

A fluorinated 2D magnetic coordination polymer

Javier López-Cabrelles,^{a+} Samuel Mañas-Valero,^{a+} Iñigo J. Vitórica-Yrezábal,^b Pablo J. Bereciartua,^{c,d} Eugenio Coronado,^a and Guillermo Mínguez Espallargas^{*a}

^a Instituto de Ciencia Molecular (ICMol), Universidad de Valencia, c/Catedrático José Beltrán, 2, 46980 Paterna, Spain

^b School of Chemistry, University of Manchester, Oxford Road, Manchester M13 9PL, UK.

^c Instituto de Tecnología Química (UPV-CSIC), Universitat Politècnica de València–Consejo Superior de Investigaciones Científicas, Av. de los Naranjos, s/n, 46022 Valencia, Spain.

^d Present address: Deutsches Elektronen-Synchrotron (DESY), Notkestraße 85, 22607 Hamburg, Germany.

Supporting Information

Contents

1. Materials and synthesis	2
2. Structural Characterization	3
2.1 Data Collection.....	3
2.2 Crystal structure determinations and refinements	3
2.3 Magnetic characterization	5
3. Contact angle	6
4. Two-dimensional approach and characterization	6
5. References	7

1. Materials and synthesis

All reagents and solvents were commercially available and used without further purification.

Synthesis. The compound **MUV-1-F** was prepared adapting a previously described method for the preparation of iron imidazolates.^{1,2} Ferrocene (30 mg, 0.16 mmol) and 5-fluorobenzimidazole (46.3 mg, 0.34 mmol) were combined and sealed under vacuum in a layering tube (4 mm diameter). The mixture was heated at 250 °C for 3 days to obtain colourless crystals suitable for X-ray single-crystal diffraction. The product was cooled down to room temperature, and the layering tube was then opened. The unreacted precursors were extracted with acetonitrile and benzene, and the main compound was isolated as colourless crystals (yield 80 %). Phase purity was established by X-ray powder diffraction.

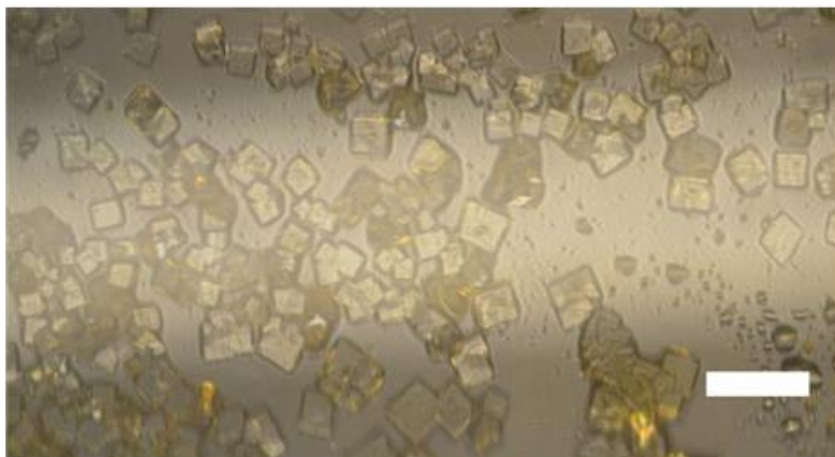


Fig S1. Crystals of **MUV-1-F** as synthesized. Scale bar is 400 μ m

2. Structural Characterization

2.1 Data Collection

X-ray data for compound **MUV-1-F** were collected at a temperature of 100 K using Rigaku FR-X rotating anode (Mo- $k\alpha$, $\lambda = 0.71073 \text{ \AA}$), equipped with a Hybrid Photon detector HyPix-6000HE and an Oxford Cryosystems nitrogen flow gas system. Data was measured using CrysAlisPro software.

2.2 Crystal structure determinations and refinements

X-ray data was processed and reduced using CrysAlisPro suite of programmes. Absorption correction was performed using empirical methods (SCALE3 ABSPACK) based upon symmetry-equivalent reflections combined with measurements at different azimuthal angles. The crystal structure was solved and refined against all F^2 values using the SHELXL and Olex 2 suite of programmes.^{3,4} Despite that the coordination polymer is intrinsically chiral, the centrosymmetric space group $C2/c$ was found as result of the racemic distribution of the disordered layers of the **MUV-1-F** coordination polymer, as previously observed for **MUV-1-H**, **MUV-1-Cl**, **MUV-1-CH₃** and **MUV-1-NH₂**.¹

The modulation in the crystal structure was treated as positional disorder. All the disordered moieties were modelled to have a 50 % occupancy, whereas the disordered fluoride groups of the ligands were refined to have a 25 % of occupancy on each of the four different positions. All the atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions refined using idealized geometries (riding model) and assigned fixed isotropic displacement parameters. The phenyl groups were restrained to have idealized geometries using AFIX commands.

CCDC 1582351 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

The crystallographic information is summarized in Table S1. Different views of the crystal lattice and the orientation of the ligand are shown in Figure S2.

Table S1. Crystallographic information for compounds **MUV-1-F**

Identification code	MUV-1-F
Empirical formula	$C_{14}H_8F_2FeN_4$
Formula weight	326.09
Temperature/K	100.00(14)
Crystal system	monoclinic
Space group	$C2/c$
$a/\text{\AA}$	8.2727(5)
$b/\text{\AA}$	8.2567(4)
$c/\text{\AA}$	19.3526(14)
$\alpha/^\circ$	90
$\beta/^\circ$	97.498(6)
$\gamma/^\circ$	90
Volume/ \AA^3	1310.58(14)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.653
μ/mm^{-1}	1.171
F(000)	656.0
Crystal size/ mm^3	$0.15 \times 0.15 \times 0.1$
Radiation	MoK α ($\lambda = 0.71073$)
2Θ range for data collection/ $^\circ$	4.246 to 52.74
Index ranges	$-10 \leq h \leq 10, -10 \leq k \leq 10, -24 \leq l \leq 24$
Reflections collected	13800
Independent reflections	1350 [$R_{\text{int}} = 0.0614, R_{\text{sigma}} = 0.0217$]
Data/restraints/parameters	1350/135/170
Goodness-of-fit on F^2	1.222
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0585, wR_2 = 0.1524$
Final R indexes [all data]	$R_1 = 0.0594, wR_2 = 0.1529$
Largest diff. peak/hole / $e \text{\AA}^{-3}$	1.53/-0.81

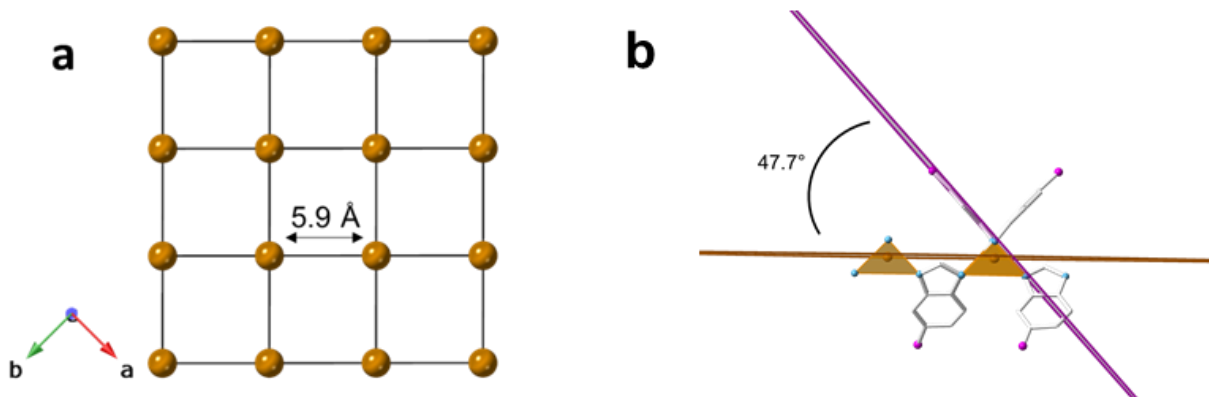


Fig S2. a) Square lattice formed by the Fe(II) with a 5.9 Å distance. b) Angle formed by the ligand and the ab plane composed by the metal centers

2.3 Magnetic characterization

Table S.2.- Magnetic data parameters for the **MUV-1-X(Fe)** compounds.

MUV	S	T _N (K)	J (cm ⁻¹)	g	C (emu·mol ⁻¹ ·K)	Θ (K)
MUV-1-F(Fe) (This work)	2	19.9	-19 ± 1	2.06 ± 0.03	6.34 ± 0.12	-114 ± 3
MUV-1-Cl(Fe)*	2	20.7	-22.9 ± 0.4	2.00 ± 0.02	3.635 ± 0.006	-80.6 ± 0.4
MUV-1-H(Fe)*	2	20.0	-23.5 ± 0.2	1.98 ± 0.02	5.76 ± 0.02	-97.5 ± 1.3
MUV-1-Br(Fe)*	2	20.0	- 22.8 ± 0.2	2.0 ± 0.2	3.693 ± 0.002	-89.32 ± 0.2
MUV-1-CH ₃ (Fe)*	2	20.1	- 22.6 ± 0.4	2.0 ± 0.2	5.13 ± 0.03	-132.0 ± 1.9
MUV-1-NH ₂ (Fe)*	2	21.2	- 23.3 ± 0.3	2.0 ± 0.2	3.976 ± 0.014	-106.8 ± 1.5

* Nat. Chem. 2018, 10, 1001

3. Contact angle

Static water contact angle measurements of the samples were performed in air using a Rame-hart 200 standard goniometer equipped with an automated dispensing system. The initial drop volume was 0.17 μL , increased by additions of 0.08 μL .

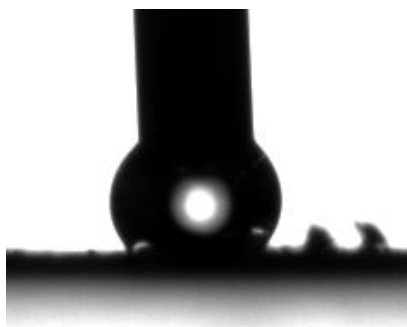


Fig S3. Contact angle measurement around 135°.

4. Two-dimensional approach and characterization

MUV-1-F was mechanically exfoliated by mechanical methods (as commonly known as the *Scotch-tape* method, developed for obtaining graphene from graphite), using an adhesive plastic film of 80 μm thick tape from Ultron Systems. The obtained flakes were deposited onto silicon substrates with 285 nm of thermally grown SiO_2 and inspected by different microscopies such as optical microscopy, atomic force microscopy, and transmission electron microscopy.

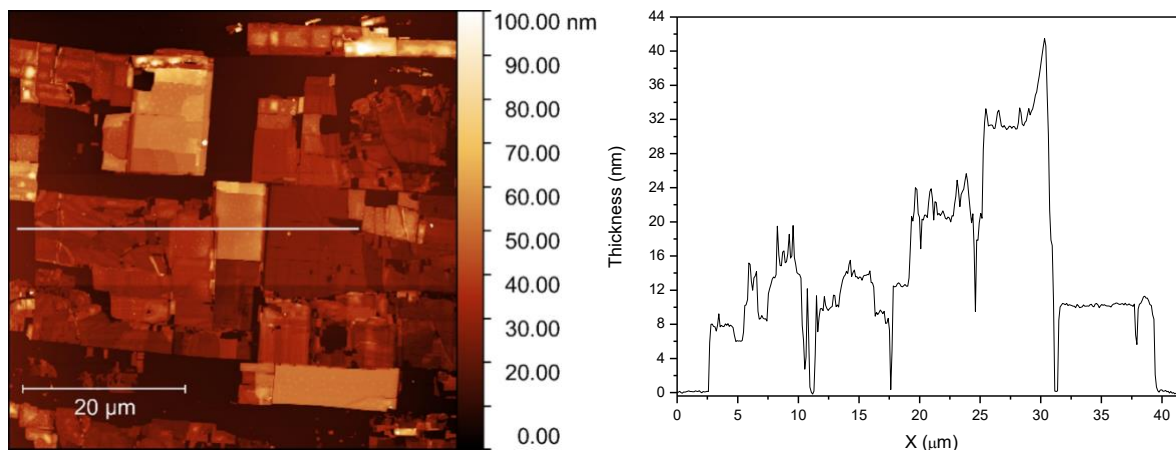


Fig S4. Atomic force microscopy for the **MUV-1-F**.

5. References

- 1 J. López-Cabrelles, S. Mañas-Valero, I. J. Vitórica-Yrezábal, P. J. Bereciartua, J. A. Rodríguez-Velamazán, J. C. Waerenborgh, B. J. C. Vieira, D. Davidovikj, P. G. Steeneken, H. S. J. van der Zant, G. Mínguez Espallargas and E. Coronado, *Nat. Chem.*, 2018, **10**, 1001–1007.
- 2 J. López-Cabrelles, J. Romero, G. Abellán, M. Giménez-Marqués, M. Palomino, S. Valencia, F. Rey and G. Mínguez Espallargas, *J. Am. Chem. Soc.*, 2019, **141**, 7173–7180.
- 3 Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr. Sect. C Struct. Chem.* **71**, 3–8 (2015).
- 4 Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. OLEX2 : a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **42**, 339–341 (2009).