Biogenic metal-organic frameworks: 2,5-furandicarboxylic acid as versatile building block

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Electronic Supplementary Information

Single crystal X-ray structure determination of Cu-FDA-1

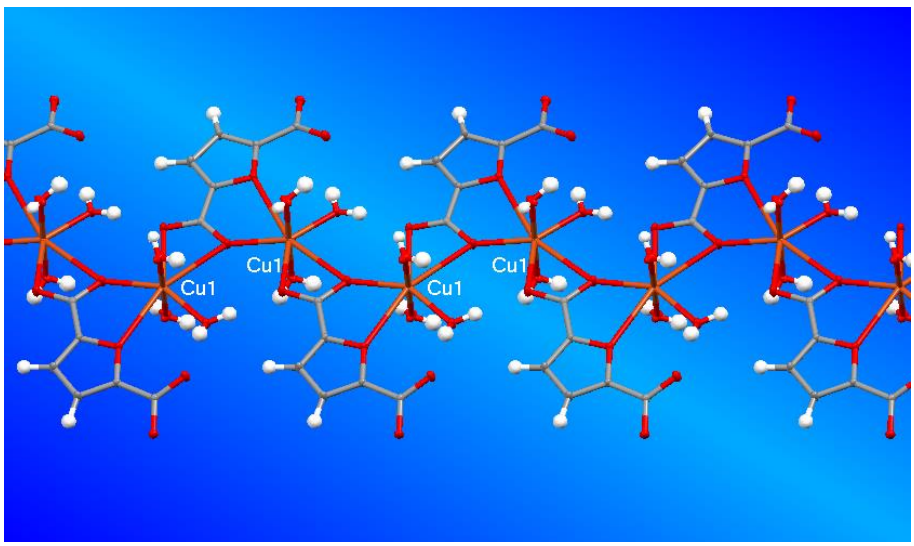

Figure S1. The crystal structure of Cu-FDA-1, viewed down [100], showing a section of the one dimensional coordination polymer, which extends along the [001] direction. Selected distances (Å) and angles (°): Cu1-O7 1.928(1), Cu1-O8 1.936(1), Cu1-O6 1.989(1), Cu1-O4 2.031(1), Cu1···O5 2.223(1), Cu1···O4* 2.656(1), Cu1···O1 2.797(1), O6···O2 2.714(1), O6···O5* 2.708(1), O4-Cu1-O5* 81.92(2), O5*-Cu1-O6 133.50(2), O4-Cu1-O6 144.33(2), O2···O6···C5* 117.6(1) [* indicates symmetry related atoms]. Atomic displacement ellipsoids are shown at the 50% probability level. H atoms are shown as circles with arbitrary radii.

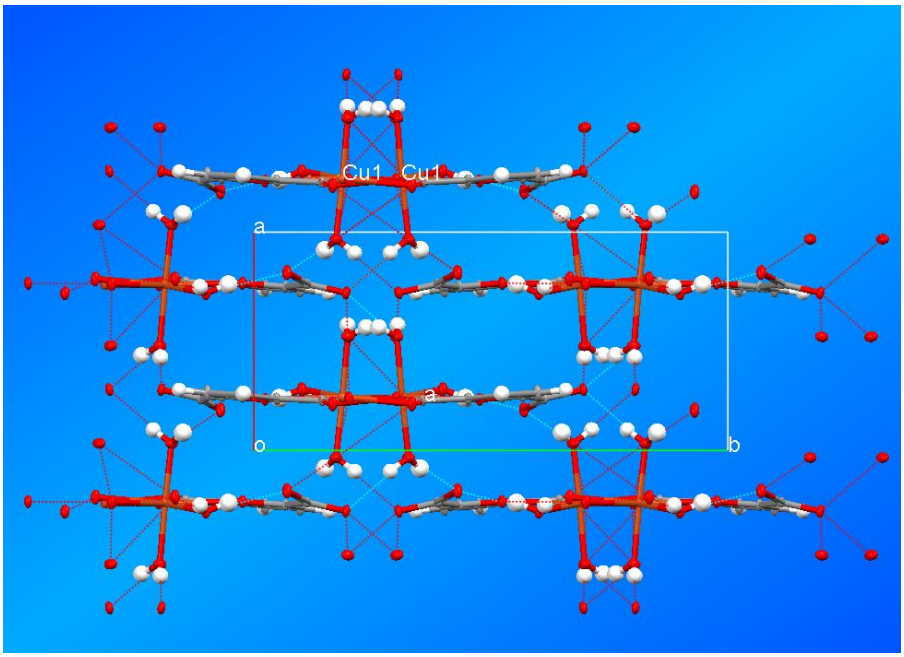

Figure S2. The arrangement of coordination polymer chains in the unit cell of Cu-FDA-1, viewed along the *c* axis. O2 and O3 are hydrogen bonded to O7 and O8 in neighbouring chains. Selected interchain hydrogen bond distances (Å) and angles (°): O7···O2* 2.702(1), O7···O3* 2.852(1), O8···O3* 2.678(1), O8···O3* 2.818(1), O2*···O7···O3* 116.8(1), O3*···O8···O3* 106.1(1) [* indicates symmetry related atoms]. Atoms are shown as circles with arbitrary radii. H atoms omitted for clarity.

X-ray Crystal Structure Analysis of Cu-FDA-1: $[C_6H_2CuO_5.3(H_2O)]_n$, M_r = 271.7 g · mol^{-1}, pale blue plate, crystal size 0.19 x 0.32 x 0.52 mm^3, monoclinic, space group $P2_1/c$, a = 6.9749(9) Å, 15.085(2) Å, c = 8.133(1) Å, β = 94.949(2)°, V = 852.5(2) Å^3, T = 160 K, Z = 4, D_{calc} = 2.117 g·cm^3, Mo-K$_\alpha$ X-radiation, λ = 0.71073 Å, μ = 2.587 mm^{-1}, Gaussian face-indexed absorption correction (T_{min} = 0.39408, T_{max} = 0.66461), scaling SADABS, Bruker AXS Kappa Mach3 AREX-II diffractometer, 2.70 < θ < 36.89°, 31971 measured reflections, 4160 independent reflections, 4079 reflections with $I > 2\sigma(I)$ (R_{int} = 0.0197). 99.9 % of the data were measured to 2θ of 70°:

INTENSITY STATISTICS FOR DATASET

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 2.51	65	67	97.0	9.00	102.1	113.45	0.0302	0.0089
2.51 - 1.64	155	157	98.7	11.13	106.2	129.19	0.0240	0.0072
1.64 - 1.30	217	217	100.0	11.71	73.1	128.43	0.0184	0.0070
1.30 - 1.13	215	215	100.0	11.07	51.1	115.99	0.0159	0.0073
1.13 - 1.02	227	228	99.6	10.15	35.0	106.77	0.0163	0.0079
1.02 - 0.95	219	220	99.5	9.40	31.8	100.95	0.0161	0.0082
0.95 - 0.90	188	188	100.0	8.88	26.8	91.97	0.0176	0.0087
0.90 - 0.85	235	236	99.6	8.58	22.6	88.97	0.0196	0.0092
0.85 - 0.81	232	232	100.0	7.97	19.6	83.67	0.0186	0.0096
0.81 - 0.78	198	198	100.0	7.91	14.7	72.47	0.0183	0.0100
0.78 - 0.75	248	248	100.0	7.29	13.4	71.46	0.0194	0.0107
0.75 - 0.73	182	182	100.0	7.11	11.5	62.17	0.0194	0.0117
0.73 - 0.71	214	214	100.0	6.75	10.3	59.98	0.0203	0.0118
0.71 - 0.69	212	212	100.0	6.55	10.3	59.72	0.0182	0.0122
0.69 - 0.67	268	268	100.0	6.21	10.4	53.25	0.0193	0.0130
0.67 - 0.66	138	138	100.0	6.36	6.9	46.91	0.0202	0.0147
0.66 - 0.64	301	301	100.0	5.79	8.9	49.22	0.0203	0.0146
0.64 - 0.63	160	161	99.4	5.51	10.1	54.21	0.0205	0.0143
0.63 - 0.62	190	190	100.0	5.22	6.3	40.37	0.0221	0.0179
0.62 - 0.61	206	206	100.0	4.95	7.9	43.83	0.0227	0.0175
0.61 - 0.59	223	363	61.4	1.52	6.2	26.16	0.0218	0.0281
0.69 - 0.59	1486	1627	91.3	4.76	8.2	44.93	0.0206	0.0164
Inf - 0.59	4293	4441	96.7	7.30	24.4	74.50	0.0198	0.0093

The structure solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.0184 [$I > 2\sigma(I)$], wR_2 = 0.0512, 168 parameters (G. M. Sheldrick, *Acta Cryst*. **A64**, 112 (2008)). The positions of the H atoms were refined together with their isotropic atomic displacement parameters, S = 1.116, residual electron density +0.61 / -0.62 e Å^{-3}.

Assignment of the XRD peaks of Cu-FDA-1 (2θ = 0-30°) according to the crystal structure deposited in the Cambridge Crystallographic Data Centre (CCDC deposition number 909483)

2θ / °	**h,k,l**
11.7	0,2,0
12.7	1,0,0
14.0	1,1,0
16.1	1,0,-1
17.2	1,1,-1
18.5	1,1,1

20.8	0,3,1
21.8	0,0,2
22.8	0,1,2
23.6	0,4,0
24.0	1,3,-1
24.5	1,0,-2
24.9	1,3,1
25.6	2,0,0
26.1	0,4,1
26.4	1,0,2
27.2	1,2,-2
28.3	0,3,2
29.0	1,2,2

Supplementary Figures and Tables

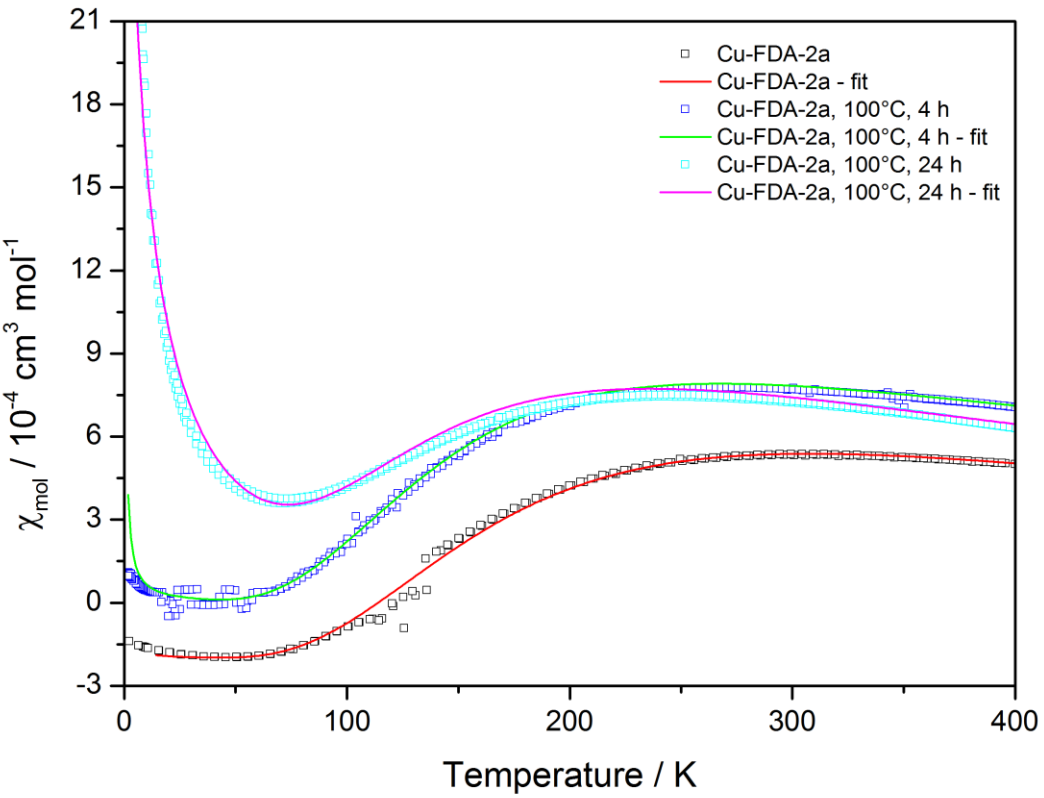

Figure S3. Results of the SQUID measurements: the magnetic susceptibility vs. temperature for Cu-FDA-2a as prepared and treated at 100 °C under vacuum for 4 and 24 h, respectively. The intra-dimer spin-exchange constants are J_{ex} = -493 K for Cu-FDA-2, J_{ex} = -433 K for 4 h heating time and J_{ex} = -416 K for 24 h heating time.

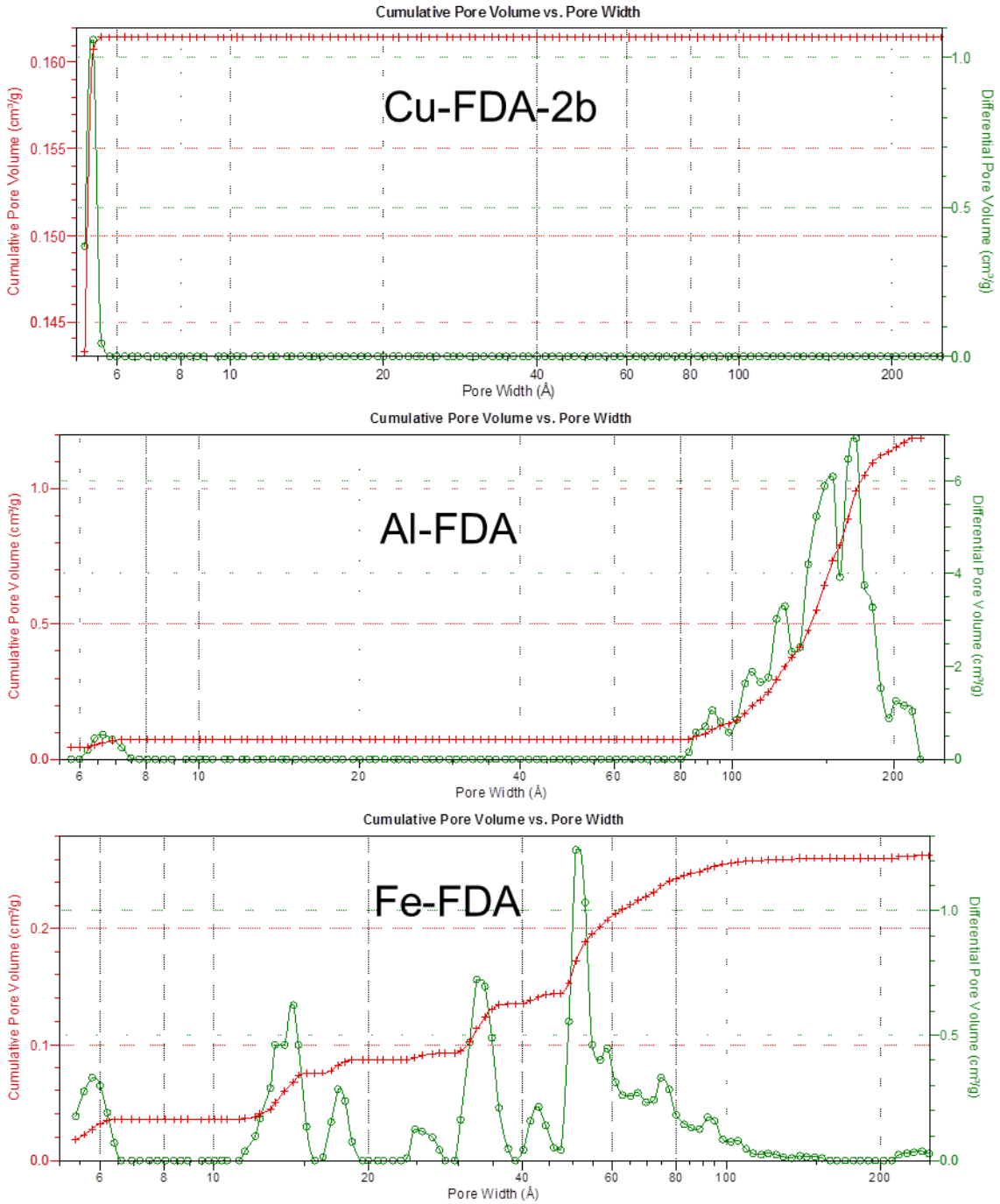

Figure S4. Pore size distribution of Cu-FDA-2b, Al-FDA and Fe-FDA determined from the nitrogen physisorption data using the following DFT model of the company Micromeritics: N_2@77K-CarbFinitePores, AS=6, 2D-NLDFT.

Table S1. Experimental results of the elemental analysis ([a] composition according to C/metal ratio, [b] composition corresponds to one coordinated DMF molecule per Cu ion (theoretical composition: C=37.2%, H=3.1%, N=4.8%, Cu=21.9%) since Cu-FDA-2a was not degassed under vacuum and heating).

	C / wt-%	H / wt-%	N / wt-%	Metal / wt-%	Composition[a]
Cu-FDA-1	26.43	2.48	0.00	22.38	$Cu_1(FDA)_{1.04}$
Cu-FDA-2a	33.84	3.35	4.08	19.70	$Cu_1(FDA)_1(DMF)_1$[b]
Cu-FDA-2b	27.49	2.89	0.00	27.13	$Cu_1(FDA)_{0.89}$
Al-FDA	33.19	3.55	4.66	9.90	$Al_1(FDA)_{1.26}$
Fe-FDA	30.42	2.77	3.81	23.39	$Fe_1(FDA)_{1.01}$

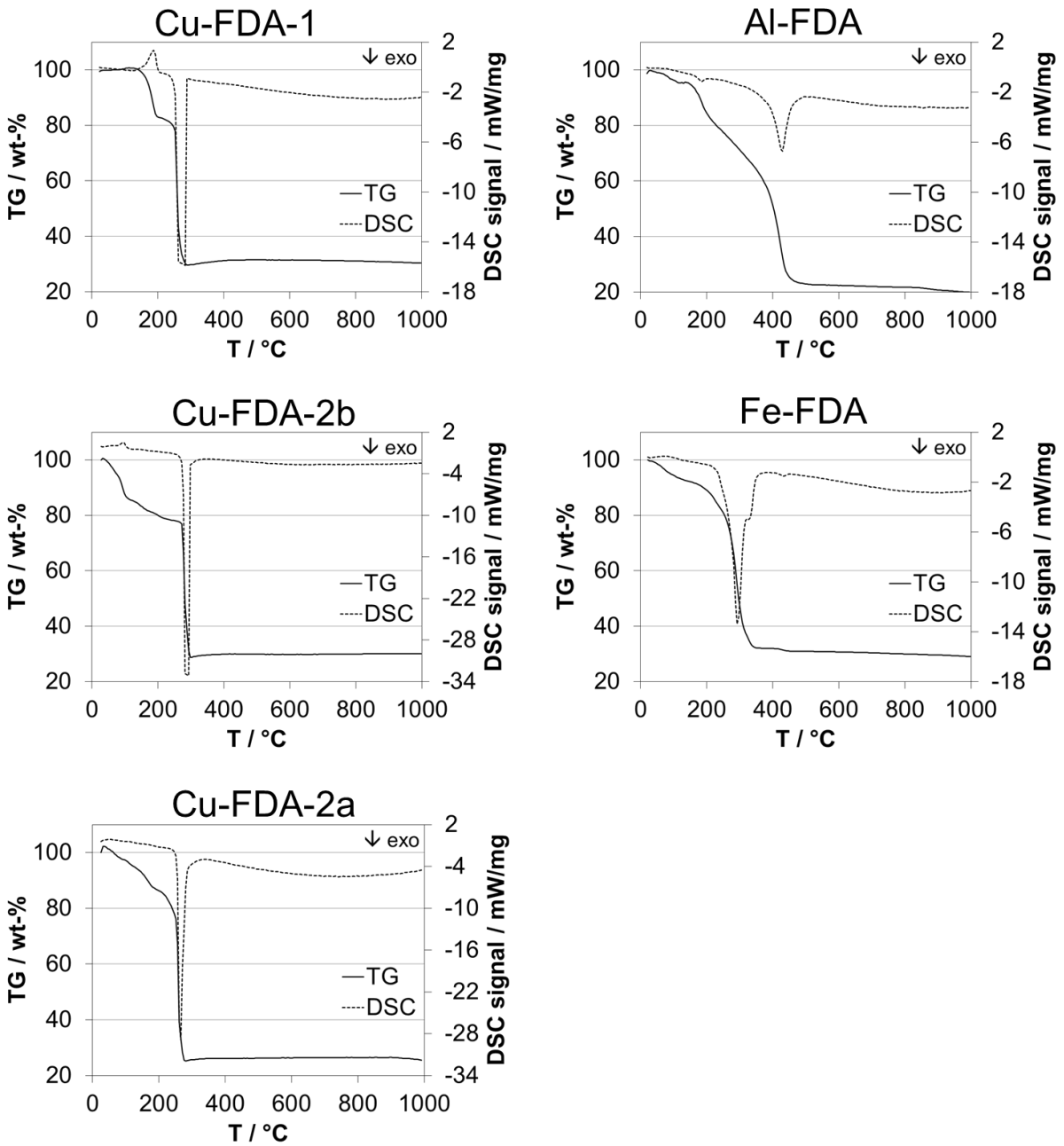

Figure S5. TG (full line) and DSC (dotted line) analysis of Cu-FDA-1, Cu-FDA-2a and -2b, Al-FDA and Fe-FDA in air.

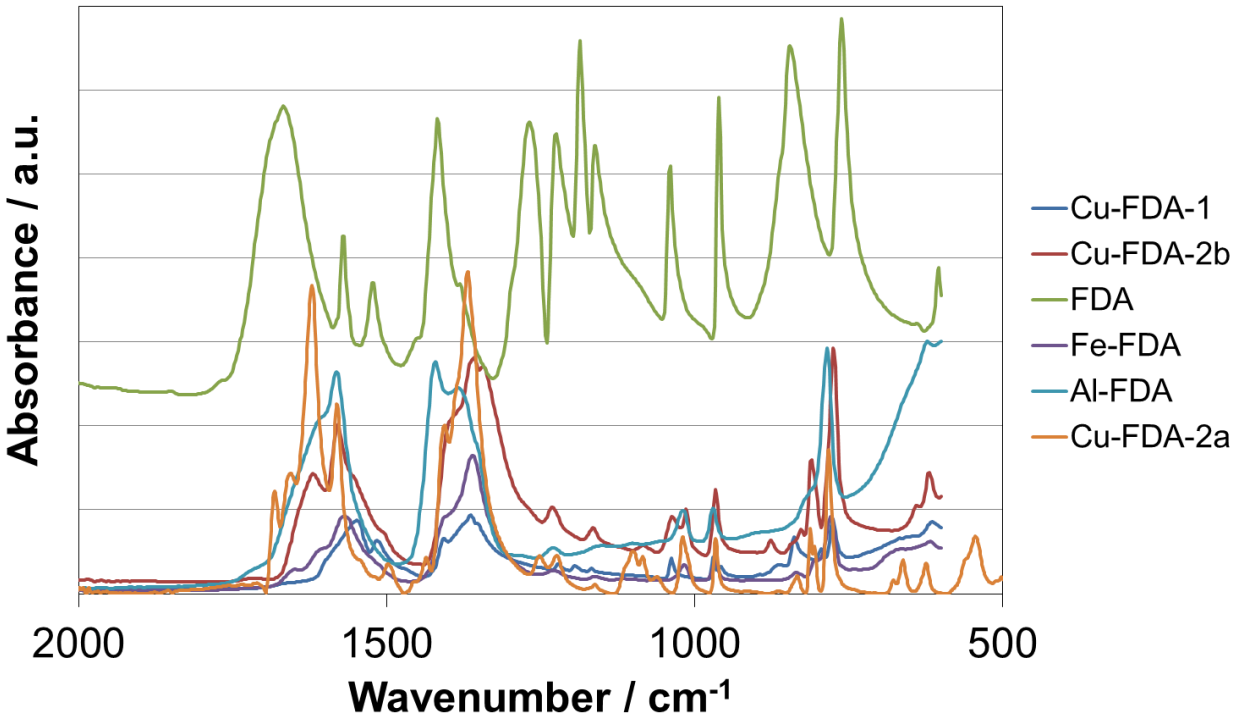

Figure S6. FT-IR spectra measured in ATR mode of Cu-FDA-1, Cu-FDA-2a, Cu-FDA-2b, Al-FDA, Fe-FDA and pure FDA for comparison. No distinct IR absorption bands indicating significant amounts of residual nitrate ions or DMF can be identified.