Experimental

Synthesis and chemical analysis

BioMIL-1 (BioMIL stands for Bioactive Material Institut Lavoisier) was prepared as single crystals (75 x 15 x 10 µm) from a reaction mixture of composition iron(III) acetate ($Fe^{III}_3O(ClO_4)(CH_3CO_2)_6$):[21] nicotinic acid ($CC_5H_4N$): dimethylformamide (DMF) = 1 : 5.4 : 580 heated at 140°C in a Teflon-lined autoclave for 24 hours. The solid was recovered by filtration and washed with deionised water.

Structure determination

The crystal structure of the title phase $Fe_2^{III}Fe_{1-x}^{III}Fe_x^{II}O(OH)_y[O_2C\text{-}C_5H_4N]_5[O_2CCH_3]$ (x~0.45, y~0.55); BioMIL-1 was determined by laboratory single crystal X-ray diffraction. Intensity data from a crystal of dimensions 0.2 x 0.2 x 0.1 mm was obtained on a Siemens SMART diffractometer equipped with a Mo anode, a graphite monochromator and a CCD camera detector. The data reduction was performed using the SAINT program[22] and the absorption correction was performed using the SADABS software.[22] The structure was solved and refined by full-matrix least-squares techniques, based on F2, using the SHELX software package.[23] The iron and oxygen atoms were located by direct methods and all other non-hydrogen atoms (C, N) placed from subsequent Fourier-difference map calculations. The hydrogen atoms were placed with geometrical restraints in the riding mode and refined anisotropically. The final refinement converged at R1(F)~0.103 and wR2(F2)~0.315 for 2737 reflections with $F_o > 4\sigma(F_o)$ and 480 parameters, highest residual e^- density, 1.43, deepest hole -0.95. Crystal data and details of the data collection are summarized in Table S1.

Table S1 Experimental and crystallographic parameters for the structure analysis of $Fe_2^{III}Fe_{1-x}^{III}Fe_x^{II}O_{1-y}(OH)_y[O_2C\text{-}C_5H_4N]_5[O_2CCH_3]$ (x~0.15) or BioMIL-1

Chemical formula		$Fe_2^{III}Fe_{1-x}^{III}Fe_x^{II}O_{1-y}(OH)_y[O_2C\text{-}C_5H_4N]_5[O_2CCH_3]$ (x~0.15)
Formula weight/g mol^{-1}		853.54
Crystal system		Monoclinic
Space Group		P 2_1/c
Final *R* indices [I>2σ(I)]		
R indices (all data)		
Unit cell	a/Å	11.064(2)
	b/Å	21.464(4)
	c/Å	19.613(3)
	β/º	122.47(2)
Unit cell volume/$Å^3$		3929.1(12)
Temperature of data collection		293K
Z		4
Measured / independent reflections and *R*(int)		11059 / 2737 [*R*(int) = 0.2721

Each trimer is connected to four other trimers parallel to the *c*-axis and two trimers from a different chain. Each chain connects to the chain above and below itself via two nicotinate linkers. The linkers which connect the chains on different levels connect to the same level through the same trimer, i.e. both nicotinate linkers will connect from one trimer to the corresponding chain above, and then the trimer located next to it on the chain will connect to the chain below via two nicotinate linkers.

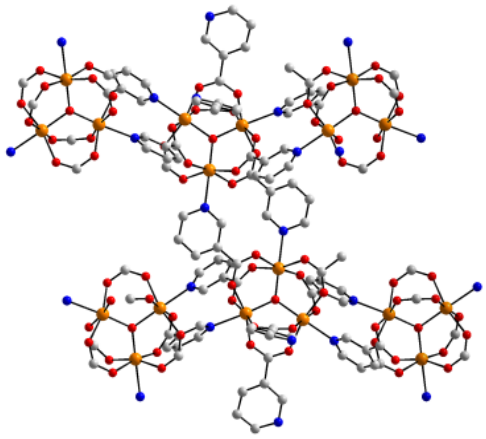

Figure S1. Representation of the undulating chains present within BioMIL-1. Iron, oxygen, carbon and nitrogen are in orange, red, grey and blue, respectively. Hydrogen atoms have been omitted for clarity.

Thermogravimetry

Thermal gravimetric analysis of BioMIL-1 was carried out on a TGA Perkin Elmer apparatus under oxygen gas flow with a heating rate of 2°C.min^{-1} (fig. S2). The TG curve shows three weight losses: first, a water weight loss up to 100°C (1%), then a second weight loss of around 6.3% corresponding to the acetate loss (up to 300°C) and finally, *ca.* 67 % of nicotinate linker combustion. The material degrades around 300°C. The remaining solid, i.e. 26.3 % of the initial weight, corresponds to iron oxide (in the dry solid: 6.4% acetate; 67.0% nicotinic acid; 26.3% Fe_2O_3). These values are in agreement with the theoretical values (6.9% acetate; 71.5% nicotinic acid, 17.9% N uncoordinated nicotinate and 53.6% nicotinate bonded by COO^- and N; 29.5% Fe_2O_3).

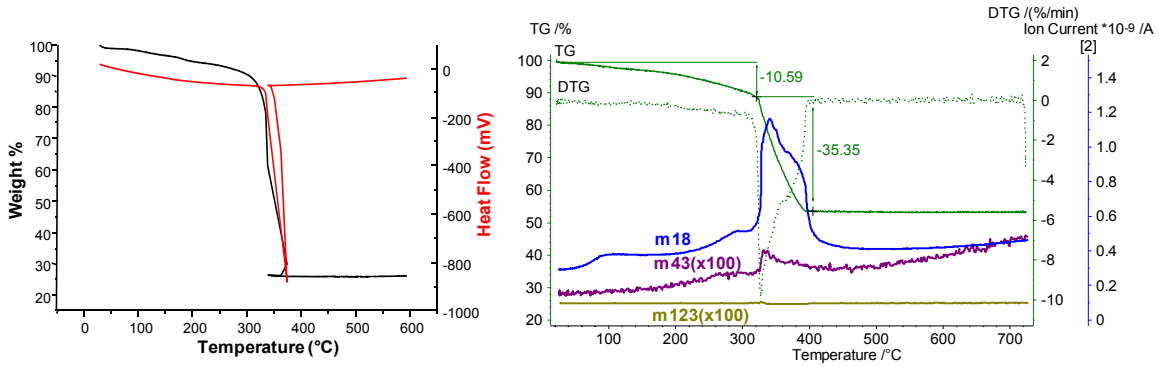

Figure S2. TGA/DTA (on the left) and TGA-mass spectrometry (on the right) of BioMIL-1 solid

Thermal gravimetric analysis coupled to mass spectrometry of BioMIL-1 was carried out under oxygen gas flow with a heating rate of 2°C.min^{-1} (fig. S2). The ion current for the mass numbers values of 18, 43 and 123 were assigned to water, acetate and nicotinate, respectively. Note that this solid contained an inorganic iron oxide impurity.

Degradation tests

The delivered nicotinic acid concentration was determined using a RP-HPLC system (Reversed phase liquid chromatography) equipped with a Waters Alliance E2695 separations module (Waters, Milford, MA, USA), a variable-wavelength diode array detector Waters 2998 and controlled by Empower software. Sunfire-C18 reverse-phase column (5 µm, 4.6x150 mm), supplied for Waters, were employed. The mobile phase consisted of 20% solution (v/v) of methanol in

phosphate buffer 0.02M pH 6.4. The flow rate was 0.8 mL·min-1 and the column temperature was 37ºC. The effluent was monitored at 262 nm and the injection volume was 50 µL.
Several nicotinic acid solutions at different concentrations in phosphate buffer 0.02M pH 6.4 were used as standards. The calibrated plot showed a good correlation coefficient > 0.99 (Figure S3).
The detection limit of this chromatographic method is 0.01µg.mL^{-1}.

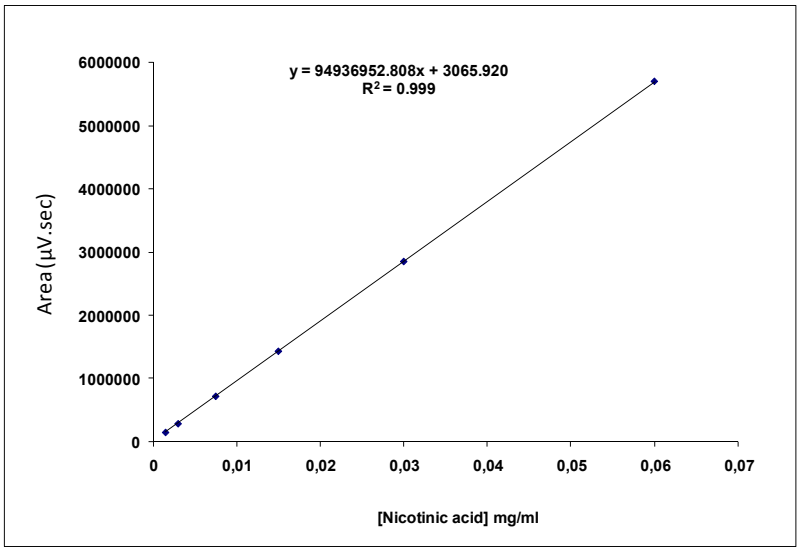

Figure S3. Calibration plot of standard nicotinic acid by HPLC method

Chromatogram of standard solutions presents only one retention time, at 2.9 min (figure S4), which was identified by UV spectra, with absorption maximum at 262 nm, in standard solutions as well in BioMIL-1 degradation as nicotinic acid (Figure S5).

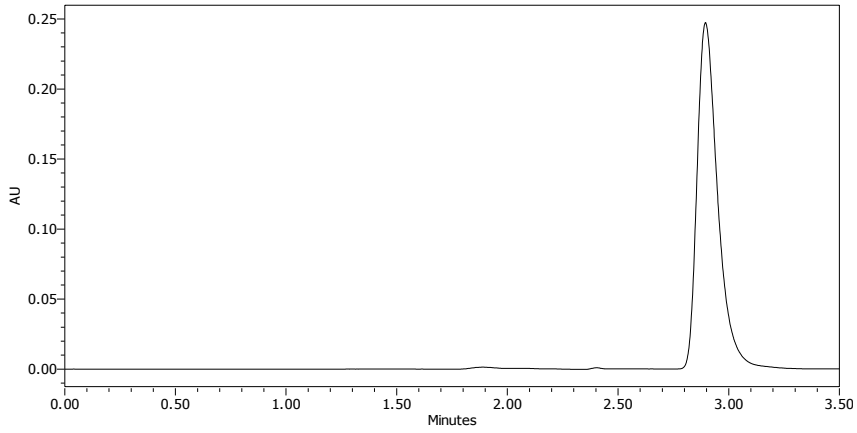

Figure S4. Chromatogram of nicotinic acid

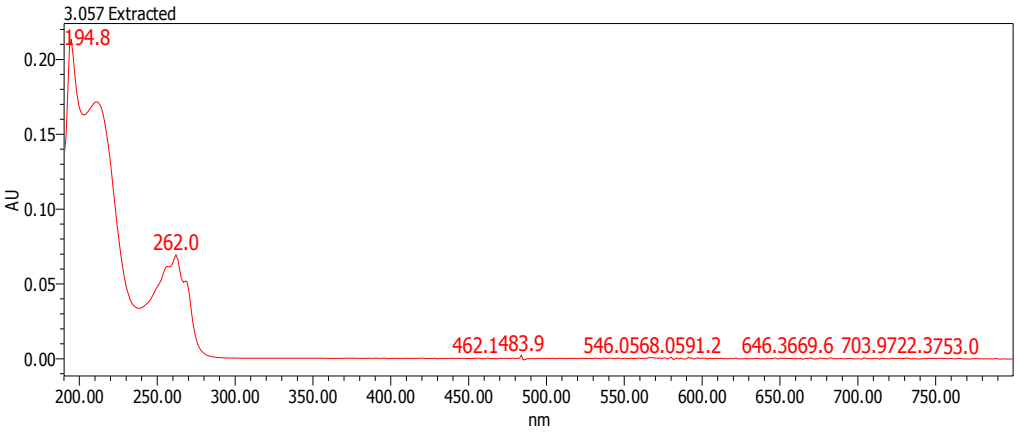

Figure S5. Spectrum of nicotinic acid

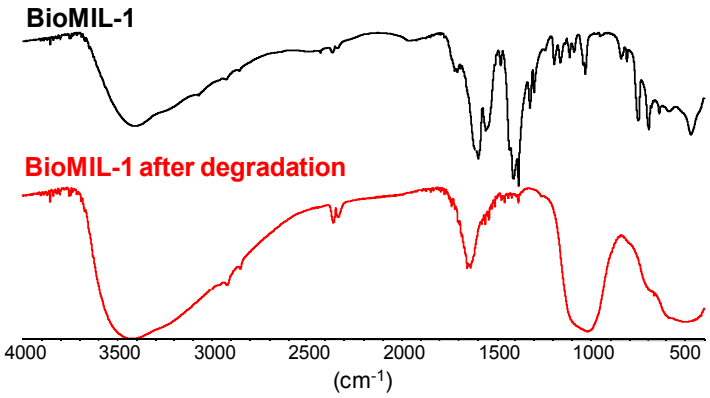

Figure S6. IR spectra of BioMIL-1 solid before and after degradation tests

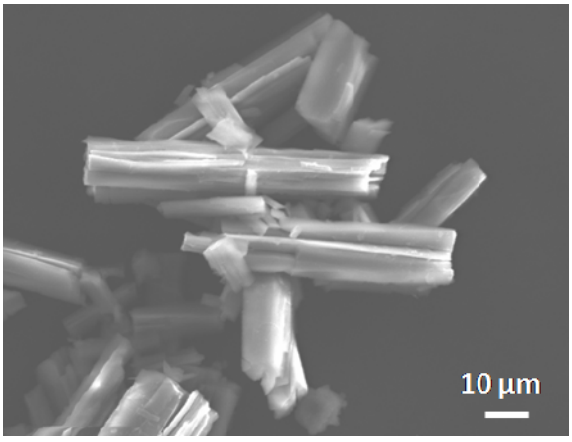

Figure S7. SEM micrograph of BioMIL-1