Highly Efficient Cu(II)-Pyrazoledicarboxylate Heterogeneous Catalysts for Base-Free Aerobic Oxidation of Benzylic Alcohol to Benzaldehyde with Hydrogen Peroxide as the Oxidant

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Oxidant reaction conditions: Benzyl alcohol:19.2 mmol; 1: 10 mg, 0.18 mol % of benzyl alcohol;
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Fig. S1 Infrared spectrum of Cu(II)-MOF 1.



Fig. S2 The 3D structure connected by intermolecular hydrogen bonds in **1**. The hydrogen atoms not involved in hydrogen bonds are omitted for clarity. Hydrogen bonds are indicated by dashed lines.



Fig. S3 The PXRD spectrum of 1.



Fig. S4 The TG-trace for 1.



Fig. S5 The corresponding PXRD patterns of **1** and after the fifth catalytic run, respectively. Oxidant reaction conditions: Benzyl alcohol:19.2 mmol; **1**: 10 mg, 0.18 mol % of benzyl alcohol; H_2O_2 : 4 mL, 2 equiv to benzyl alcohol; Temperature: 55 °C; Reaction time: 2 h.



Fig. S6 Resonance Raman spectra of catalyst **1** and after the fifth catalytic run, respectively, using an excitation wavelength of 532 nm.

1						
Cu1–N1	1.969(18)	Cu1–N3	1.9819(19)			
Cu1–N2A	1.9934(17)	Cu1–O4A	1.9969(16)			
Cu1–O3B	2.3831(17)					
N1–Cu1–N3	94.31(8)	N1–Cu1–N2A	97.42(7)			
N3-Cu1-N2A	163.50(8)	N1–Cu1–O4A	174.14(8)			
N3-Cu1-O4A	85.88(7)	N2A–Cu1–O4A	81.27(7)			
N1–Cu1–O3B	95.46(7)	N3-Cu1-O3B	107.31(7)			
N2A-Cu1-O3B	83.12(7)	O4-Cu1-O3B	90.07(7)			
Symmetry code: A:1 – x, 1 – y, 2 – z; B: 1 – x, $-0.5 + y$, 1.5 – z.						

Table S1. Main bond lengths (Å) and angles (°) in 1.

Table S2. Bond lengths (Å) and angles (°) of hydrogen bonds for 1.

D−H···A	D–H / Å	H····A / Å	D…A / Å	D–H…A / °
O2–H2…O3	0.82	1.79	2.610(3)	178
N4–H4…O1D	0.82	2.04	2.847(3)	170
С8–Н8…О4В	0.93	2.32	3.102(3)	141

Symmetry code: B: 1 – x, –0.5 + y, 1.5 – z; D: 2 – x, –0.5 + y, 1.5 – z;