Electronic supplementary information (ESI)

New porous coordination polymers based on expanded pyridyl-dicarboxylate ligands and a paddle-wheel cluster†

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Table S1. Crystallographic data.

Complex	**1**	**1**
Method	single crystal	single crystal
Formula	$C_{24}H_{14}CuN_2O_4$	$C_{24}H_{14}CuN_2O_4$
Formula weight	457.92	457.92
Temperature (K)	150(2)	298(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	13.8932(6)	13.8641(6)
b/Å	14.9017(8)	18.1349(9)
c/Å	28.2244(15)	26.5914(12)
β/^{o}	117.982(6)	117.3390(10)
V/Å^3	5160.2(4)	5939.0(5)
Z	4	4
D_c /g cm^{-3}	0.589	0.512
μ (mm^{-1})	0.713	0.379
$R_1{}^a$ $[I > 2\sigma(I)]$[a]	0.0484	0.0411
$wR_2{}^b$ (all data)[b]	0.1107	0.0867
GOF	1.018	1.014

$^aR_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^bwR_2 = [\Sigma w_c(F_o^2 - F_c^2)^2/\Sigma w_c(F_o^2)^2]^{1/2}$, and $w_c = (\sigma^2(F_o^2)^2 + \{0.1[\max(0,F_o^2) + 2F_c^2]/3\}^2)^{-1}$. $^cR_p = \Sigma|cY^{sim}(2\theta_i) - I^{exp}(2\theta_i) + Y^{back}(2\theta_i)|/\Sigma|I^{exp}(2\theta_i)|$. $^dR_{wp} = \{w_p[cY^{sim}(2\theta_i) - I^{exp}(2\theta_i) + Y^{back}(2\theta_i)]^2/\Sigma w_p[I^{exp}(2\theta_i)]^2\}^{1/2}$, and $w_p = 1/I^{exp}(2\theta_i)$.

Table S1. (Continued)

Complex	**2**	**2**	**3**	**3**
Method	single crystal	single crystal	single crystal	powder
Formula	$C_{24}H_{14}CuN_2O_4$	$C_{24}H_{14}CuN_2O_4$	$C_{48}H_{68}CuN_8O_{10}$	$C_{48}H_{68}CuN_8O_{10}$
Formula weight	457.92	457.92	980.65	980.65
Temperature (K)	150(2)	298(2)	150(2)	298(2)
Crystal system	Trigonal	Trigonal	Orthorhombic	Orthorhombic
Space group	*R*-3*m*	*R*-3*m*	*Pbca*	*Pbca*
a/Å	33.2878(9)	33.5037(5)	21.732(5)	23.014(3)
b/Å	33.2878(9)	33.5037(5)	22.850(6)	23.075(8)
c/Å	25.768(1)	26.8482(6)	22.848(7)	23.076(5)
V/Å^3	24728(2)	26099.4(8)	11346(5)	12254(5)
Z	/	18	/	8
D_c /g cm^{-3}	/	0.524	/	1.06
μ (mm^{-1})	/	0.634	/	0.93
R_1[a] $[I > 2\sigma(I)]$[a]	/	0.0360	/	R_p[c] = 4.66%
wR_2[b] (all data)[b]	/	0.0791	/	R_{wp}[d] = 7.39%
GOF	/	1.064	/	/

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w_c(F_o^2 - F_c^2)^2/\Sigma w_c(F_o^2)^2]^{1/2}$, and $w_c = (\sigma^2(F_o^2)^2 + \{0.1[\max(0,F_o^2) + 2F_c^2]/3\}^2)^{-1}$. [c] $R_p = \Sigma|cY^{sim}(2\theta_i) - I^{exp}(2\theta_i) + Y^{back}(2\theta_i)|/\Sigma|I^{exp}(2\theta_i)|$. [d] $R_{wp} = \{w_p[cY^{sim}(2\theta_i) - I^{exp}(2\theta_i) + Y^{back}(2\theta_i)]^2/\Sigma w_p[I^{exp}(2\theta_i)]^2\}^{1/2}$, and $w_p = 1/I^{exp}(2\theta_i)$.

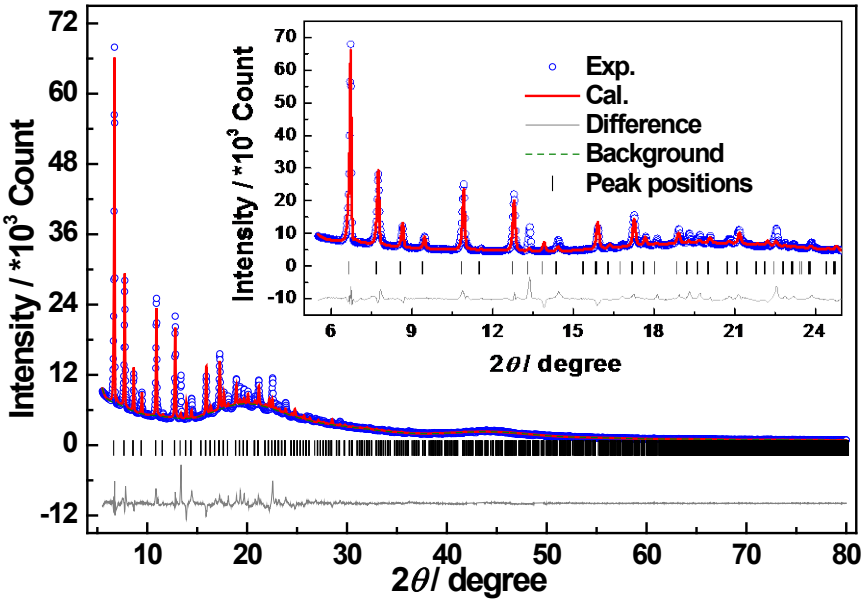

Fig. S1. The final Rietveld refinement plots of **3**.

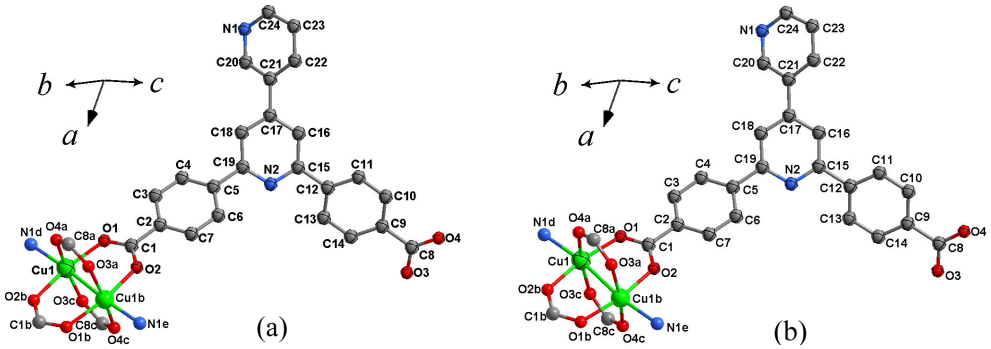

Fig. S2. Perspective views of the coordination environments in **1** at (a) 150 K and (b) 298 K. Hydrogen atoms are omitted for clarity (probability drawn at 50%). Symmetry codes: a = 1-*x*, 1-y, -z; b = 1+x, 1.5-y, -0.5+z; c = 1+x, 1+y, z; d = x, 1.5-y, -0.5+z; e = 2-x, 0.5+y, 0.5-z.

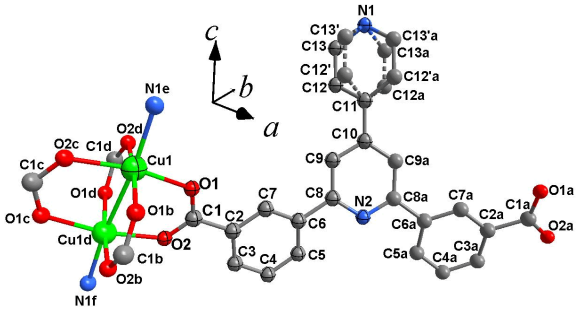

Fig. S3. Perspective views of the coordination environments in **2** at 298 K. Dashed bonds represent the secondary disordering parts. Hydrogen atoms are omitted for clarity (probability drawn at 50%). Symmetry codes: a = 2/3+x-y, 1/3+x, 4/3-z; b = 2/3-x, 1/3-y, 4/3-z; c = x, x-y, z; d = x, y, z; e = 2/3-y, 1/3+x-y, 1/3+z; f = y, x, 1-z.

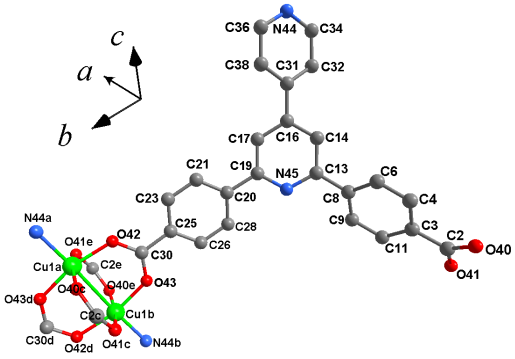

Fig. S4. Perspective views of the coordination environments in **3** at 298 K. Hydrogen atoms are omitted for clarity. Symmetry codes: a = 0.5+x, y, 1.5-z; b = 0.5-x, 1-y, -0.5+z; c = x, y, z; d = 0.5+x, 1.5-y, 1-z; e = 1-x, 1-y, 1-z.

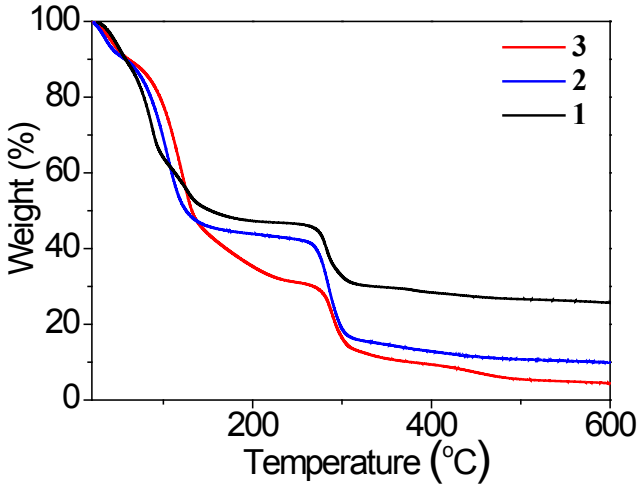

Fig. S5. TGA curves of **1**-**3**.

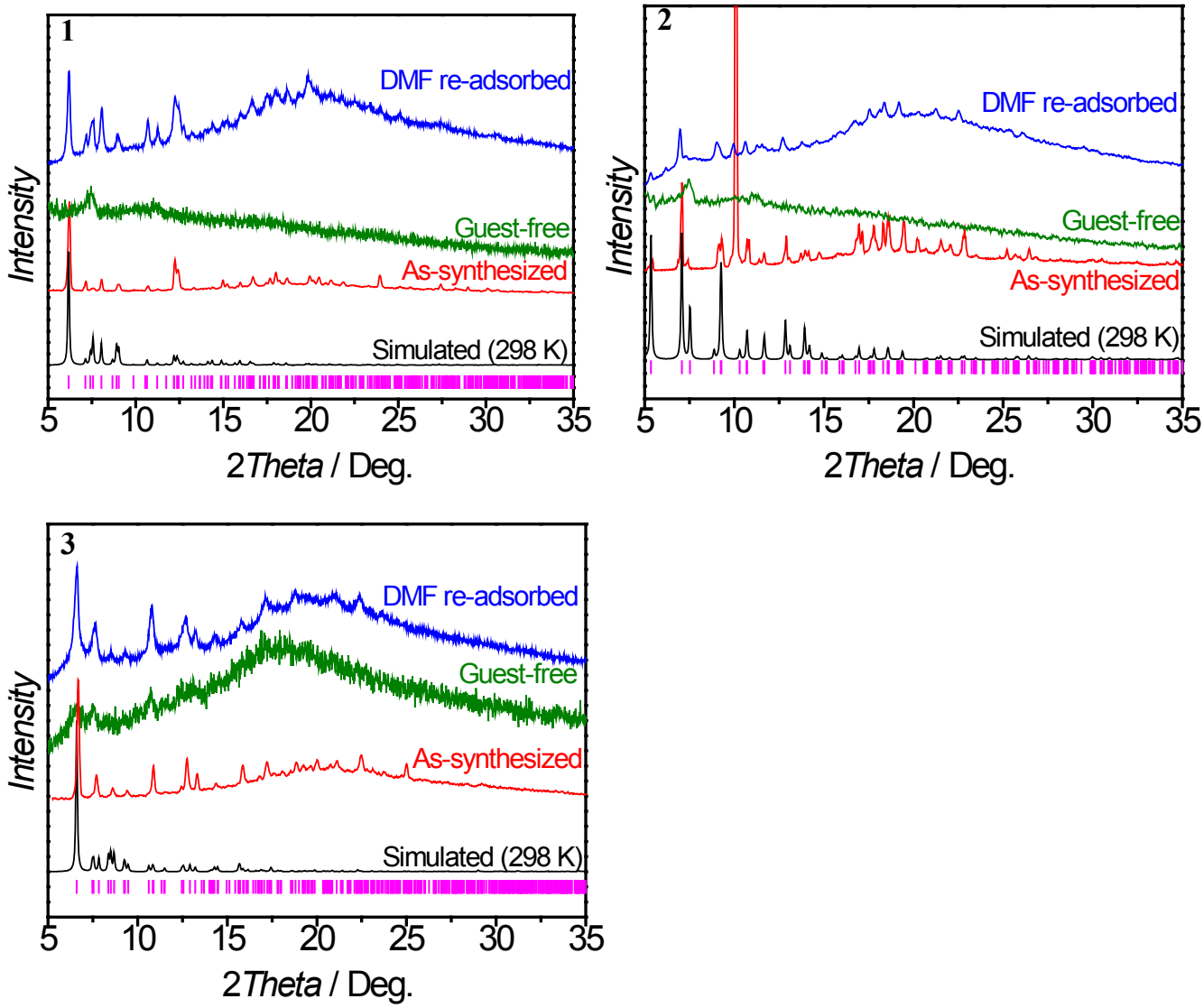

Fig. S6. Room-temperature PXRD patterns of **1**-**3**.

Table S2. CO_2 adsorption data (195 K, 1 atm).

	saturated uptake ($cm^3\ g^{-1}$)	BET ($m^2\ g^{-1}$)[a]	Langmuir ($m^2\ g^{-1}$)[a]	pore volume ($cm^3\ g^{-1}$)[a]	pore volume ($cm^3\ g^{-1}$)[b]
1	80	212	362	0.142	1.46
2	51	137	366	0.090	1.38
3	82	231	378	0.146	1.47

[a] calculated from CO_2 saturated uptakes.

[b] calculated from crystal structures.

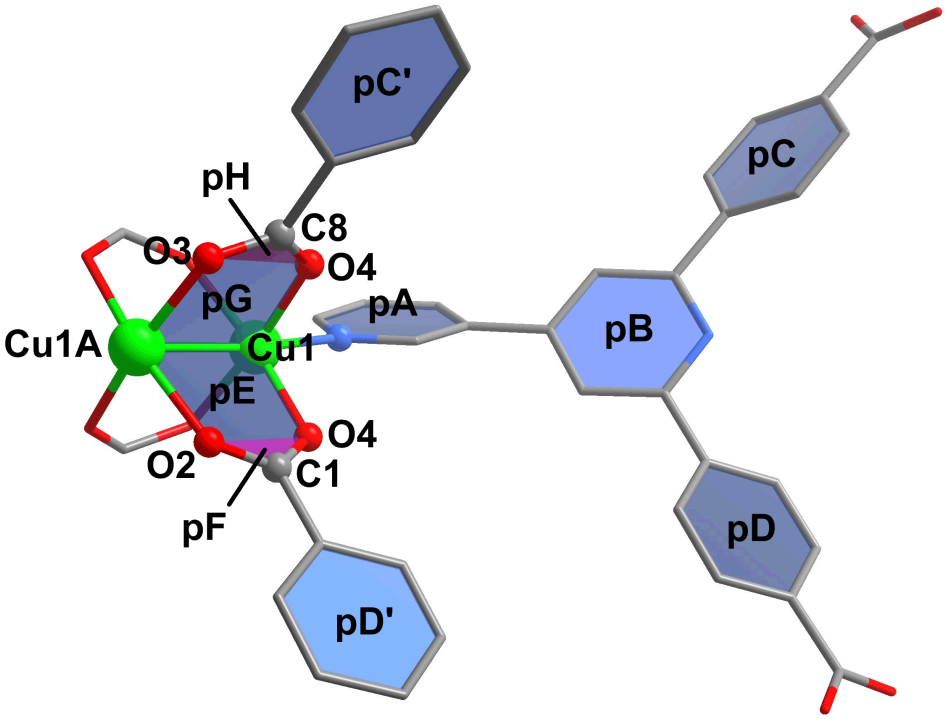

Fig. S7. A representative portion of the crystal structures of **1**. Definition of planes: pA (pA' is a symmetric equivalent of pA) for the pyridyl rings, pB (pB' is a symmetric equivalent of pB) for the central pyridyl ring, pC and pD for the phenyl ring. pF and pH for the carboxylate group composed of O1, O2, C1 and O3, O4 C8, pE and pG for the Cu_2O_2 plane composed of Cu1, Cu1A, O1, O2 and Cu1, Cu1A, O3, O4, respectively.

Table S3. Comparison of important bond lengths, bond angles, and dihedral angles in **1**. Atom and plane numbering scheme is shown in Fig. S7.

	150 K	298 K
∠Cu-O1-C1 (°)	120.6(2)	120.1(1)
∠Cu-O2-C2 (°)	126.0(2)	126.3(1)
∠Cu-O3-C8 (°)	122.5(2)	123.9(1)
∠Cu-O4-C8 (°)	123.6(2)	122.0(1)
∠O3-Cu-O1 (°)	90.06(9)	89.52(6)
∠O4-Cu-O2 (°)	89.47(8)	88.80(6)
Cu1-O1 (Å)	1.960(2)	1.957(2)
Cu1-O2 (Å)	1.973(3)	1.977(2)
Cu1-O3 (Å)	1.969(2)	1.969(1)
Cu1-O4 (Å)	1.963(2)	1.962(1)
Cu1-N1 (Å)	2.160(2)	2.170(2)
O1-C1 (Å)	1.257(4)	1.261(1)
O2-C1 (Å)	1.249(4)	1.260(3)
O3-C8 (Å)	1.260(3)	1.258(2)
O4-C8 (Å)	1.241(4)	1.256(3)
∠Cu1A-Cu1-N1 (°)	4.72(7)	7.34(5)
∠Cu1A-Cu1-pA (°)	11.83(8)	6.73(4)
∠Cu1-N1-pA (°)	7.94(9)	4.09(6)
∠pB-pC (°)	34.0(1)	31.97(7)
∠pB-pD (°)	33.70(9)	26.72(7)
∠pB-pA (°)	45.2(1)	37.75(6)
∠pE-pF (°)	0.5(2)	1.9(2)
∠pF-pD' (°)	14.9(2)	6.1(1)
∠pG-pH (°)	0.7(1)	1.0(2)
∠pH-pC' (°)	8.2(1)	9.3(1)