Supporting Information

A first Cyclodextrin-Transition Metal Coordination Polymer

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S1 Experimental Section

S1.1. General considerations

All chemical reagents and solvents were purchased from commercial sources and used as received without further purification. Purity of all bulk material batches was confirmed by X-ray powder diffraction (PXRD) patterns collected on an X'Pert PRO MPD analytical diffractometer (Panalytical) at 45 kV, 40 mA using Cu Kα radiation (λ = 1.5419 Å), and compared with single crystal simulated patterns. Thermogravimetric analyses were performed under nitrogen flow using an STA 449 F1 Jupiter–Simultaneous TGA-DSC (NETZSCH) at a heating rate of 10 °C/min. Elemental Analysis measurements were performed on a Flash EA 2000 CHNS (Thermo Fisher Scientific) analyser. N_2 and CO_2 adsorption and desorption measurements were done at 77 K and 194 K, respectively, using an Autosorb-IQ-AG analyser (Quantachrome Instruments). Water vapour adsorption–desorption isotherms were measured using a gravimetric instrument DVS Advantage-1 (Surface Measurement Systems Ltd). The weight of the dry powder was constantly monitored and recorded at 25 ºC and different relative humidity values. The relative humidity inside the chamber was adjusted by bobbling a carrier gas (N_2) in pure water until stream saturated in water (95% Relative Humidity). The adsorbed moisture was expressed as $g_{water}/g_{dried\ sample}$. Prior to the water adsorption measurements, air-dried samples were outgassed under vacuum at 80 ºC during 2 hours.

S1.2. Synthesis of $[Cu_4(SD)(H_2O)_4]\cdot 46H_2O$

An aqueous solution (1.5 ml) containing SD (sodium salt, 20 mg; 0.009 mmol) was initially placed into the bottom of a glass tube. Then, a mixture of H_2O/EtOH (1:1, 4 ml) was carefully added on top of this solution as a buffer zone. Finally, an ethanolic solution (1.5 ml) containing $CuCl_2\cdot 2H_2O$ (20 mg; 0.117 mmol) was added slowly above the H_2O/EtOH mixture. The diffusion proceeded at room temperature for a week in static conditions, resulting in blue cubic crystals suitable for single-crystal X-ray diffraction (SCXRD). The resulting crystals were collected by centrifugation, and washed two times with a H_2O/EtOH (1:1) mixture solution (2 ml each step) followed by another three times with pure EtOH (2 ml each step). Yield: 40 %. The obtained crystal samples were air-dried and kept in a vial in ambient for further characterization.

Table S1. Crystal and refinement data of **Cu-SD**.

Compound	**Cu-SD**
Emp. formula	$C_{36}H_{52}O_{26}S_4Cu_2$
Formula weight	1156.16
Temperature (K)	293(2)
Wavelength (Å)	0.79474
Crystal system	Tetragonal
Space group	$P4_12_12$
CCDC ref.	1495256
Unit cell dimensions	
a (Å)	17.010(5)
c (Å)	49.050(5)
V (Å^3)	14192(8)
Z	8
F (000)	4784
Crystal size (mm^3)	0.11 x 0.11 x 0.10
θ range (°)	0.9-33.8
Flack parameter	-0.003(10)
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	17305 / 12 / 630
Goodness-of-fit on F^2	1.130
Ind. Refln. (R_{int})	17305 (0.077)
Final R indices [I > 2σ(I)]	R1 = 0.1287 wR2 = 0.3846
Largest diff. peak and hole	1.234 and -0.530 e. Å^{-3}

Table S2. Selected bond distances (Å) and angles (°) in **Cu-SD**.[a]

Cu(1)-O(1w)	2.130(15)	O(1w)-Cu(1)-O(1)	93.4(5)
Cu(1)-(O1)	1.84(2)	O(1w)-Cu(1)-O(7)	94.5(5)
Cu(1)-(O7)	1.962(19)	O(1)-Cu(1)-O(7)	85.6(8)
		O(1)-Cu(1)-O(1)$^{\#1}$	165.3(4)
		O(1)-Cu(1)-O(7)$^{\#1}$	85.8(8)
		O(7)-Cu(1)-O(7)$^{\#1}$	167.5(8)
Cu(2)-O(3w)	2.09(2)	O(3w)-Cu(2)-O(9)	94.1(7)
Cu(2)-O(9)	1.930(16)	O(3w)-Cu(2)-O(15)	98.7(7)
Cu(2)-O(15)	1.936(17)	O(3w)-Cu(2)-O(12)$^{\#2}$	91.1(6)
Cu(2)-O(12)$^{\#1}$	1.947(14)	O(3w)-Cu(2)-O(19)$^{\#2}$	99.8(6)
Cu(2)-O(19)$^{\#1}$	1.972(12)	O(9)-Cu(2)-O(15)	89.7(7)
		O(9)-Cu(2)-O(12)$^{\#2}$	90.7(7)
		O(9)-Cu(2)-O(19)$^{\#2}$	166.1(7)
		O(15)-Cu(2)-O(12)$^{\#2}$	169.4(7)
		O(15)-Cu(2)-O(19)$^{\#2}$	87.4(6)
		O(12)$^{\#2}$-Cu(2)-O(19)$^{\#2}$	89.7(6)
Cu(3)-O(2w)	2.173(15)	O(2w)-Cu(3)-O(2)	95.2(3)
Cu(3)-O(2)	1.960(12)	O(2w)-Cu(3)-O(6)	94.6(3)
Cu(3)-O(6)	1.961(10)	O(2w)-Cu(3)-O(2)$^{\#1}$	95.2(3)
		O(2w)-Cu(3)-O(6)$^{\#1}$	94.6(3)
		O(2)-Cu(2)-O(6)	89.1(5)
		O(2)-Cu(2)-O(2)$^{\#1}$	169.6(4)
		O(2)-Cu(2)-O(6)$^{\#1}$	90.1(5)
		O(2)$^{\#1}$-Cu(3)-O(6)	90.1(5)
		O(6)-Cu(2)-O(6)$^{\#1}$	170.9(4)
		O(2)$^{\#1}$-Cu(3)-O(6)$^{\#1}$	89.1(5)

[a] Symmetry code: #1 2-x, 1-y, -z; #2 y, x, -z.

Table S3 H-bond interactions (Å/°) in **Cu-SD**.[a]

D-H…A	**d (D-H)**	**d (H…A)**	**d (D..A)**	**< (DHA)**
H-bonds in a single sheet				
O(5)-H(5)…O(21)	*0.82*	*1.94*	*2.759(12)*	*172.0*
O(17)-H(17)…O(8)	*0.82*	*2.16*	*2.865(11)*	*145.0*
H-bonds between the 2-fold interpenetrated sheets				
O3w…O2$^{\#1}$			*2.912(16)*	
H-bonds participating in the packing along the c axes				
O(3)-H(3)…O(5)$^{\#2}$	*0.82*	*2.26*	*2.981(10)*	*146.0*
O(11)-H(11)…O(5)$^{\#2}$	*0.82*	*2.27*	*3.080(13)*	*171.0*
O(18)-H(18)…O(17)$^{\#2}$	*0.82*	*1.96*	*2.646(10)*	*141.0*
O(23)-H(23)…O(21)$^{\#3}$	*0.82*	*2.17*	*2.823(9)*	*137.0*

[a] *Symmetry code: #1 x-1, y, z; #2 1/2+x, -y+1/2, -z+1/2; #3 -x+3/2, y-1/2, -z+1/2.*

Figure S1. H-bond interactions between the two-fold interpenetrated networks, involving the coordinated water molecule (O3w) and an O atom belonging to carboxylate group.

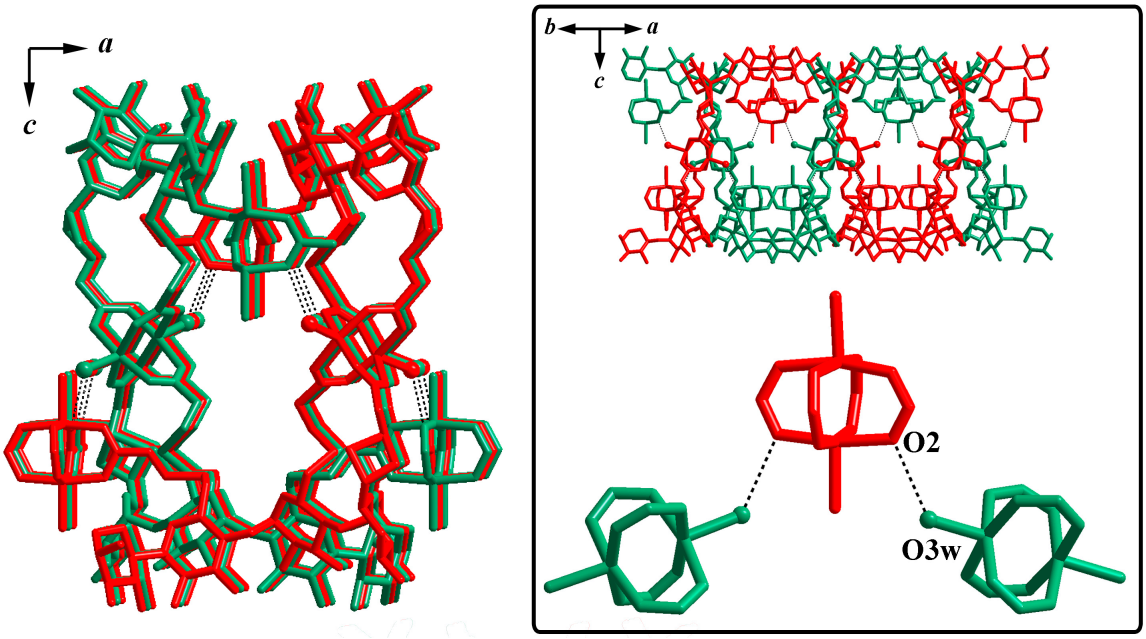

Figure S2. Representation of the accessible void volume of **Cu-SD**, showing that the free volume is mainly located inside the two-fold interpenetrated sheets.

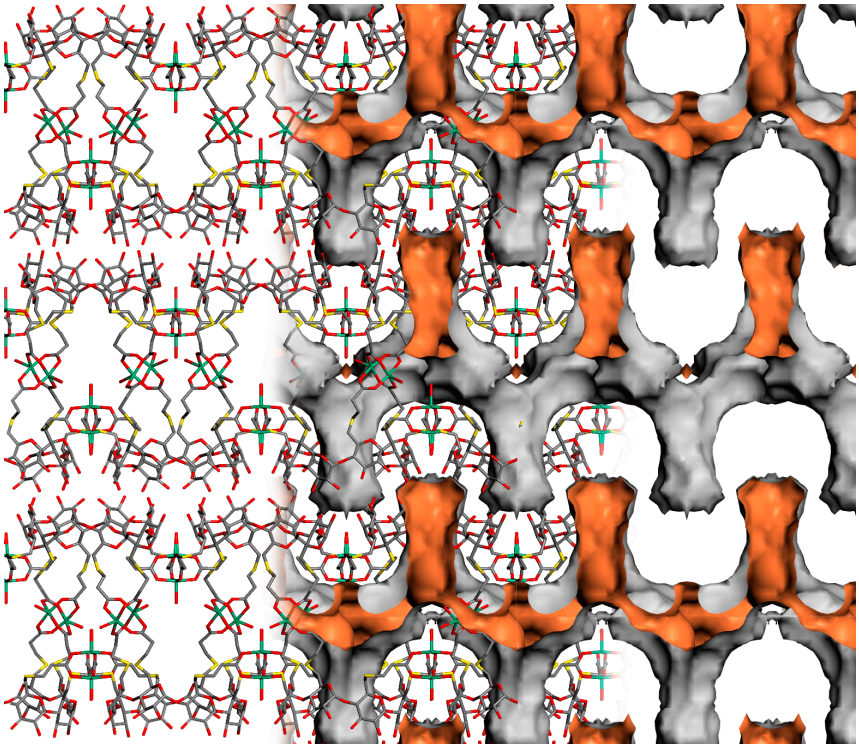

Figure S3. Thermogravimetric (TGA) analysis of **Cu-SD** after activation (80 ºC and high vacuum -0.05 torr- during 1 hour). Note that there is not any significant weight loss up to 200 ºC, confirming the removal of all guest water molecules. After 200 ºC, the structure of **Cu-SD** decomposes in two consecutive steps.

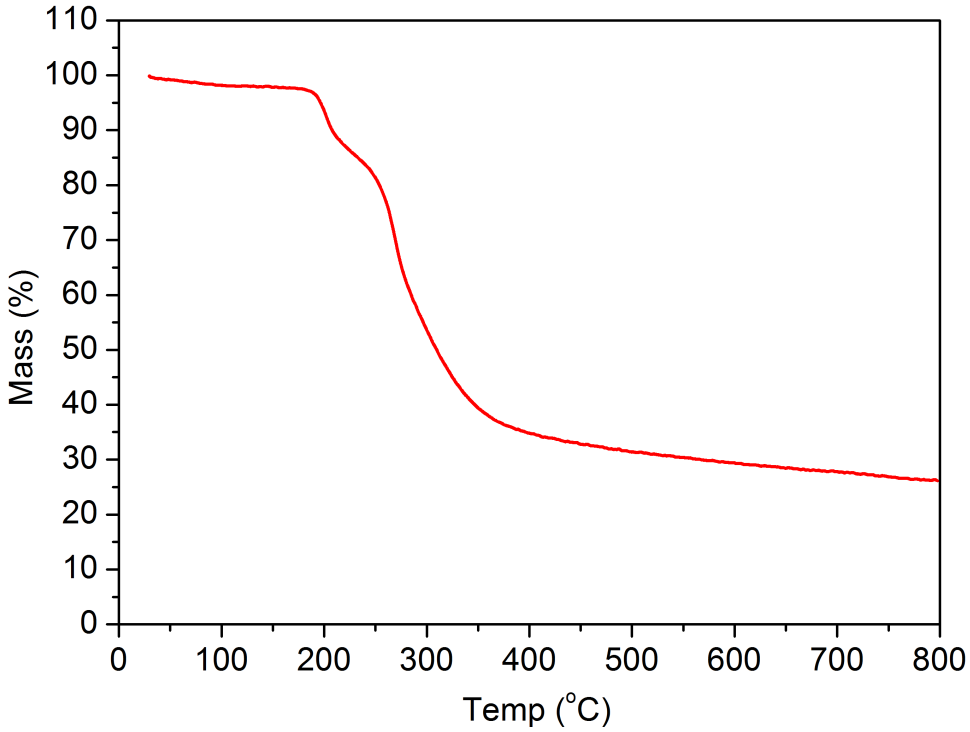

Figure S4. N2 (77 K, top) and CO2 (194 K, bottom) adsorption-desorption isotherms for **Cu-SD**. Solid and open symbols represent for adsorption and desorption, respectively.

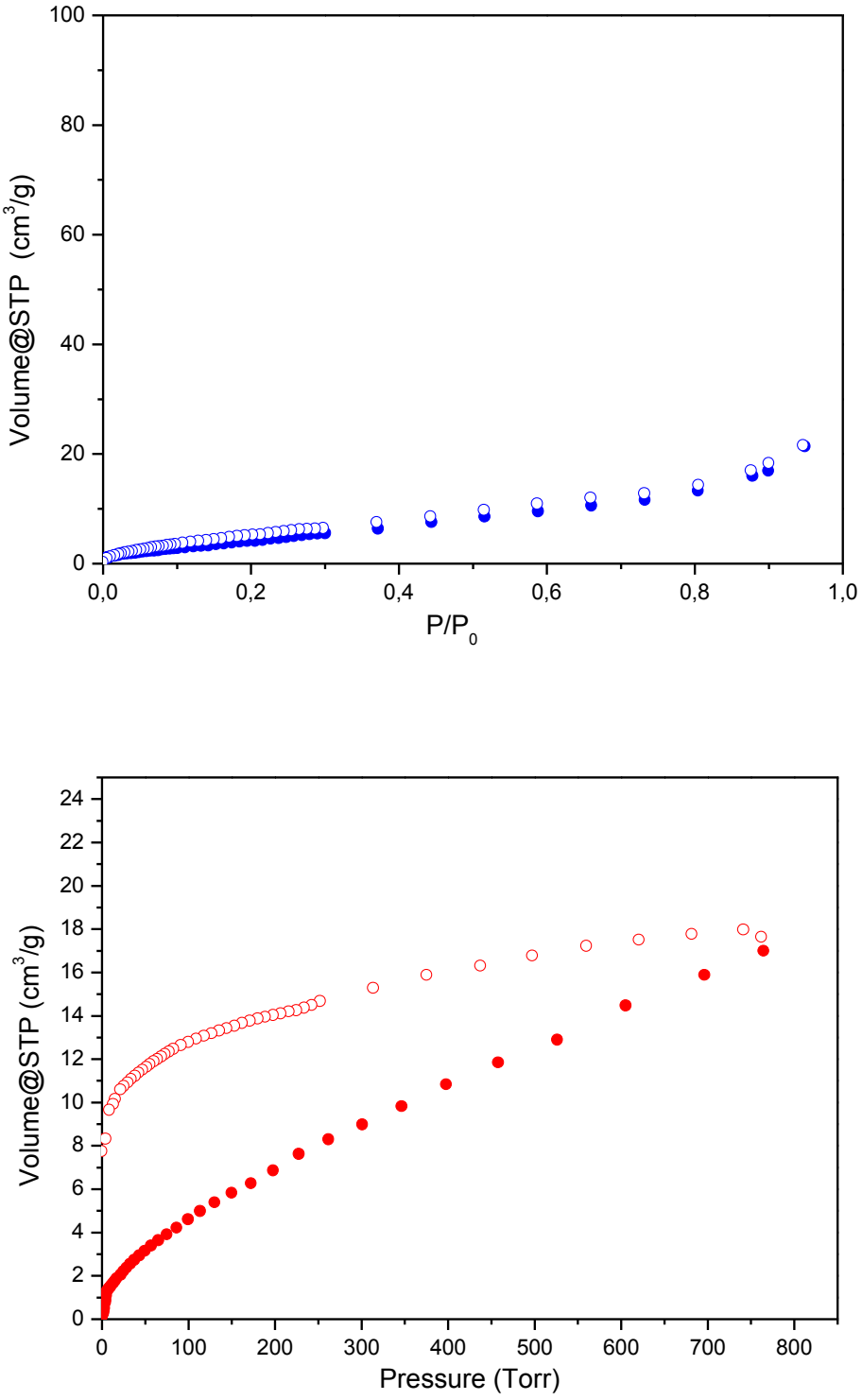

Figure S5. XRPD patterns of as-synthesized **Cu-SD** (red) and air-dried **Cu-SD** (brown), in comparison to those obtained when an air-dried **Cu-SD** was soaked in ethanol (green), acetonitrile (purple) and dimethylformamide (black).