aqueous copper(II)-aminoalcohol-pyromellitic acid system: Self-assembly synthesis, structural features and catalysis

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⁺Electronic supplementary information (ESI) contains: additional structural (Tables S1 and S2, Figs. S1–S3) and catalytic (Figs. S4–S7) data, as well as crystallographic CIF files for **1a** and **1b** (CCDC 1857110-1857111). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x

1a	1b	
Cu1-N1 2.027(2)	Cu1-O1 1.9272(18)	
Cu1-O6B 2.031(9)	Cu1-O1* 1.9294(19)	
Cu1-O6A 2.294(9)	Cu1-O3 1.9324(18)	
Cu1-O5 2.160(2)	Cu1-N3 2.059(3)	
Cu2–O7 2.326(2)	Cu1-O2 2.393(2)	
Cu2-N2 2.038(3)	Cu1…Cu1* 2.8559(6)	
Cu2-O8 2.035(2)		
Symmetry operator * -x+1/2, y, -z	-	

Table S1. Selected bond distances in 1a and 1b (in Å).

 Table S2. Hydrogen bonding details for compounds 1a and 1b.

	Symmetry Operator	D−H …A	d (H···A) (Å)	d (D …A) (Å)	DĤA (°)
1a	x, y, z	$O_5 - H_5 \cdots O_1$	1.66(5)	2.525(3)	175(2)
	x, y, z	O_{6A} - H_{6A} ··· O_2	1.81	2.608(10)	165
	2-x, -y, 2-z	$O_{6B} – H_{6B} \cdots O_2$	1.77	2.484(10)	153
	x, y, z	$O_4-H_4\cdots O_8$	1.94(5)	2.652(4)	169(5)
	x, y, z	$O_7 - H_{70} \cdots O_3$	1.63	2.483(3)	177
1b	x, y, z	$O_2 - H_{10} \cdots O_4$	2.01(4)	2.670(3)	167(5)
	x, y, z	$O_{1w}\!\!-\!\!H_{1w}\!\cdots\!O_2$	2.21(5)	3.013(4)	153(7)



Fig. S1. Experimental (blue) and calculated (black) PXRD patterns of 1a.



Fig. S2. Additional structural fragments of **1a**. (a) Interlinkage of H_2pma^{2-} anion with four monocopper(II) units via strong H-bonding interactions (dotted lines); CH hydrogen atoms were omitted for clarity. (b) Crystal packing pattern along the *c* axis showing the formation of several 2D H-bonded layers. Further details: Cu (green balls), N (blue), O (red), C (pale green), H (gray).



Fig. S3. Crystal packing patterns of **1b** along the c (a) and b (b) axis showing the 3D+3D interpenetrated metal-organic framework and guest water molecules (red balls); H atoms are omitted for clarity. Further details: Cu (green balls), N (blue), O (red), C (pale green).



Fig. S4. Effect of the catalyst type on the total product yield in the cyclooctane oxidation with H_2O_2 catalyzed by **1a**, Cu(NO₃)₂, or a mixture of Cu(NO₃)₂/H₂mdea/H₄pma (1:2:1). Reaction conditions: Cu catalyst (0.01 mmol), TFA (0.1 mmol), C₈H₁₆ (2.0 mmol), H₂O₂ (50% in H₂O, 10.0 mmol), CH₃CN (up to 5.0 mL total volume), 50 °C.



Fig. S5. Oxidation of C_5-C_8 cycloalkanes (yields of alcohol, ketone and total vs. time) with H₂O₂ catalyzed by **1a** in the presence of TFA promoter. Reaction conditions: **1a** (0.01 mmol), TFA (0.1 mmol), cycloalkane (2.0 mmol), H₂O₂ (50% in H₂O, 10.0 mmol), CH₃CN (up to 5.0 mL total volume), 50 °C.



Fig. S6. Effect of TFA amount on (a) the total product yield and (b) the maximum initial reaction rate (W_0) in the cyclooctane oxidation with H₂O₂ catalyzed by **1a**. Reaction conditions: catalyst **1a** (0.01 mmol), TFA (0.01–0.10 mmol), C₈H₁₆ (2.0 mmol), H₂O₂ (50% in H₂O, 10.0 mmol), CH₃CN (up to 5.0 mL total volume), 50 °C.



Fig. S7. Effect of catalyst amount on (a) the total product yield and (b) the maximum initial reaction rate (W_0) in the cyclooctane oxidation with H₂O₂ catalyzed by **1a**/TFA. Reaction conditions: catalyst **1a** (0.0025–0.01 mmol), TFA (0.1 mmol), C₈H₁₆ (2.0 mmol), H₂O₂ (50% in H₂O, 10.0 mmol), CH₃CN (up to 5.0 mL total volume), 50 °C.