Experimental section

2,6-dibromoisonicotinic acid and the 2,6-di(1H-pyrazol-1-yl)isonicotinic acid (bppCOOH) were prepared according to the literature methods.[1] All other chemicals are commercially available and were used as received without further purification.

Synthesis of [Fe(bppCOOH)$_2$](ClO$_4$)$_2$.

A solution of Fe(ClO$_4$)$_2$,xH$_2$O (25 mg, 0.10 mmol) in acetone (2 mL) was added to a solution of bppCOOH (57 mg, 0.20 mmol) in acetone (10 mL) and the mixture was stirred for 15 minutes. Red prismatic crystals of [Fe(bppCOOH)$_2$](ClO$_4$)$_2$ suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into this solution. The composition of crystals of [Fe(bppCOOH)$_2$](ClO$_4$)$_2$, checked by microanalysis, shows a Fe:Cl ratio close to 1:2.

Structural characterization. A single crystal of [Fe(bppCOOH)$_2$](ClO$_4$)$_2$ was mounted on a glass fibre using a viscous hydrocarbon oil to coat the crystal and then transferred directly to the cold nitrogen stream for data collection. X-ray data were collected at 120 K on a Supernova diffractometer equipped with a graphite-monochromated Enhance (Mo) X-ray Source (λ = 0.71073 Å). The program CrysAlisPro, Oxford Diffraction Ltd., was used for unit cell determinations and data reduction. Empirical absorption correction was performed using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm. Crystal structure was solved by direct methods with the SIR97 program,[2] and refined against all F^2 values with the SHELXL-97 program,[3] using the WinGX graphical user interface.[4] Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated positions refined using idealized geometries (riding model) and assigned fixed isotropic displacement parameters. A summary of the data collection and structure refinements is provided in Table 1. A 0.5 mm glass capillary was filled with a polycrystalline sample of [Fe(bppCOOH)$_2$](ClO$_4$)$_2$ and mounted and aligned on a Empyrean PANalytical powder diffractometer, using CuKα radiation (λ = 1.54177 Å). A total of 2 scans were collected at room temperature in the 2θ range 5-40°.

Physical characterizations. The Fe:Cl ratios were measured on a Philips ESEM X230 scanning electron microscope equipped with an EDAX DX-4 microsonde.

Differential scanning calorimetry (DSC) measurements under nitrogen atmosphere were performed in a Mettler Toledo DSC 821e apparatus with warming and cooling rates equal to 5 K·min^{-1}. A correction from the sample holder was automatically applied. The heat flow thus measured ($\Delta H/\Delta t$) was used in the calculation of the approximate specific heat function as follows:

$$\frac{\Delta H}{\Delta T} = \frac{\Delta H}{\Delta t} \cdot \frac{M}{\beta \cdot m}$$

where m is the mass of the sample, M its molecular weight and β the heating (cooling) rate.

Magnetic measurements were performed with a Quantum Design MPMS-XL-5 SQUID magnetometer in the 2 to 400 K temperature range with an applied magnetic field of 0.1 T at a scan rate of 1 K/min on a polycrystalline sample with a mass of 18.07 mg. Photomagnetic measurements were performed irradiating with a Diode Pumped Solid State Laser DPSS-532-20 from Chylas coupled *via* an optical fibre to the cavity of the SQUID magnetometer. The optical power at the sample surface was adjusted to 3.4 mW.cm^{-2}, and it was verified that it resulted in no significant change in magnetic reponse due to heating of the sample. The photomagnetic samples consisted of a thin layer of compound whose weight was obtained by comparison of a thermal spin crossover curve with that of a more accurately weighted sample of the same compoud.

References

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Table S1. Crystallographic data for [Fe(bppCOOH)$_2$](ClO$_4$)$_2$. **[Fe(bppCOOH)$_2$](ClO$_4$)$_2$.**

Formula	FeC$_{24}$H$_{18}$N$_{10}$O$_{12}$Cl$_2$
M$_r$	765.23
Crystal size	0.03*0.03*0.02
T /K	120
Crystal system	Monoclinic
Space group	$C2/c$
a /Å	17.2679(8)
b /Å	16.0585(6)
c /Å	10.7907(5)
α /°	90.000(5)
β /°	105.264(5)
γ /°	90.000(5)
V /Å^3	2886.7(2)
Z	4
ρ_{calc} /g.cm^{-3}	1.761
μ(Mo$_{K_a}$) /mm^{-1}	0.793
Reflns collected	3312
Independent reflns	2368
$R1$(F),[a] I >2σ(I)	0.0517
$wR2$(F^2),[b] all data	0.1171

[a] $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. [b] $R_w = \{ \sum [w(|F_o| - |F_c|)]^2 / \sum [w|F_o|^2] \}^{1/2}$

Table S2. DSC data for [Fe(bppCOOH)$_2$](ClO$_4$)$_2$.

T (K)	ΔH (KJ.mol^{-1})	ΔS (J.mol^{-1}.K^{-1})
383	18.9	45.3
381	17.2	44.9

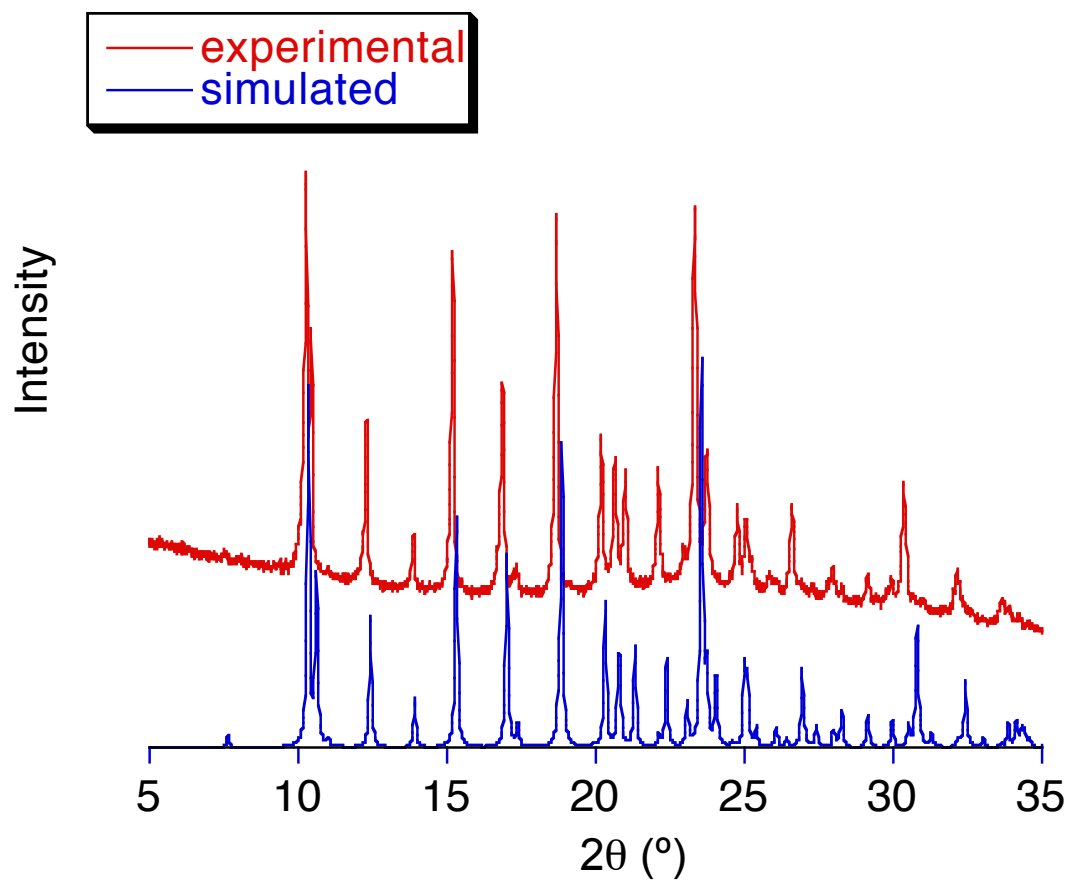**Fig. S1** Experimental powder X-ray diffraction pattern (top) and simulated one (bottom) of [Fe(bppCOOH)$_2$](ClO$_4$)$_2$ at room temperature.

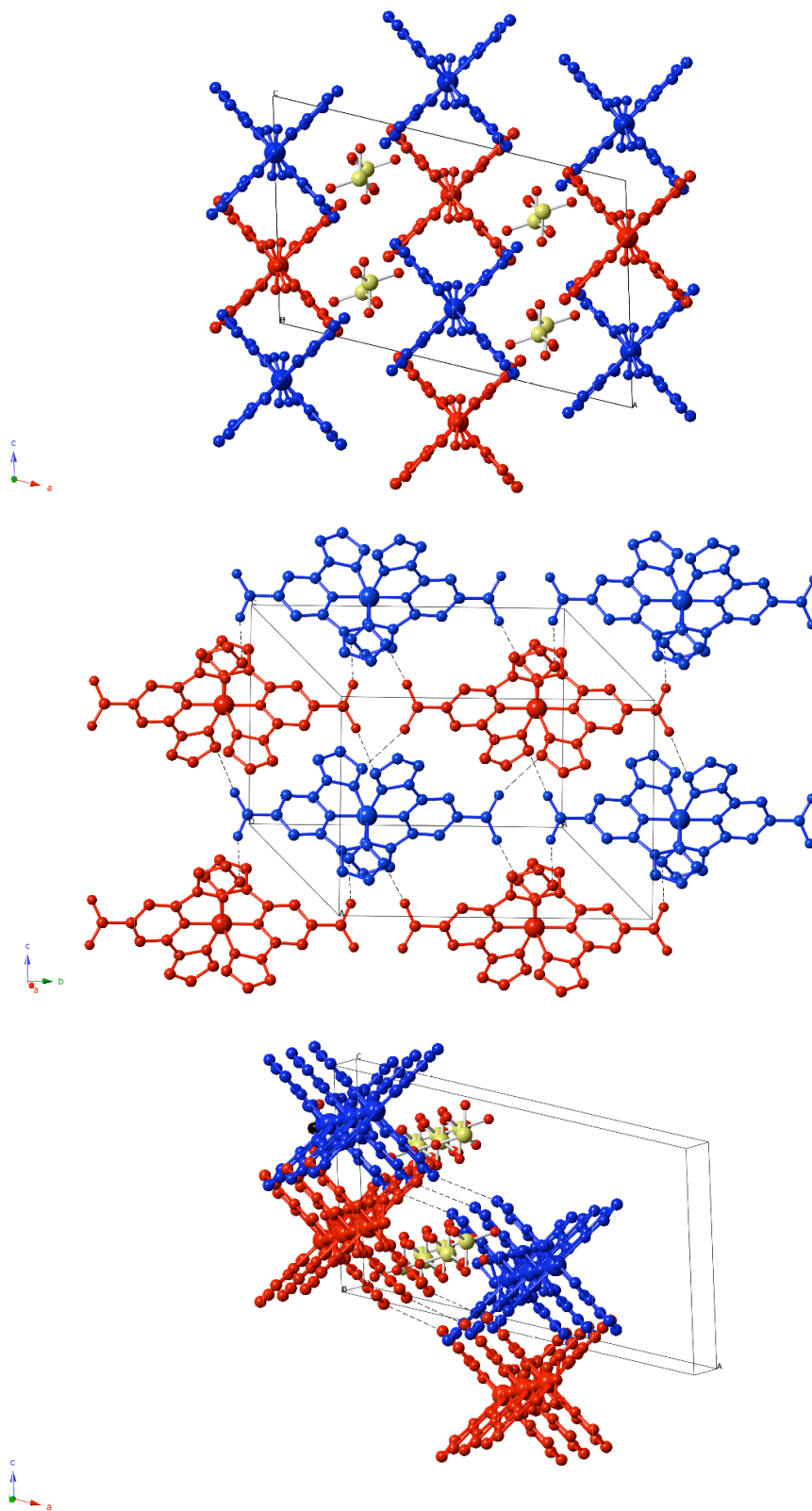**Fig. S2** Projection of the structure of [Fe(bppCOOH)$_2$](ClO$_4$)$_2$ in the *ac* plane with the [Fe(bppCOOH)$_2$]$^{2+}$ belonging to the same hydrogen-bonded chain coloured in red or blue (top); view of a layer of [Fe(bppCOOH)$_2$]$^{2+}$ complexes with the intermolecular interactions between complexes belonging to different hydrogen-bonded chains as dashed lines (centre); view of two layers of [Fe(bppCOOH)$_2$]$^{2+}$ complexes with the intermolecular interactions between complexes belonging to different layers as dashed lines (bottom).

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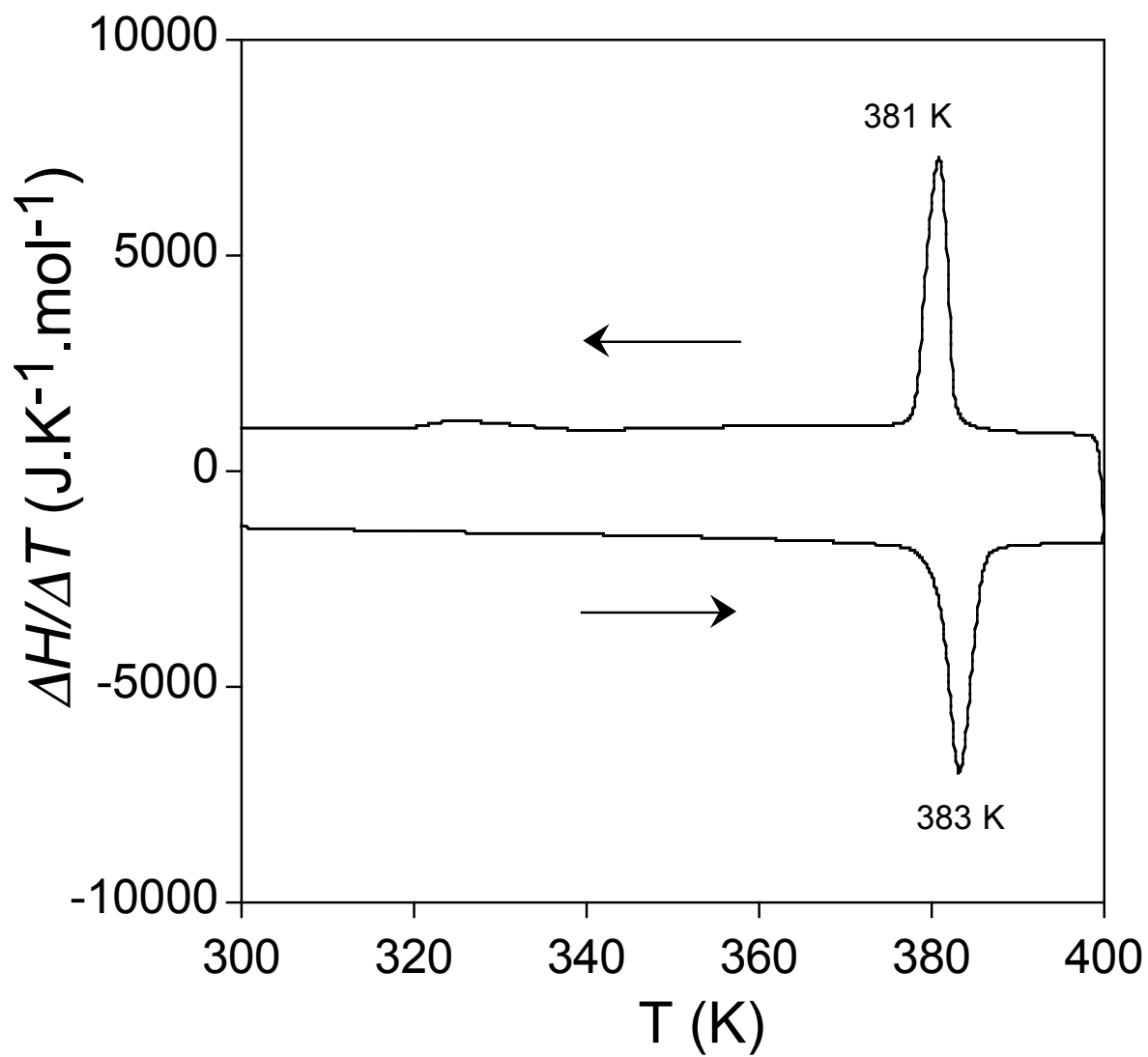**Fig. S3** Differential scanning calorimetry of [Fe(bppCOOH)$_2$](ClO$_4$)$_2$: The corresponding thermodynamic parameters are gathered in Table S2.