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Supporting information

Copper-based coordination polymers from thiophene and furan dicarboxylates with high isosteric heats of hydrogen adsorption

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X-ray crystal structure of Cu-TDC

Cu-TDC crystallizes in the trigonal space group R**Error!**c (no. 167). The asymmetric unit contains one Cu^{2+} ion, one TDC ligand and a DMF molecule (Fig. S1). Both carboxylate groups of the TDC ligand are deprotonated resulting in a dianion. Each carboxylate group acts as a bridge between two symmetries related copper ions. Overall, there are four carboxylate bridges between the two copper ions leading to a $Cu_2O_8C_4$ unit and a Cu1-Cu1^{i} distance of 2.6471(5) Å (*i*: 1-x, 1-y, 1-z). A simplified representation of the cluster is shown in Fig. S2. In addition to the Cu-Cu contact and the four carboxylate oxygen atoms, the coordination environment of Cu1 is completed by O5 from a coordinated *N,N'*-dimethylformamide molecule. As expected, the neutral oxygen O5 has a longer Cu-O distance than the negatively charged carboxylate oxygen atoms. The environment of Cu1 is best described as distorted octahedron. Selected bond distances and angles are given in Table S1.

The thiophene core of the TDC ligand links the Cu_2 dimers into an infinite two-dimensional network in the crystallographic a,b-plane (Fig. S3). Due to the space group symmetry, the Cu ions occupy the corners of a triangle. The Cu1···Cu1^{ii} and Cu1···Cu1^{iv} distances between the corners are 9.2917(5) Å (*ii*: 1-x+y, 1-x, z; *iv*: 1-y, x-y, z).

The two dimensional coordination layers are stacked on top of each other in the direction of the c-axis. They are connected in this direction by weak intermolecular C-H···O hydrogen bonds (Fig. S4). Hereby, the thiophene carbon atoms C3 and C4 act as hydrogen bond donors and carboxylate oxygens O2 and O4 as acceptors (Table S2).

The framework structure of Cu-TDC is loosely packed. Most characteristic are channels in the direction of the c-axis (Fig. S5), but solvent accessible voids extend also perpendicular to these channels. Overall, the unit cell contains approximately 36% solvent accessible voids, as determined with the PLATON software.

The crystal structure of Cu-TDC shows pseudo-translational symmetry on the c-axis. Reflections with l=even (average intensity 53304) are much stronger than the reflection with l=odd (average intensity 782). A test for pseudo-translational symmetry[1] with the program SIR2011[2] results consequently in a m.f.s.p. of 97% for l=2n. Nevertheless, the reflections with l=odd are not completely absent (Table S3 and Fig. S6).

If the c-axis is half, the space group changes from R**Error!**c (no. 167) to R**Error!**m (no. 166). The substructure of Cu-TDC is thus identical to structure MOF-110 in reference.[3] We cannot say if we indeed obtained a new modification or if the original authors of MOF-110 overlooked the weak superstructure reflections.

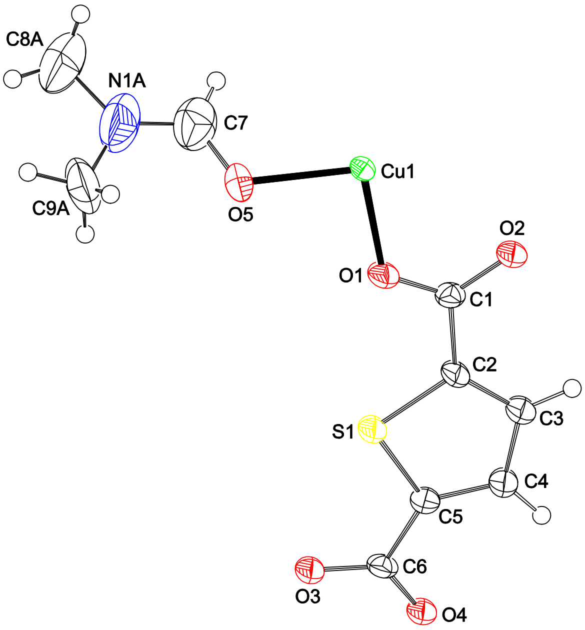

Fig. S1 Asymmetric unit of the Cu-TDC crystal structure. Viewed along the crystallographic a-axis. Displacement ellipsoids are drawn at the 50% probability level. Only the major form of the disordered *N,N'*-dimethylformamide (DMF) is shown. Non-coordinated solvent molecules are treated as diffuse electron density (see Experimental section) and are omitted in the drawing.

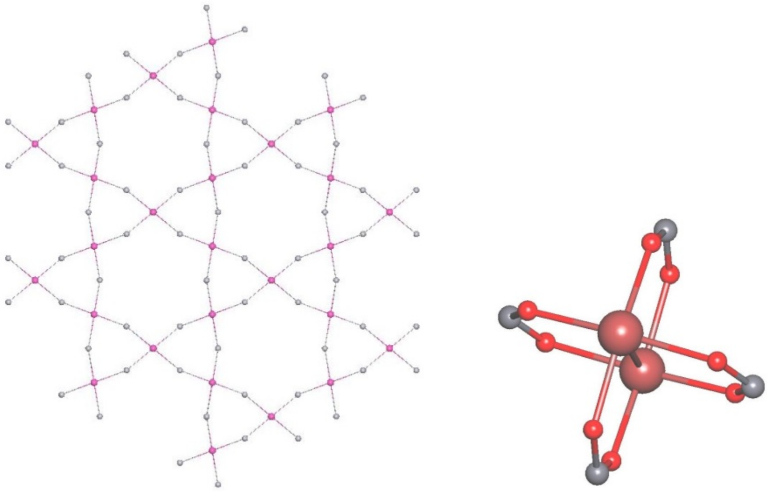

Fig. S2 Simplified view of the two-dimensional network in the crystal structure of Cu-TDC as determined with the TOPOS software.[4] Viewed along the c-axis. *Left:* Purple spheres represent the $Cu_2O_8C_4$ nodes, grey spheres represent the thiophene linkers. *Right:* Representation of the $Cu_2O_8C_4$ node.

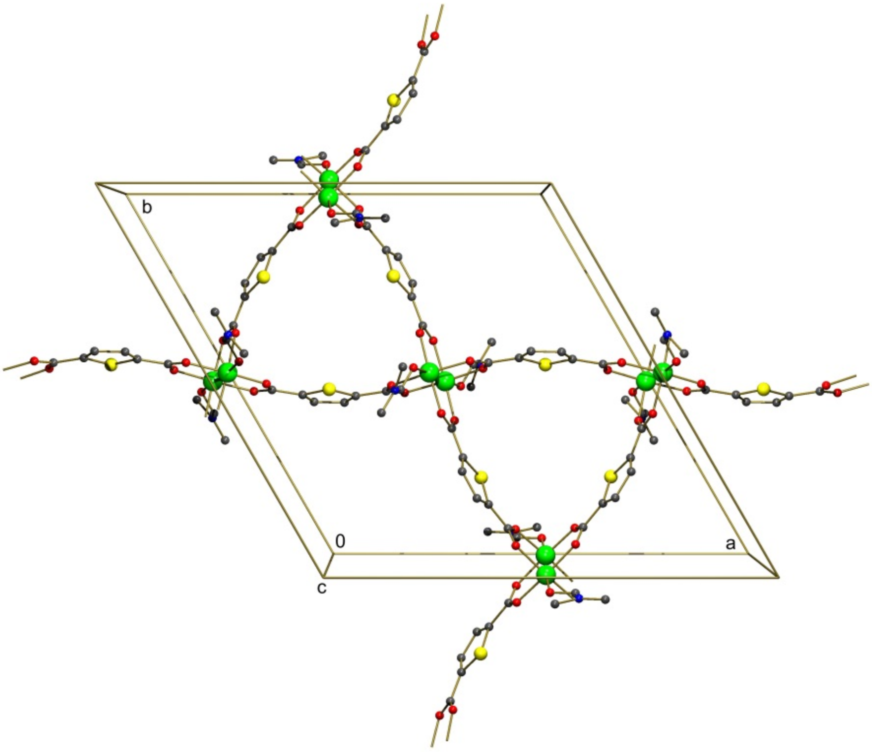

Fig. S3 Infinite two-dimensional coordination layer in the crystal structure of Cu-TDC. Hydrogen atoms are omitted for clarity. Only the major disordered form of *N,N'*-dimethylformamide is shown.

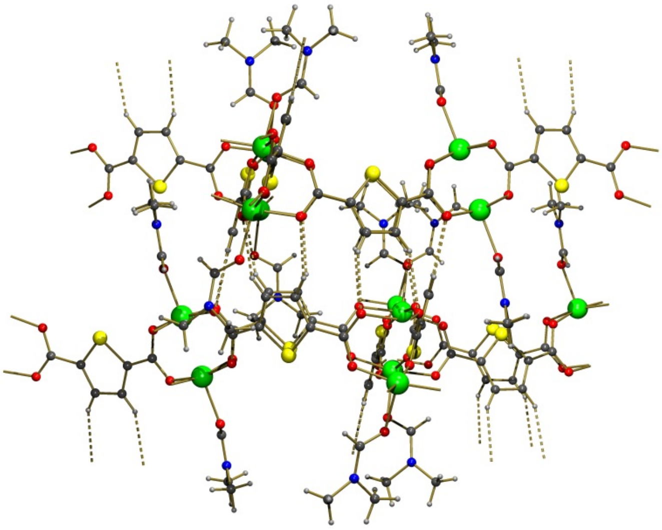

Fig. S4 Weak C-H···O hydrogen bonding in the crystal structure of Cu-TDC. Viewed along the crystallographic a-axis. The two-dimensional coordination planes are shown horizontally. Hydrogen bonds are shown as dashed lines. Only the major disordered form of *N,N'*-dimethylformamide (DMF) is shown.

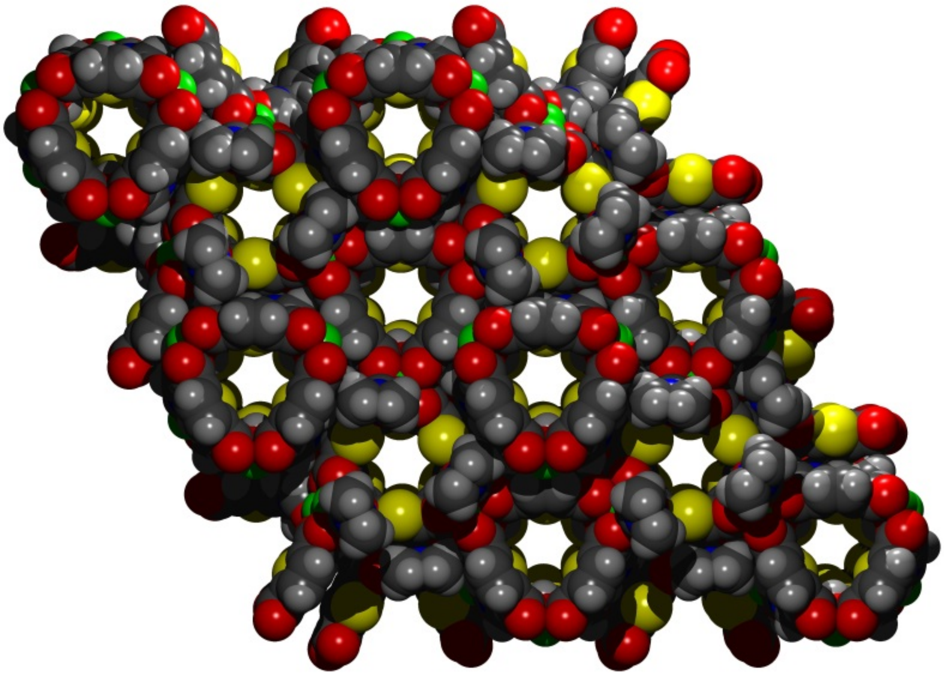

Fig. S5 Space filling plot of the crystal structure of Cu-TDC. Viewed along the crystallographic c-axis.

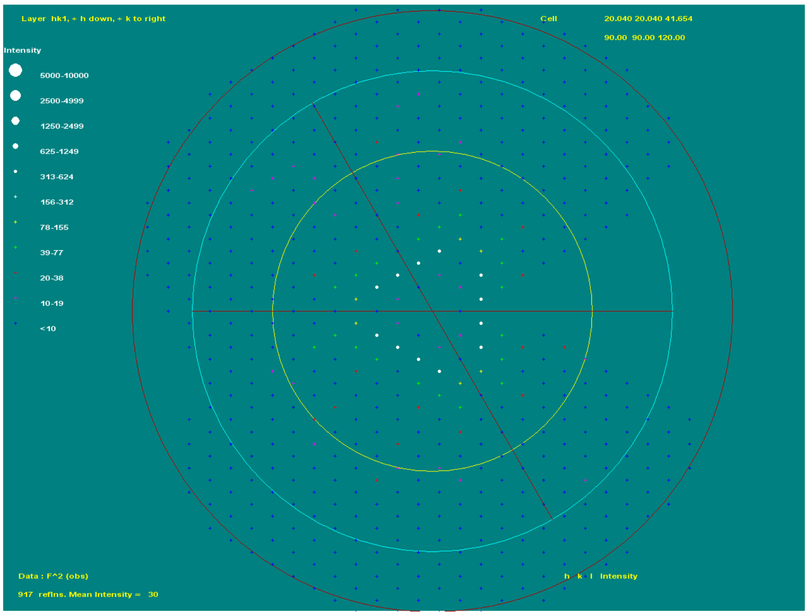

Fig. S6 Simulated precession photo of the plane *hk1*, prepared with the WinGX software.[5] The displayed reflections are weak but not absent.

Table S1 Selected distances [Å] and angles [º] in the crystal structure of Cu-TDC.

Cu1-O1	1.9592(16)	O4^{iii} -Cu1- O2^{i}	88.57(8)
Cu1-O3^{ii}	1.9631(17)	O1-Cu1-O5	96.81(7)
Cu1-O4^{iii}	1.9656(16)	O3^{ii} -Cu1-O5	92.18(7)
Cu1-O2^{i}	1.9730(16)	O4^{iii} -Cu1-O5	99.43(7)
Cu1-O5	2.1310(18)	O2^{i} -Cu1-O5	94.72(7)
Cu1-Cu1^{i}	2.6471(5)	O1-Cu1-Cu1^{i}	84.68(5)
O1-Cu1-O3^{ii}	88.74(9)	O3^{ii} -Cu1-Cu1^{i}	83.24(5)
O1-Cu1- O4^{iii}	90.45(8)	O4^{iii} -Cu1-Cu1^{i}	85.14(5)
O3^{ii} -Cu1- O4^{iii}	168.38(7)	O2^{i} -Cu1-Cu1^{i}	83.75(5)
O1-Cu1- O2^{i}	168.43(7)	O5-Cu1-Cu1^{i}	175.16(5)
O3^{ii} -Cu1- O2^{i}	89.91(8)		

Symmetry operations, *i*: 1-x, 1-y, 1-z; *ii*: 1-x+y, 1-x, z; *iii*: x-y, x, 1-z.

Table S2 Weak C-H···O hydrogen bonds in the crystal structure of Cu-TDC.

D-H...A	D-H [Å]	H...A [Å]	D....A [Å]	D-H...A [º]
C3-H3...O2^{v}	0.95	2.57	3.417(3)	148
C4-H4...O4^{vi}	0.95	2.53	3.393(3)	151

Symmetry operations, *v*: 1/3+x-y, 2/3-y, 7/6-z; *vi*: 1/3+y, x-1/3, 7/6-z.

Table S3 Strongest reflections with l=odd in the crystal structure of Cu-TDC.

hkl	I	σ(I)	I/σ(I)
-2,3,7	87618.73	349.62	250.61
-1,4,1	83255.92	332.64	250.29
-3,5,1	82655.55	335.50	246.37
-1,2,9	42277.76	175.23	241.70
-4,5,3	59845.30	249.85	239.52

X-ray crystal structure of Cu-m-BDC

Cu-m-BDC forms a monomeric cluster containing 24 copper centers (Fig. S7). Similar 24-core metal-organic polyhedra have been reported in the literature.[6-10] The cluster of Cu-m-BDC is located on the inversion center of the triclinic space group P**Error!**. The building unit is again the $Cu_2O_8C_4$ unit, here with Cu···Cu distances of 2.6297(11)-2.6438(11) Å. A simplified representation of the cluster is shown in Fig. S8. The fifth coordination site of the copper centers is partially occupied by water and partially by *N,N'*-dimethylformamide. Due to the disorder, the exact composition could not be determined reliably. These water and DMF ligands are pointing to the center of the polyhedron as well as to the outside of the surface. Cu···Cu distances through the center of the polyhedron (via the crystallographic inversion center) are in the range 15.8871(17)-16.0285(17) Å for the atoms on the inside of the shell, and 21.168(2)-21.2924(19) Å for the atoms on the outside of the shell. The packing of the approximately spherical clusters in the crystal leaves large volumes unoccupied. The PLATON software calculates solvent accessible voids of 4440 Å^3 (43%) for this structure.

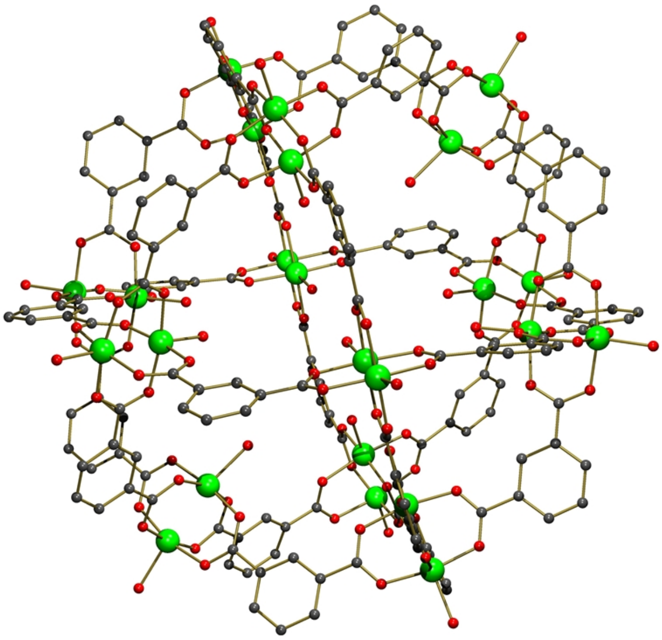

Fig. S7 Unit cell content in the crystal structure of Cu-m-BDC. Viewed along the crystallographic c-axis. Of the disordered terminal water/DMF ligands, only the oxygen atoms are shown. Hydrogen atoms are omitted for clarity. Non-coordinated solvent molecules were treated as diffuse electron density and were omitted in the drawing.

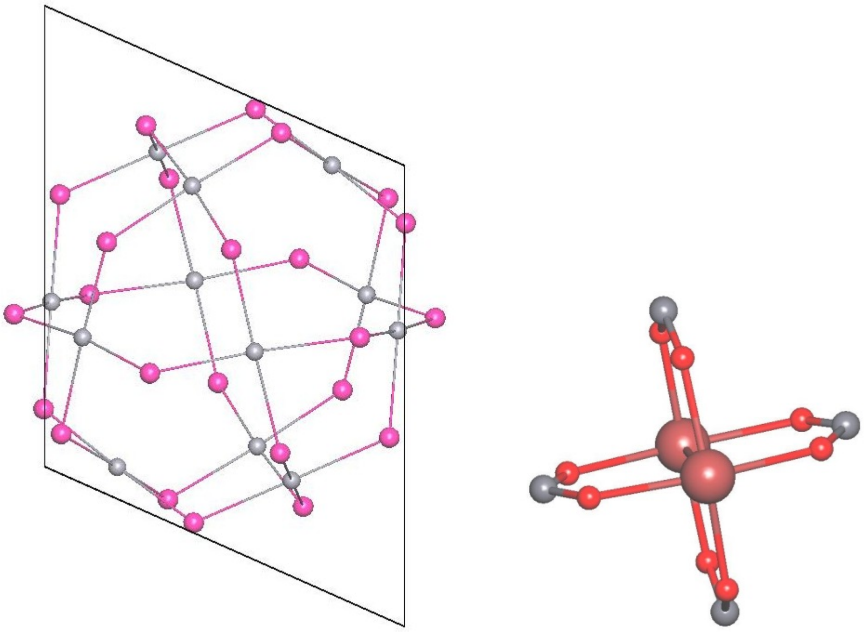

Fig. S8 Simplified net of Cu-m-BDC as determined with the TOPOS software.[4] Viewed along the c-axis. Terminal water/DMF molecules are omitted. *Left:* Grey spheres represent the $Cu_2O_8C_4$ nodes, purple spheres the phenyl linkers. *Right:* Representation of the $Cu_2O_8C_4$ paddlewheel building unit.

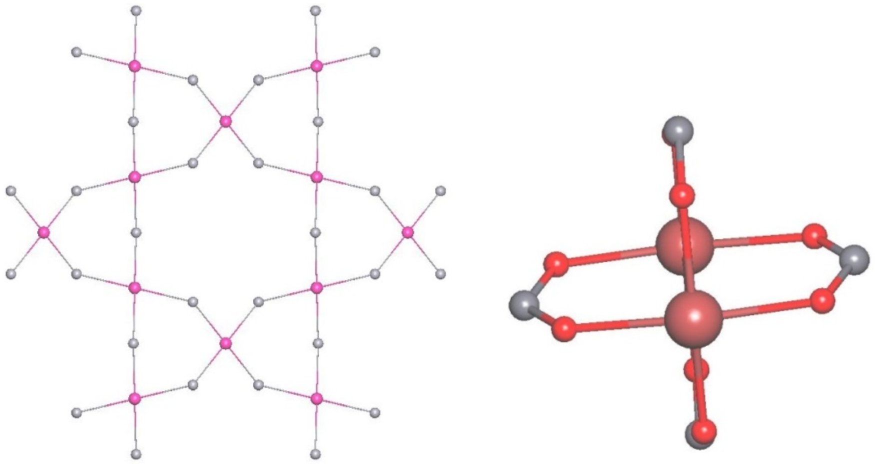

Fig. S9 Simplified view of the two-dimensional network in the crystal structure of Cu-FDC as determined with the TOPOS software.[4] Viewed along the (1,0,2) direction. *Left:* Purple spheres represent the $Cu_2O_8C_4$ nodes, grey spheres the furan linkers. *Right:* Representation of the $Cu_2O_8C_4$ node.

Table S4 Selected distances [Å] and angles [º] in the crystal structure of Cu-FDC.

Cu1-O21^{i}	1.9628(14)	O21^{iii}-Cu1-O21^{i}	88.88(9)
Cu1-O11	1.9740(14)	O21^{iii}-Cu1-O11	168.28(6)
Cu1-O1	2.124(2)	O1-Cu1-Cu1^{i}	178.27(7)
Cu1-Cu1^{i}	2.6518(6)	O22^{ii}-Cu2-O12	167.72(6)
Cu2-O22^{ii}	1.9583(15)	O12-Cu2-O31^{ii}	89.00(7)
Cu2-O12	1.9626(15)	O12-Cu2-O41	91.09(7)
Cu2-O31^{ii}	1.9721(14)	O31^{ii}-Cu2-O41	167.54(6)
Cu2-O41	1.9762(15)	O31^{ii}-Cu2-O2	97.35(7)
Cu2-O2	2.1201(17)	O41-Cu2-Cu2^{ii}	82.92(5)
Cu2-Cu2^{ii}	2.6782(5)	O2-Cu2-Cu2^{ii}	177.25(6)

Symmetry operations, *i*: -x, y, 1-z; *ii*: ½-x, ½-y, -z; *iii*: -x, 1-y, 1-z.

Table S5 Weak C-H···O hydrogen bond in the crystal structure of Cu-FDC.

D-H...A	D-H [Å]	H...A [Å]	D....A [Å]	D-H...A [°]
C32-H32...O11^{iv}	0.95	2.38	3.211(3)	146

Symmetry operations, *iv*: x+½, ½-y, -z.

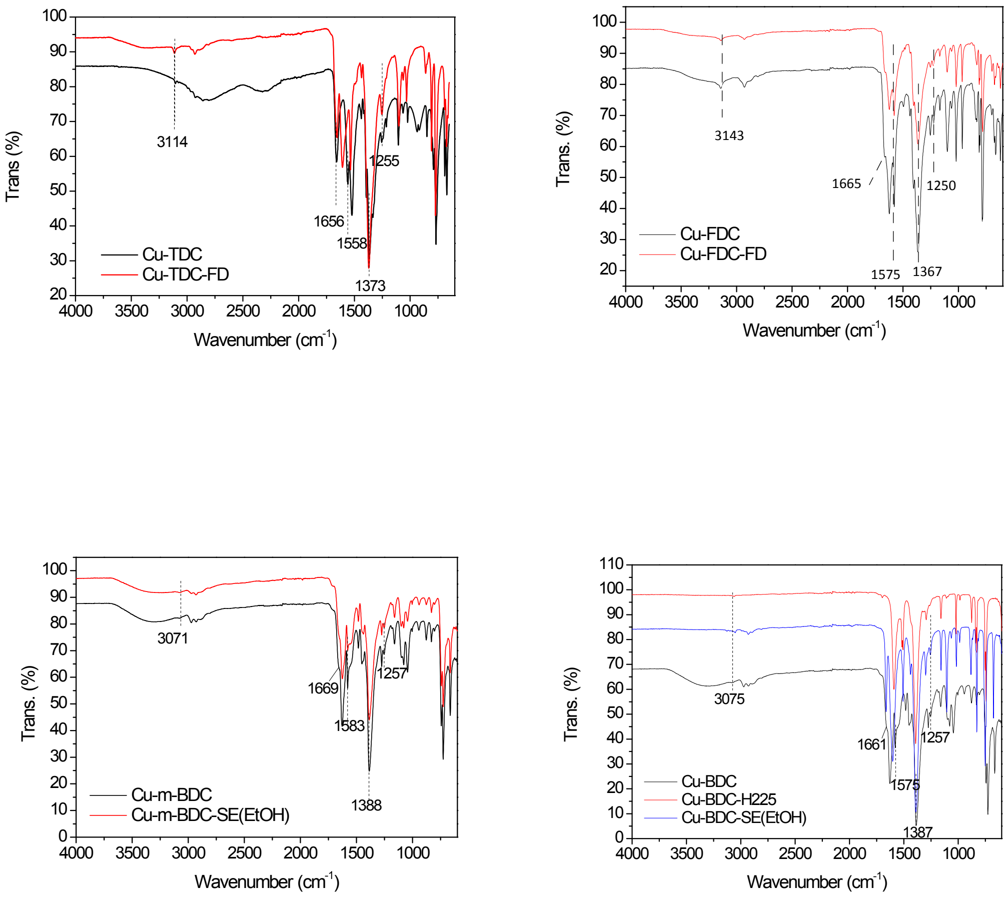

Fig. S10 IR spectra of the as prepared and activated Cu-TDC, Cu-FDC, Cu-m-BDC and Cu-BDC.

Cu-TDC: 3114 cm^{-1} ν(CH) (thiophene ring), 1656 cm^{-1} ν(CO) (DMF), 1558 cm^{-1} ν_a(COO), 1373 cm^{-1} ν_s(COO), 1255 cm^{-1} ν_a(CN) (DMF).

Cu-FDC: 3143 cm^{-1} ν(CH) (furan ring), 1665 cm^{-1} ν(CO) in DMF, 1575 cm^{-1} ν_a(COO), 1367 cm^{-1} ν_s(COO), 1250 cm^{-1} ν_a(CN) (DMF).

Cu-m-BDC:3071 cm^{-1} ν(CH) (*m*-benzene ring), 1669 cm^{-1} ν(CO) (DMF), 1583 cm^{-1}ν_a (COO), 1388 cm^{-1} ν_s(COO), 1257 cm^{-1} ν_a(CN) (DMF).

Cu-BDC: 3075 cm^{-1} ν(CH) (*p*-benzene ring), 1661 cm^{-1} ν(CO) (DMF), 1575 cm^{-1} ν_a(COO), 1387 cm^{-1} ν_s(COO), 1257 cm^{-1} ν_a(CN) (DMF).

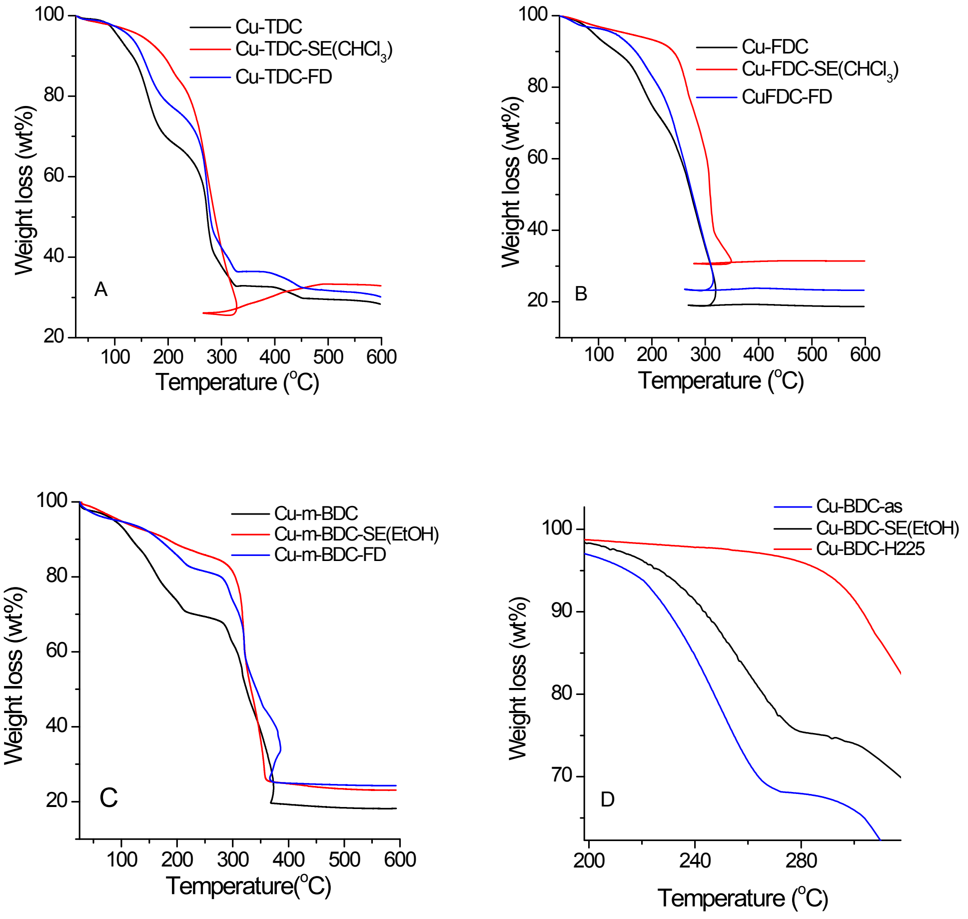

Fig. S11 TG curves of the as prepared and activated Cu-TDC(A), Cu-FDC(B), Cu-m-BDC(C) and Cu-BDC(D).

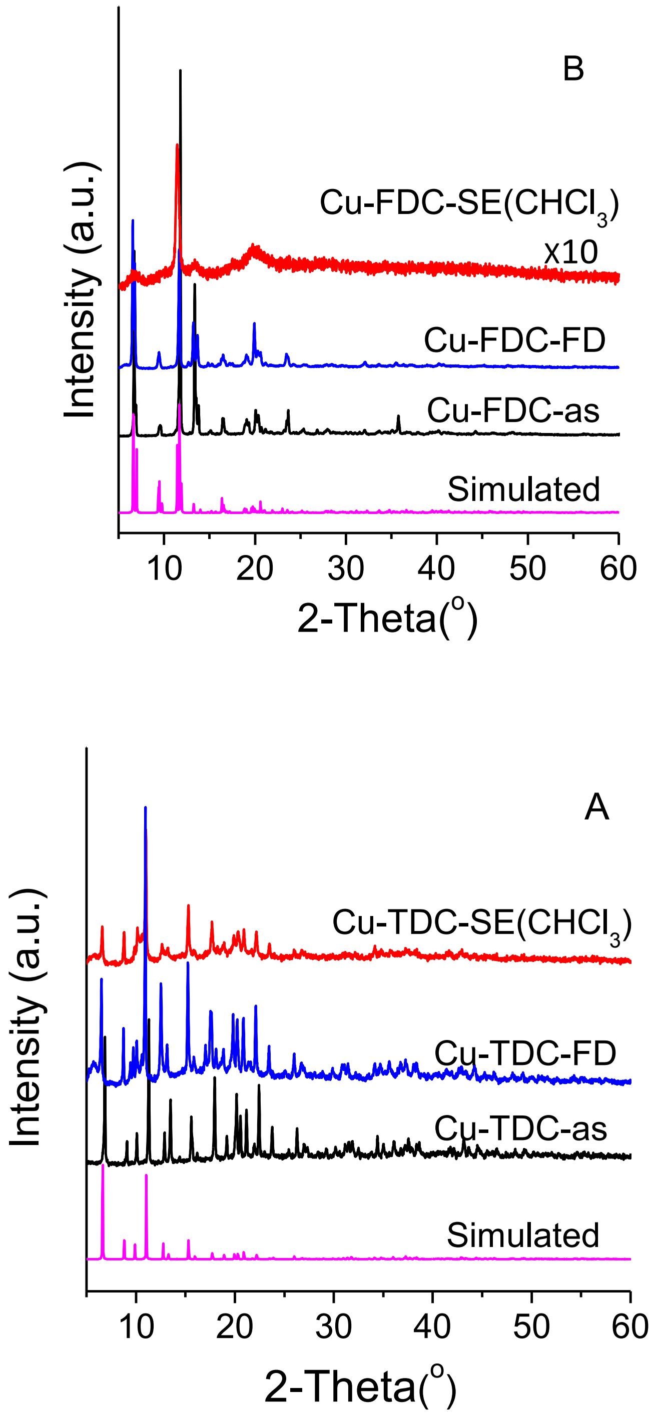

Fig. S12 As measured and simulated XRD patterns for Cu-TDC and Cu-FDC.

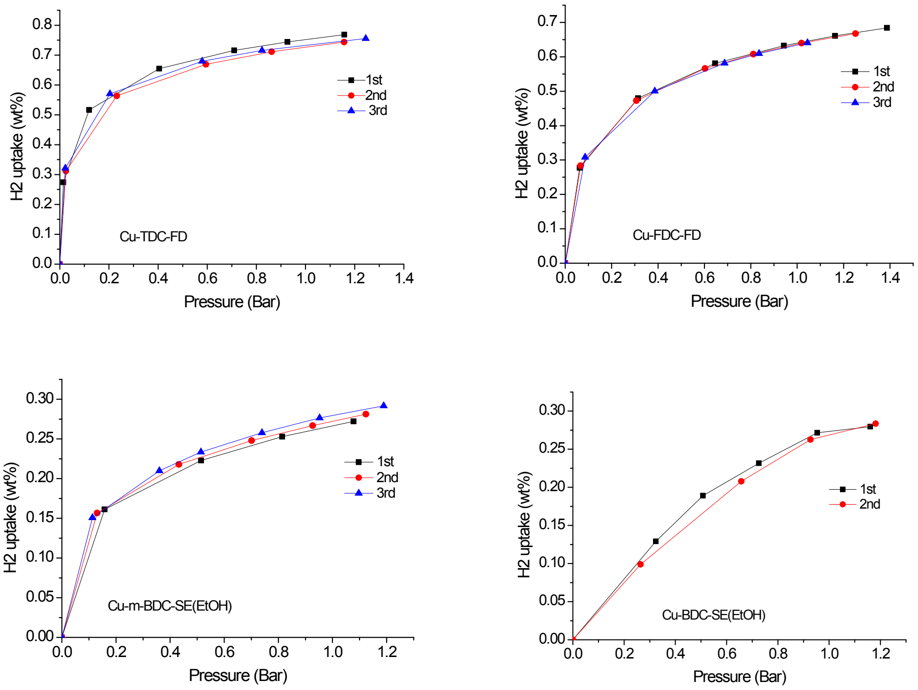

Fig. S13 The low-pressure hydrogen adsorption isotherms of the activated Cu-TDC, Cu-FDC, Cu-m-BDC and Cu-BDC at 77 K.

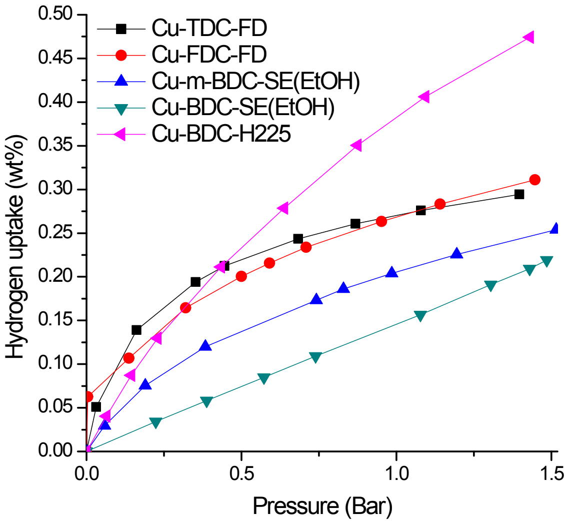

Fig. S14 The low-pressure hydrogen adsorption isotherms of the activated Cu-TDC, Cu-FDC, Cu-m-BDC and Cu-BDC at 100 K.

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