Electronic Supplementary Material (ESI) for CrystEngComm.

Hexahalorhenate(IV) Salts of Protonated Ciprofloxacin: Antibiotic-Based Single-Ion Magnets

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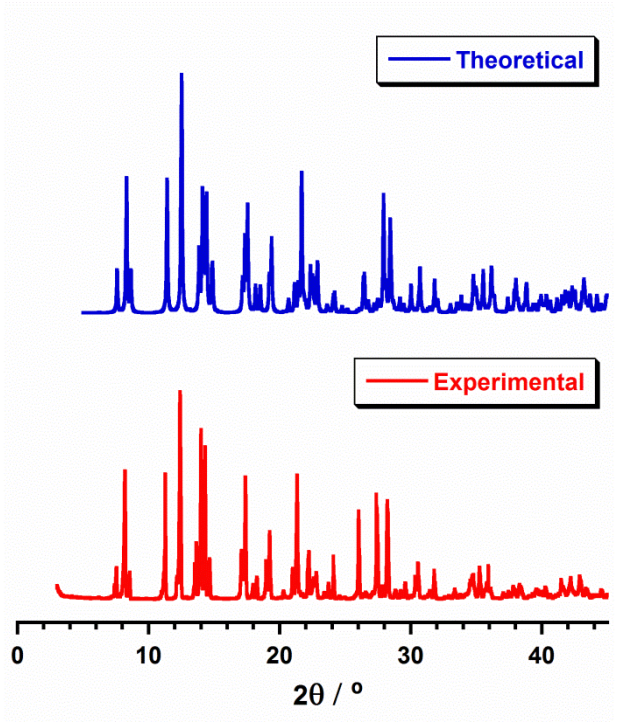

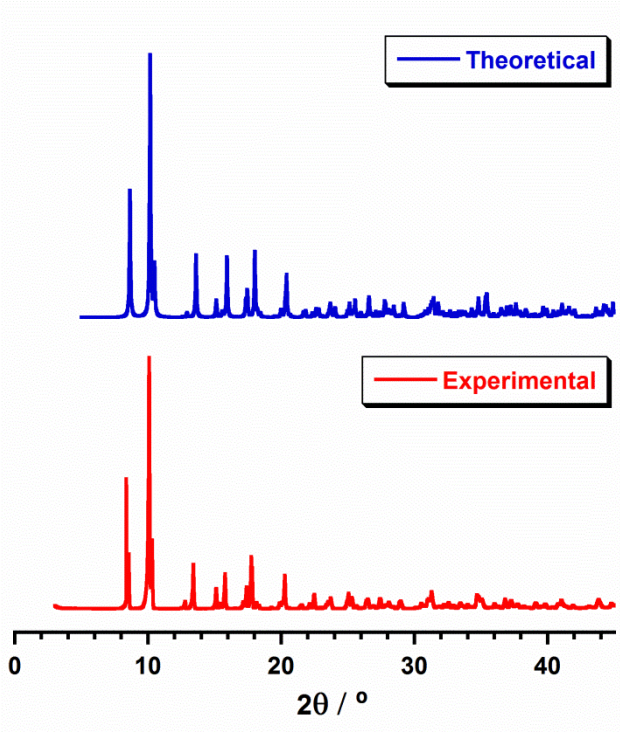

Figure S1. Plot of the theoretical and experimental XRD patterns profile (2θ/°) in the range 0-45° for compounds **1** (top) and **2** (bottom).

Table S1. Summary of the crystal data and structure refinement parameters for 1 and 2.

Compound	1	2
CCDC	2112864	2112865
Formula	$C_{34}H_{41}Cl_7F_2N_6O_7Re$	$C_{34}H_{38}Br_6F_2N_6O_6Re$
M_r/g mol^{-1}	1118.08	1330.36
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	*Pbca*
a/Å	15.357(1)	16.864(1)
b/Å	20.431(1)	11.704(1)
c/Å	13.482(1)	20.444(1)
α/°	90	90
β/°	112.67(1)	90
γ/°	90	90
V / Å^3	3903.1(3)	4035.3(2)
Z	4	4
D_c/g cm^{-3}	1.903	2.190
μ(Mo-K$_\alpha$)/mm^{-1}	3.660	9.013
F(000)	2220	2540
Goodness-of-fit on F^2	1.095	1.050
R_1 [$I > 2\sigma(I)$] / (all data)	0.0127 / 0.0139	0.0192 / 0.0329
wR_2 [$I > 2\sigma(I)$] / (all data)	0.0360 / 0.0371	0.0280 / 0.0354
$\Delta\rho$ peak and hole / e.Å^{-3}	0.493 and -0.808	0.441 and -0.387

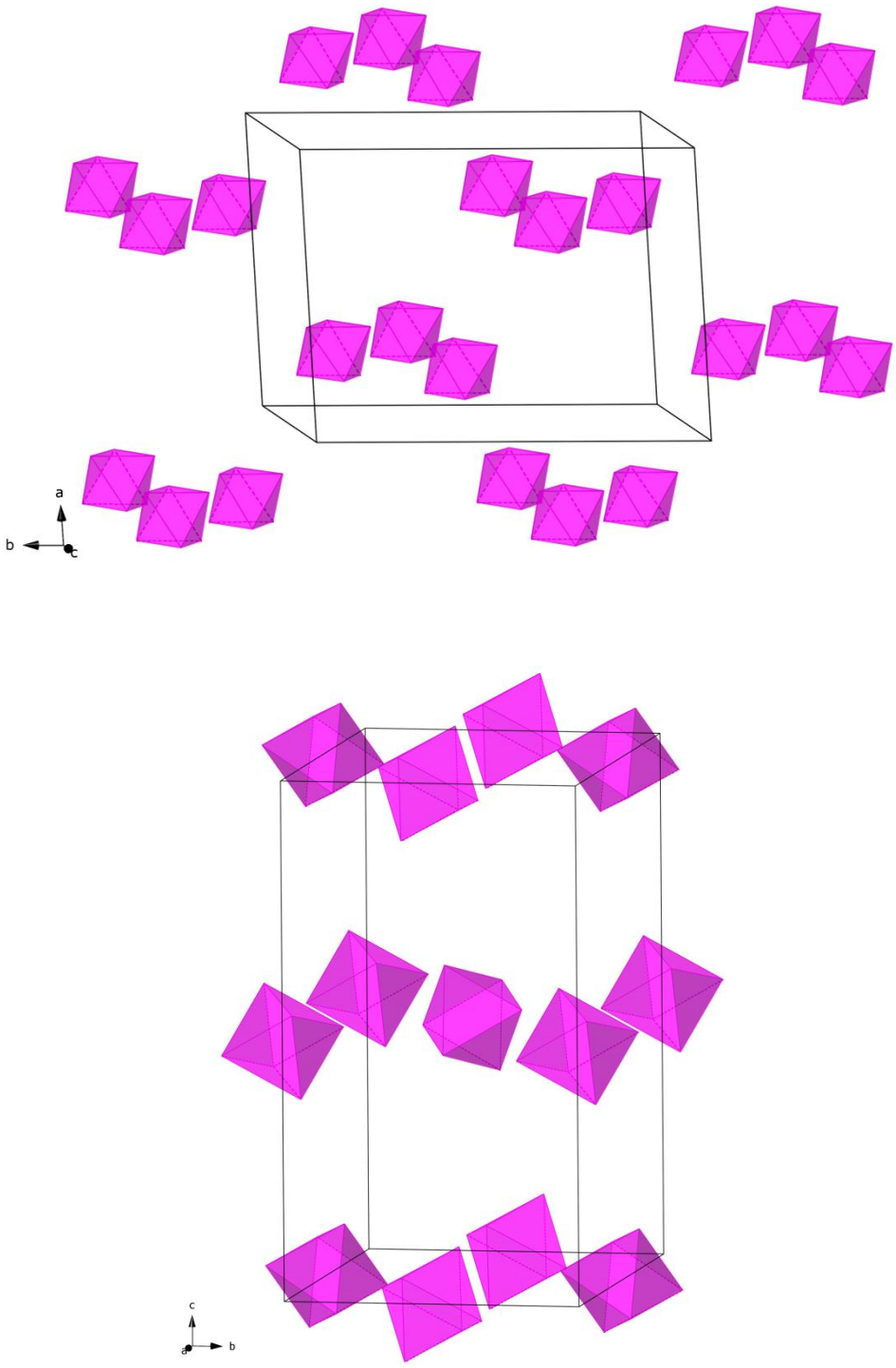

Figure S2. Perspective view of the arragment of adjacent $[ReX_6]^{2-}$ [X = Cl(**1**) and Br(**2**)] anions (pink polyhedra) in the crystal of **1** (top) and **2** (bottom). Crystallization water molecules and Cl^- anions (**1**) and protonated organic cations (**1** and **2**) have been omitted for clarity.

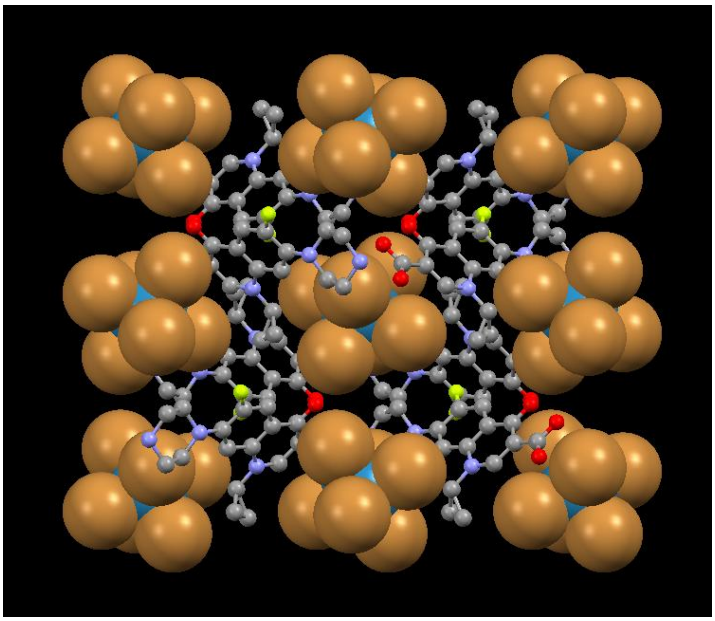

Figure S3. Perspective view along the *b*-axis direction of the packing between $[Hcip]^+$ cations (ball-and-stick model) and $[ReBr_6]^{2-}$ anions (space-filling model) in the crystal of **2**.

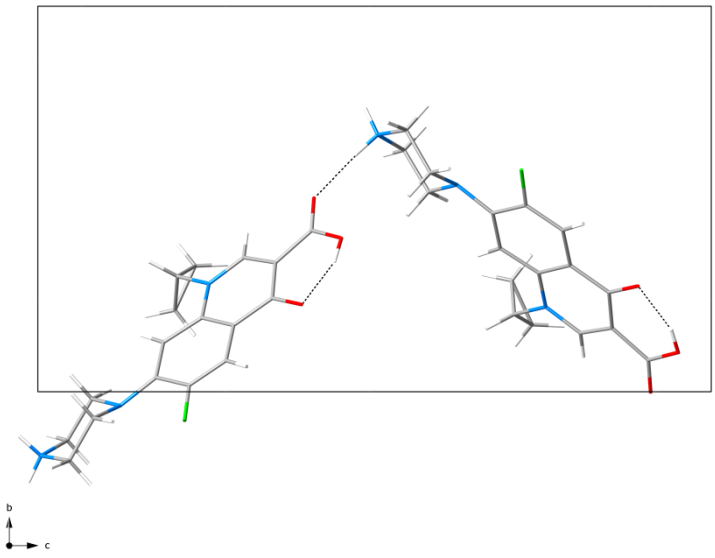

Figure S4. Detail of the H-bonding interaction between neighboring -COOH and $-NH_2$ groups connecting the $[Hcip]^+$ cations in the crystal structure of **2** [O(1)···N(3e) distance of *ca*. 2.85(1) Å; (e) = x, 1/2-y, -1/2+z].

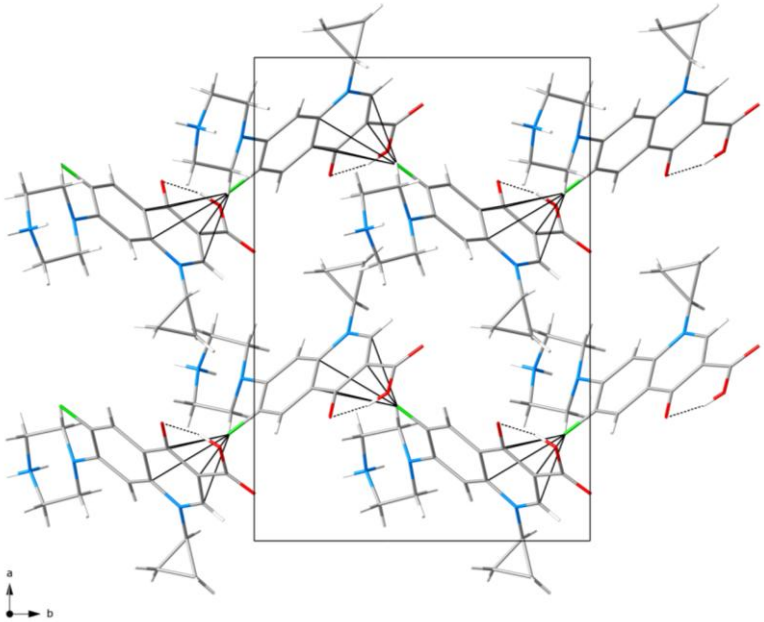

Figure S5. View along the *c*-axis direction of the intermolecular π···F type interactions (solid lines) involving quinoline rings and fluorine atoms of adjacent $[Hcip]^+$ cations in the crystal structure of **2** [the shortest centroid···fluorine distance being approximately 2.95(1) Å; (f) = -x+1/2, y+1/2, z].

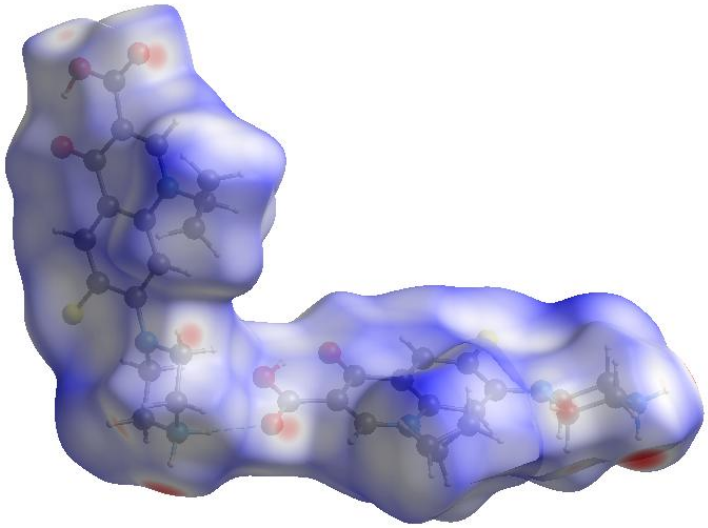

Figure S6. Hirshfeld surface mapped with d_{norm} function for two $[Hcip]^+$ cations interacting through -COOH and $-NH_2$ groups in compound **2**.

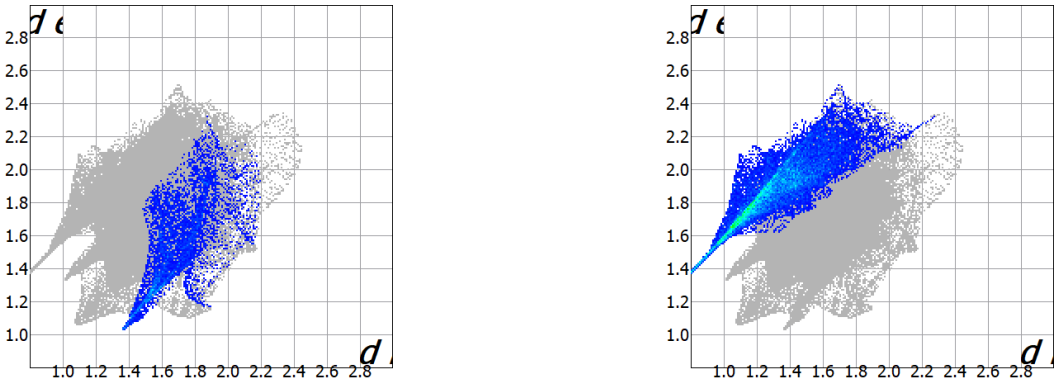

Figure S7. Intermolecular O···H (left) and Cl···H (right) interactions highlighted from the full fingerprint of the Hirshfeld surface of compound **1**.

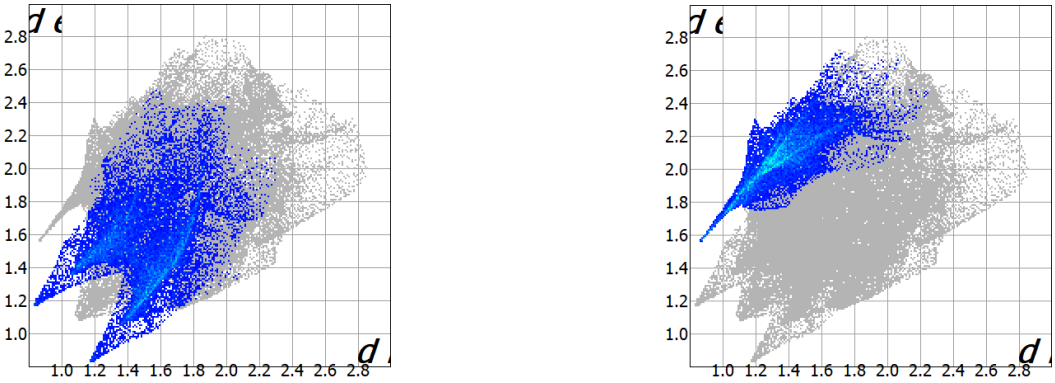

Figure S8. Intermolecular O···H (left) and Br···H (right) interactions highlighted from the full fingerprint of the Hirshfeld surface of compound **2**.

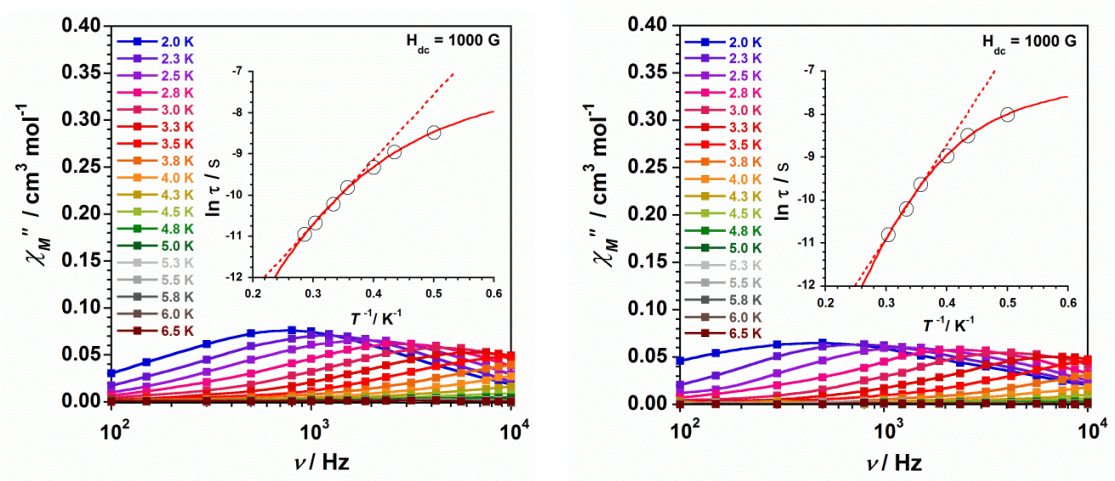

Figure S9. Frequency dependence of the out-of-phase ac susceptibility signals under a dc field of 1000 G for **1** (left) and **2** (right). The inset shows the ln(τ) *versus* 1/T plot with the fit to the Arrhenius law (dashed line) and the fit considering the contribution of two mechanisms (direct + Raman).

Table S2. Energy barrier (U_{eff}) and preexponential factor (τ_o) values obtained through the dc applied magnetic fields of 1000 and 5000 G and the Arrhenius law for 1 and 2.

Compound	H_{dc} / G	U_{eff} / K	τ_o / s
1	1000	15.8	1.94×10^{-7}
	5000	15.0	3.41×10^{-7}
2	1000	19.7	2.80×10^{-8}
	5000	17.3	1.62×10^{-7}

Table S3. Parameters of the magnetic relaxation obtained through dc applied magnetic fields of 1000 and 5000 G and considerating Direct and Raman processes for 1 and 2.

Compound	H_{dc} / G	A / $s^{-1}K^{-1}$	C / $s^{-1}K^{n}$	n
1	1000	1242.4	45.5	5.6
	5000	2536.4	11.2	6.3
2	1000	1065.6	3.2	8.0
	5000	2152.0	2.9	7.6

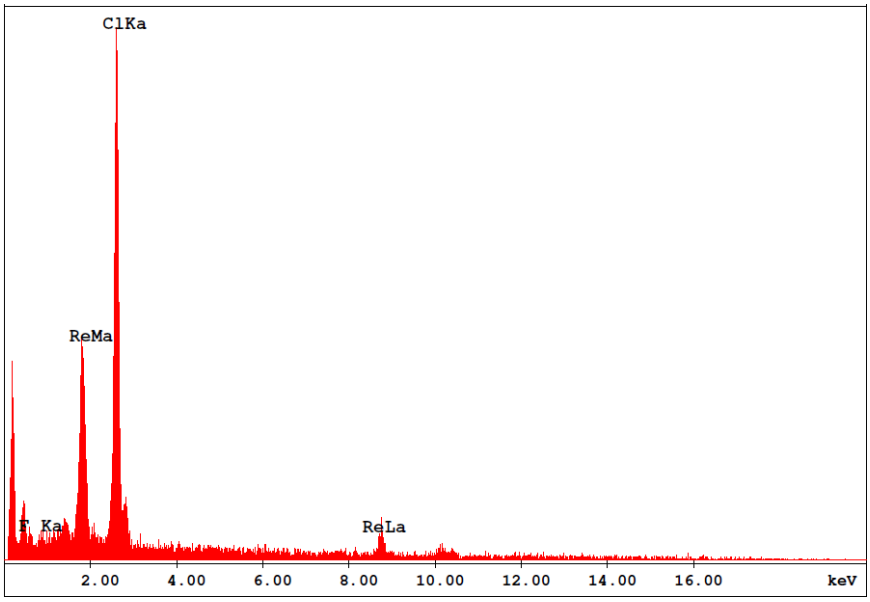

Figure S10. SEM-EDX spectrum for compound **1**.

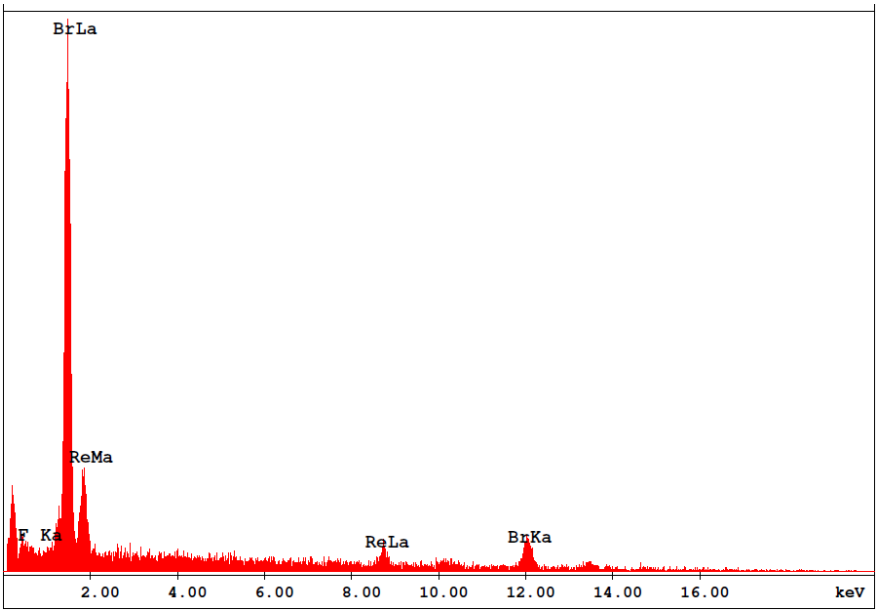

Figure S11. SEM-EDX spectrum for compound **2**.