

# Fructose-Based Metal–Organic Framework as a Means to Synthesize Sr-Loaded Chitosan Nanospheres with NLO Properties for Theranostic Applications in Radiotherapy

Alma Cioci <sup>1,\*</sup>, Paola Benzi <sup>1,2</sup>, Carlo Canepa <sup>1</sup>, Leonardo Mortati <sup>3</sup>, Antonio Alvarez de la Paz <sup>4</sup>, Itzel Marisol Garnica-Palafox <sup>4</sup>, Francisco Manuel Sánchez-Arévalo <sup>4</sup>, Roberto C. Dante <sup>5</sup> and Domenica Marabello <sup>1,2,\*</sup>

<sup>1</sup> Dipartimento di Chimica, University of Torino, 10124 Torino, Italy; paola.benzi@unito.it (P.B.); carlo.canepa@unito.it (C.C.)

<sup>2</sup> Crisdi-Interdepartmental Center for Crystallography, University of Torino, 10124 Torino, Italy

<sup>3</sup> INRIM—Istituto Nazionale di Ricerca Metrologica, 10135 Torino, Italy; l.mortati@inrim.it

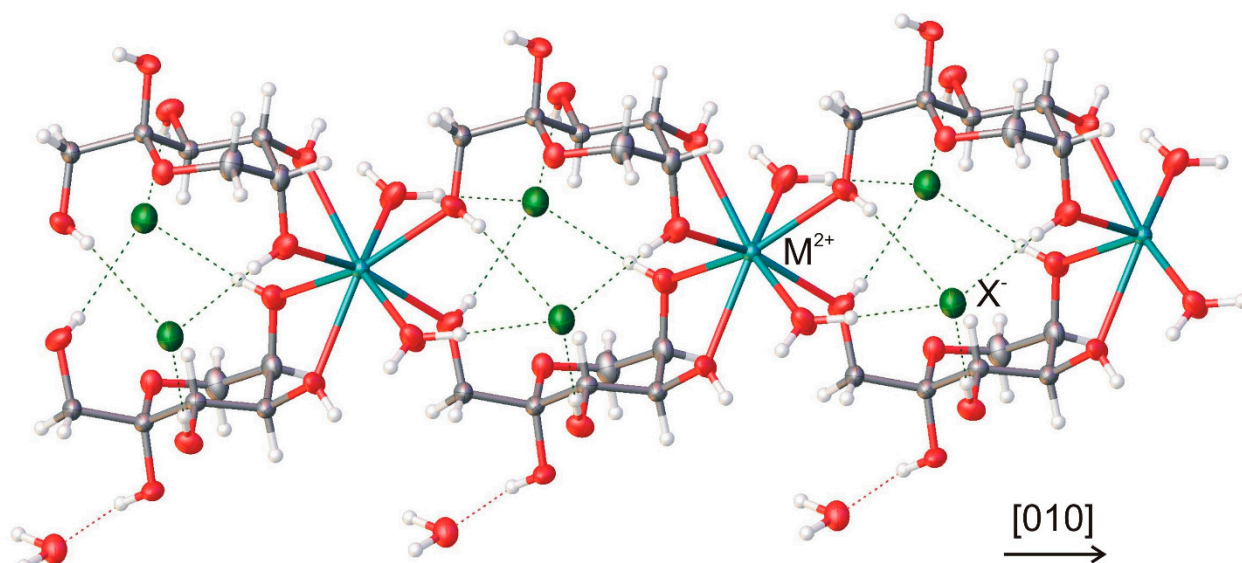
<sup>4</sup> Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, México 04510, Mexico; antonio.adlp@iim.unam.mx (A.A.d.l.P.); marisol.garnica@gmail.com (I.M.G.-P.); fsanchez@materiales.unam.mx (F.M.S.-A.)

<sup>5</sup> R&D Laboratory, 2Dto3D S.r.l.s., Via G. Quarello 15/a, 10135 Turin, Italy; rcdante@2dto3dmaterials.com

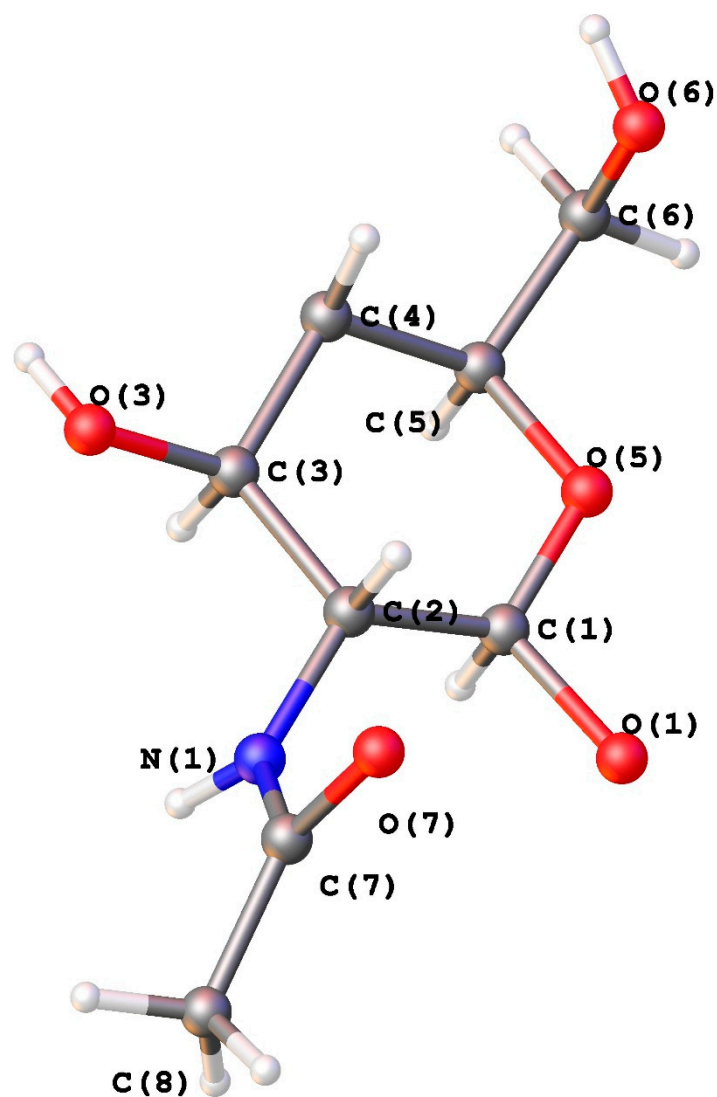
\* Correspondence: alma.cioci@unito.it (A.C.); domenica.marabello@unito.it (D.M.)

## X-ray Diffraction Structure of the SrFruCl MOF.

The asymmetric unit of the SrFruCl MOF contains one fructose molecule, one-half of a calcium ion, one chloride, one water molecule coordinated to the calcium ion, and one-half of a free water molecule. In the crystal packing, two fructose molecules bridge two metal ions, and an infinite thread of fructose and calcium ions develops in the [010] direction (Figure 1s). Consequently, this compound is a uni-dimensional Metal Organic Framework (1D-MOF) of a particular type, since the multi-dentate ligand is a neutral molecule (fructose), while the metal atom is charged +2. The halogen ions and the free water molecules are inserted between the Ca-fructose threads, strictly connected through strong hydrogen bonds to the sugar molecules and to the water molecules coordinated to the metal. Those bonds contribute to stabilize the crystal.



**Figure S1.** The infinite network of metal and halogen ions and sugar molecules for the structure of the SrFruCl MOF. Red=oxygen, grey=carbon, white=hydrogen, light blue=Sr, green=Cl.



**Figure S2.** X-ray molecular structure of chitin, downloaded from the crystallographic CSD databank (CCDC 1425611), with non-hydrogen atoms labelled.

**Table S1.** Crystal data of chitin (CCDC 1425611).

Crystal System	Monoclinic
Space group	P112 <sub>1</sub>
a/Å	4.8190(10)
b/Å	9.239(2)
c/Å	10.384(2)
$\alpha/^\circ$	90.00
$\beta/^\circ$	90.00
$\gamma/^\circ$	97.16(5)
Z	2

**Computational Details****Table S2.** Computationally optimized coordinates (Å) for **FRAG1** (E(RB3LYP) = −1410.81134050).

Center Number	Atomic Number	Atomic Type	Coordinates		
			X	Y	Z
1	6	0	1.992575	−2.49954	−1.79752
2	1	0	2.456324	−3.15381	−1.04928
3	6	0	0.733812	−1.87151	−1.17277
4	1	0	−0.02303	−3.56253	−1.64011
5	6	0	1.087744	−1.12964	0.135741
6	1	0	0.959668	−1.83291	0.971222
7	6	0	2.560932	−0.67045	0.090846
8	1	0	3.202249	−1.49847	0.420288
9	8	0	−4.81781	0.716421	0.050153
10	8	0	−0.21722	−2.90363	−0.93731
11	8	0	2.932683	−0.30893	−1.25565
12	6	0	2.894351	0.545277	0.949976
13	1	0	2.622987	0.355339	1.992643
14	8	0	4.286995	0.808129	0.923987
15	6	0	3.012795	−1.40775	−2.14699
16	8	0	4.280944	−2.02142	−2.13575
17	6	0	−0.94354	−0.17424	1.060698
18	6	0	−1.40941	1.218378	1.555013
19	1	0	−1.0116	1.967365	0.866345
20	6	0	−2.94911	1.278047	1.504056
21	6	0	−3.45213	1.110308	0.065972
22	1	0	−3.33626	2.081998	−0.44122
23	6	0	−2.57703	0.069765	−0.66075
24	1	0	−1.78925	0.596906	−1.21409
25	6	0	−3.29545	−0.85271	−1.64032
26	1	0	−3.83856	−0.25475	−2.37859
27	8	0	0.26199	0.020834	0.355667
28	8	0	−3.45511	2.519273	1.982158
29	8	0	−1.94371	−0.80025	0.300653
30	8	0	−2.36608	−1.65543	−2.34246
31	7	0	1.581168	−3.36904	−2.90045
32	1	0	1.294206	−2.81957	−3.71059
33	1	0	2.352464	−3.96428	−3.19295
34	1	0	4.518115	0.887054	−0.01589
35	1	0	−1.83814	−2.14587	−1.67804

36	1	0	−3.20631	2.590031	2.918362
37	7	0	−0.89514	1.514133	2.882047
38	1	0	−0.96091	0.790147	3.590101
39	6	0	−0.24911	2.648429	3.335277
40	6	0	−0.07033	3.787402	2.345045
41	1	0	0.598945	3.497636	1.526375
42	1	0	0.371132	4.628068	2.881082
43	1	0	−1.02775	4.088881	1.907273
44	1	0	2.310732	1.405533	0.597609
45	1	0	−4.03225	−1.45329	−1.08976
46	1	0	4.935496	−1.35779	−2.40773
47	8	0	0.140711	2.711461	4.492098
48	1	0	0.316148	−1.12928	−1.86978
49	1	0	−5.30186	1.392904	0.551499
50	1	0	−3.35832	0.443137	2.092538
51	1	0	−0.77292	−0.85449	1.907343
52	1	0	2.795904	−0.97447	−3.13466

Table S3. Computational optimized coordinates (Å) for FRAG2 (E(RB3LYP) = −1871.63065312).

Center Number	Atomic Number	Atomic Type	Coordinates		
			X	Y	Z
1	8	0	0	0	0
2	6	0	0	0	1.416637
3	6	0	1.443821	0	1.976571
4	6	0	2.412122	0.485746	0.881744
5	6	0	2.390569	−0.46532	−0.31718
6	6	0	0.937713	−0.91885	−0.58489
7	8	0	−0.66212	−1.10655	1.970498
8	6	0	−2.09756	−1.07478	1.991089
9	6	0	−2.69473	−1.73349	0.72528
10	6	0	−4.10278	−2.24255	1.045886
11	6	0	−4.09674	−3.32575	2.165882
12	8	0	−2.91544	−3.18377	2.920487
13	6	0	−2.61355	−1.81277	3.247454
14	7	0	−4.74303	−2.74894	−0.20318
15	8	0	−2.82369	−0.85798	−0.37967
16	6	0	−1.6519	−1.8791	4.429518
17	8	0	−2.29097	−2.44517	5.554987
18	8	0	−5.19121	−3.22466	3.011953
19	7	0	1.549482	0.798486	3.184289
20	6	0	2.06742	0.450305	4.421508
21	8	0	2.040608	1.254789	5.339187
22	8	0	3.75675	0.53887	1.335771
23	8	0	2.930747	0.161398	−1.47274
24	6	0	0.589442	−1.01129	−2.05861
25	8	0	−0.72783	−1.57243	−2.1411
26	6	0	2.666992	−0.93854	4.55831
27	17	0	−7.38674	−3.45361	0.744754
28	1	0	−4.73414	−1.40939	1.370005
29	1	0	−1.97741	−0.85678	−0.87514
30	1	0	−2.4309	−0.02801	2.020922

---

31	1	0	−3.53602	−1.32893	3.591349
32	1	0	−1.32815	−0.87233	4.711372
33	1	0	1.701502	−1.03044	2.232599
34	1	0	2.993014	−1.34858	−0.05238
35	1	0	0.782682	−1.90632	−0.13051
36	1	0	1.319756	−1.64901	−2.57115
37	1	0	−4.62368	−2.03093	−0.92668
38	1	0	−2.7385	−3.2475	5.236063
39	1	0	−1.03322	−1.49213	−3.05743
40	1	0	3.790685	1.178885	2.065954
41	1	0	1.141804	1.728014	3.178976
42	1	0	1.900003	−1.71319	4.442242
43	1	0	3.098919	−1.01719	5.556289
44	1	0	3.443674	−1.11481	3.8063
45	1	0	−0.76182	−2.45165	4.12998
46	1	0	0.626856	−0.01172	−2.50422
47	1	0	−6.0182	−3.35153	2.47994
48	1	0	−2.05168	−2.59017	0.474818
49	1	0	3.818204	0.470888	−1.22702
50	1	0	2.083953	1.473925	0.52467
51	1	0	−0.52404	0.927737	1.682133
52	1	0	−4.01968	−4.32716	1.708499
53	1	0	−5.82605	−2.98593	0.011315
54	1	0	−4.2933	−3.60712	−0.53412

---

**Disclaimer/Publisher’s Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.