

Supporting Information for:

Incorporation of Pyrazine and Bipyridine Linkers with High-Spin Fe(II) and Co(II) in a Metal-Organic Framework

Airi Kawamura,[†] Arin R. Greenwood,[‡] Alexander S. Filatov,[†] Audrey T. Gallagher,[§]

Giulia Galli,^{*‡||} and John S. Anderson.^{*†}

[†] Department of Chemistry, The University of Chicago, Chicago, IL, 60637, United States.

[‡] Institute for Molecular Engineering, The University of Chicago, Chicago, IL, 60637, United States.

[§] Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113, United States

^{||}Materials Science Division, Argonne National Laboratory, Argonne, IL, 60439, United States.

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Characterization Methods

Crystal Structure Determination. The diffraction data were measured at 100 K on a Bruker D8 VENTURE with PHOTON 100 CMOS detector system equipped with a Mo-target micro-focus X-ray tube ($\lambda = 0.71073 \text{ \AA}$). Data reduction and integration were performed with the Bruker APEX3 software package (Bruker AXS, version 2015.5-2, 2015). Data were scaled and corrected for absorption effects using the multi-scan procedure as implemented in SADABS (Bruker AXS, version 2014/5, 2015, part of Bruker APEX3 software package). The structure was solved by the dual method implemented in SHELXT (Sheldrick, G. M. *Acta Cryst.* **2015**, A71, 3-8) and refined by a full-matrix least-squares procedure using OLEX2 (O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann. *J. Appl. Cryst.* (2009). 42, 339-341) software package (XL refinement program version 2014/7, Sheldrick, G. M. *Acta Cryst.* **2008**, A64, 112-122; Sheldrick, G. M. *Acta Cryst.* **2015**, C71, 3-8). The porous frameworks are known to contain large accessible solvent voids that can be filled with disordered solvent molecules degrading the overall quality of the single crystal X-ray diffraction experiments. Crystal of **1** contained large pores and the diffuse contribution to scattering from the disordered solvent molecules located in them was treated by application of the program SQUEEZE [Spek, A.L. *Acta Cryst.* **2015**, C71, 9-18] as implemented in Platon [Spek, A. L., *Acta Cryst.* 2009, D65, 148-155] using the “fab” file construct. This construct allows the solvent density distribution to be added to calculation of structure factors without modifying the observed intensities through the subtraction of a solvent contribution. Overall, the SQUEEZE algorithm located “Solvent Accessible Volume” of $2255 \text{ \AA}^3$ with an electron count of 507. This can account for approximately 12 molecules of DMF per unit cell or 2 molecules of DMF per 1 Fe atom. Crystallographic data and details of the data collection and structure refinement are listed in Table S6.

Gas Adsorption Measurements. Activation and measurements were performed on a Micromeritics ASAP 2020. Surface area was calculated from the N_2 adsorption isotherm using Brunauer–Emmett–Teller (BET) theory. Samples were loaded into a quartz tube fitted with a TranSeal cap and activated as described in the synthetic protocol. Measurements were performed at 77 K, in a liquid N_2 bath.

FT-IR Spectroscopy. Powder samples for FT-IR were formed into pellets in a potassium bromide matrix. Spectra were acquired in absorbance mode on a Bruker Tensor II with background subtractions used to account for air.

Magnetometry. Magnetic measurements were performed on a Quantum Design MPMS 3 equipped with a superconducting quantum interference device (SQUID). Corrections were made for the diamagnetic contributions from the polycarbonate capsules and eicosane used to secure the sample by measuring field vs. moment in triplicate for each to determine a moment per gram correction. The χ values reported are the molar magnetic susceptibilities. χT vs. T data was calculated as a $[\text{M}(\text{BDC})\text{L}]_2$ dimer and fit to an isotropic Heisenberg model with axial zero-field splitting (Eq. S1) in MagProp (Azuah, R. T. et al, *J. Res. Natl. Inst. Stand. Technol.* **2009**, 114 (6), 341-358) where ions i and j are nearest neighbors and have the same values. The axial zero-field splitting parameter (D) was used to fit the data, however there was large error in the D value for all data sets making their values unreliable.

$$\hat{H} = g\mu_B \mathbf{H} \cdot (\mathbf{S}_i + \mathbf{S}_j) - J \mathbf{S}_i \mathbf{S}_j + D_i [S_{zi}^2 - S_i(S_i + 1)/3] + D_j [S_{zj}^2 - S_j(S_j + 1)/3] \quad (\text{Eq. S1})$$

Where g is the electron g-factor, μ_B is the Bohr magneton, $\mathbf{H}$ is the magnetic field, $\mathbf{S}$ is the spin, J is the exchange constant, and D is the axial zero-field splitting parameter.

Magnetic data (χT vs. T) plots and reported values have been normalized to one formula unit. All reported literature J values of magnetic systems have been normalized to Eq. S1.

PXRD. Powder X-ray diffraction patterns were acquired on a Bruker D8 powder X-ray diffractometer with a General Area Detector Diffraction System (GADDS) using Cu K α radiation ($\lambda = 0.15418$ nm). Samples were measured under heavy mineral oil to reduce air exposure. Powder diffraction data were analyzed by the Le Bail method (A. Le Bail Powder Diffr. 20, 316-326) as implemented in TOPAS ((a) Coelho, A. A. J. Appl. Crystallogr. 2003, 36, 86. (b) TOPAS version 5.0; Bruker AXS, 2015.).

Thermogravimetric Analysis. TGA was performed on activated samples of **1** (4.889 mg) and **2** (4.778 mg) in platinum pans. Measurements were acquired on a Shimadzu TGA-50H from 15 °C to 800 °C at a ramp rate of 2 °C/minute in air.

Differential Scanning Calorimetry. DSC was performed on activated samples of **1** (7.3 mg) and **2** (5.7 mg) in aluminum pans with lids handled under N₂. Measurements were acquired on a TA Instruments DSC 2920 from 25 °C to 400 °C at a ramp rate of 20 °C/minute in an inert N₂ atmosphere.

Mössbauer Measurements. Zero-field iron-57 Mössbauer spectra were obtained at 80 K with a constant acceleration spectrometer and a cobalt-57 rhodium source. Prior to measurements, the spectrometer was calibrated at 295 K with α -iron foil. Samples were prepared in a N₂-filled glovebox where powdered **1** was placed in a polyethylene cup, covered in Paratone-N oil and frozen in liquid nitrogen prior to handling in air. The sample contained approximately 100 mg. All spectra were analyzed using the WMOSS Mössbauer Spectral Analysis Software (www.wmoss.org).

X-ray Absorption Spectroscopy. X-ray near-edge absorption spectra (XANES) and X-ray absorption fine structure (XAFS) spectra were employed to probe the local environment around Co. Data were acquired at the Advanced Photon Source at Argonne National Labs with a bending magnet source with ring energy at 7.00 GeV. Co K-edge data were acquired at the MRCAT 10-BM beam line. EXAFS data were collected in the fluorescence mode using fluorescence ion chamber in Stern-Heald geometry. Absorption was calibrated and concurrently referenced during measurement to a Co foil set to 7709.00 keV. Data collected was processed using Athena software [Ravel, B., Newville, M., ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. J. Synchr. Radn., 12, 537-541 (2005)] by extracting the EXAFS oscillations $\chi(k)$ as a function of photoelectron wavenumber k [Newville, M., IFEFFIT: interactive EXAFS analysis and FEFF fitting. J. Synchr. Radn. 8 322-324 (2001).]. The theoretical paths were generated using FEFF6 [Rehr, J. J.; Albers, R. C. *Rev. Mod. Phys.* **2000**, 72, 621-654] and the models were done in the conventional way using the fitting program Artemis [Ravel, B., Newville, M., ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. J. Synchr. Radn., 12, 537-541 (2005)]. The initial model was taken from an X-ray crystal structure of an Fe-containing analogue compound. EXAFS data were modelled in R-space with k -weights of 1, 2 and 3 until a satisfactory fit describing the system was obtained.

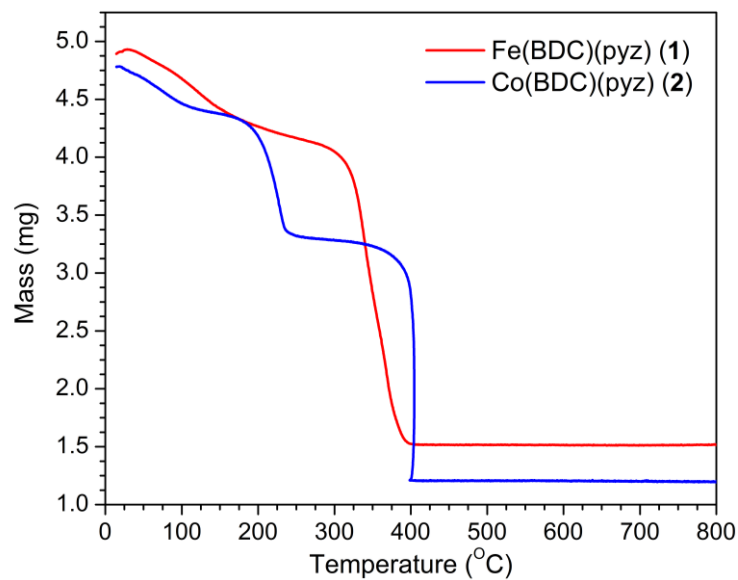


Figure S1. Thermogravimetric analysis plots of Fe(BDC)(pyz) **1** and Co(BDC)(pyz) **2**.

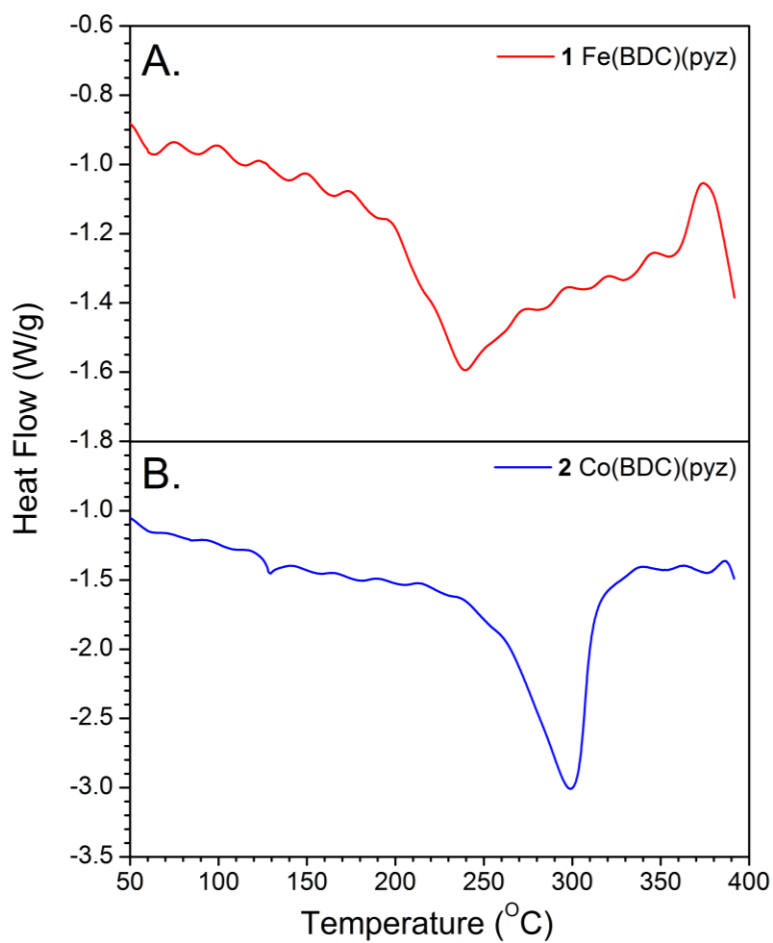


Figure S2. Differential scanning calorimetry plots of (a) **1** and (b) **2**.

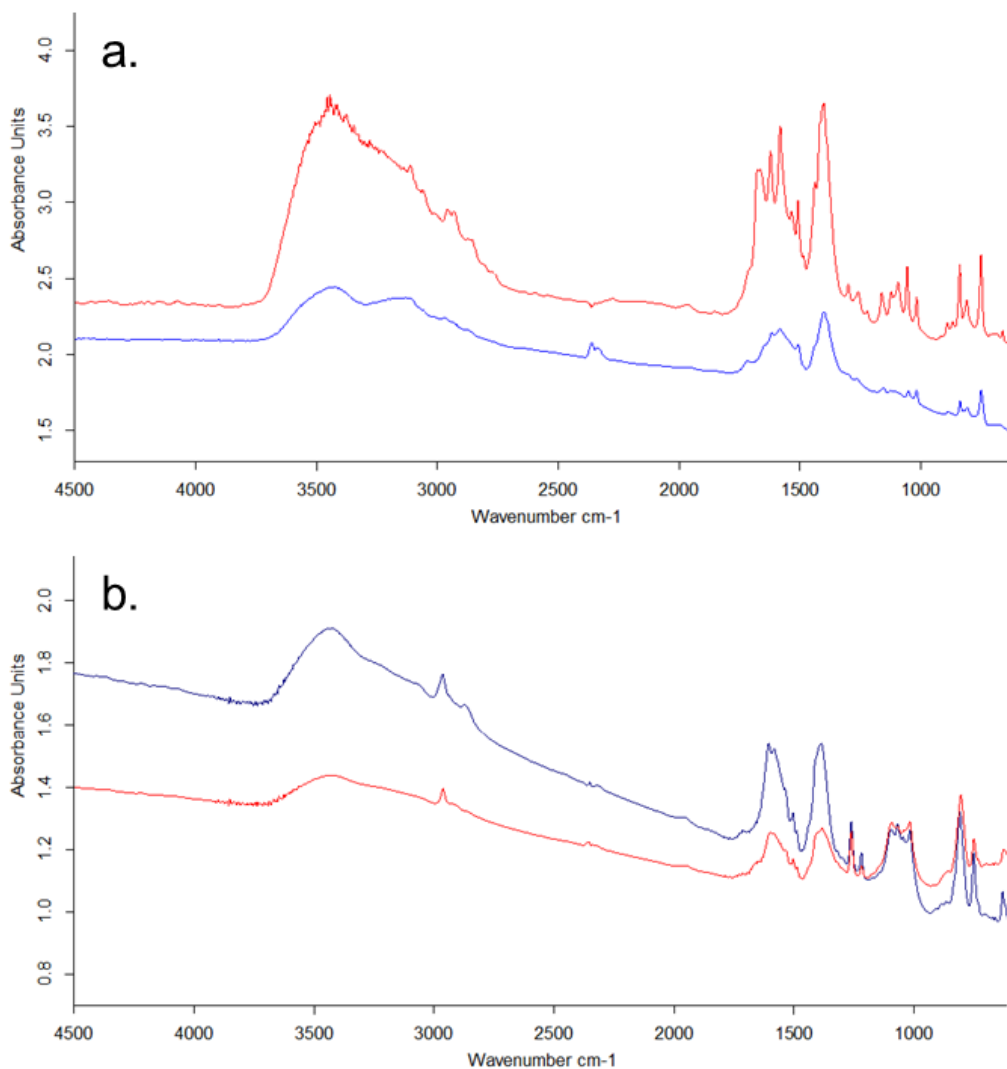


Figure S3. FT-IR spectra of A) Fe(BDC)(pyz) (**1**) (red) and Co(BDC)(pyz) (**2**) (blue) and B) Fe(BDC)(bipy) (**3**) (red) and Co(BDC)(bipy) (**4**) (blue).

	Fe(BDC)(pyz)	Fe(BDC)(bipy)	Co(BDC)(pyz)	Co(BDC)(bipy)
<i>a</i>	25.020(2)	24.957(2)	25.06(1)	24.83(1)
<i>c</i>	7.238(1)	11.598(3)	7.23(1)	11.53(1)
V	3924(1)	6256(2)	3930(5)	6153(5)

Table S1. PXRD fit parameters for **1**, **2**, **3** and **4** from the Le Bail fit to space group *P6/m*.

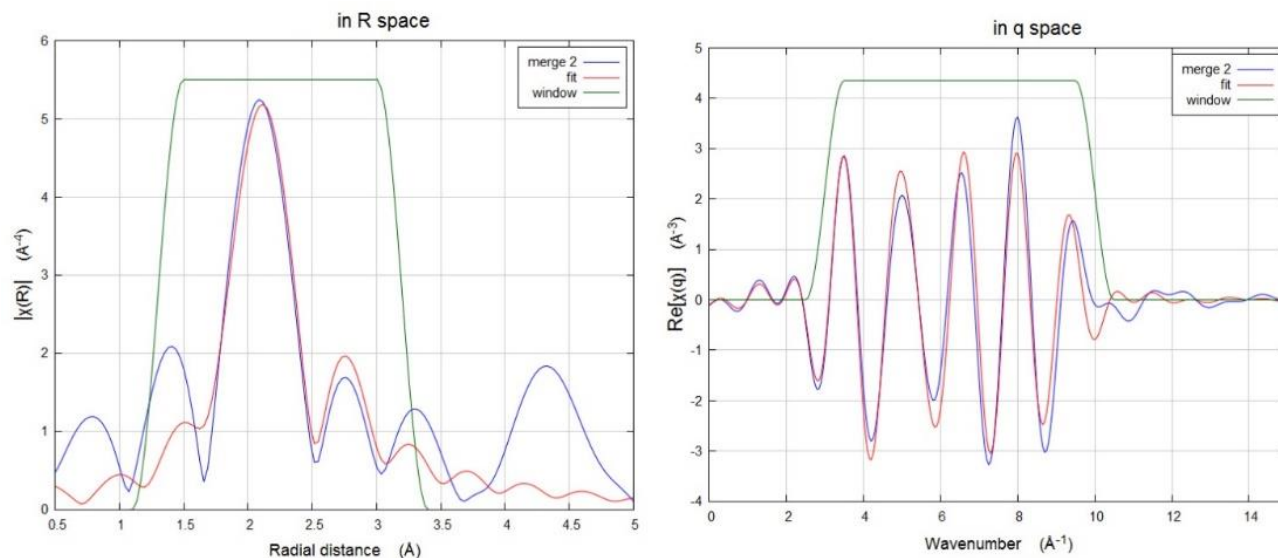


Figure S4. Fit results of EXAFS data for **2** at the Co K-edge.

Edge	Fitting range	Paths	Bond length R (ang)	Coordination Number (n)	Debye Waller Factor	Energy Shift ΔE (eV)
Co edge $S_0^2=1.00$	R=1.3-3.2 Å dr=0.4 k= 3.0-10.5 Å ⁻¹ dk = 1	Co-O	2.02 ± 0.04	1	0.009 ± 0.002	9.4 ± 1.7
		Co-O	2.06 ± 0.04	1	0.009 ± 0.002	
		Co-N	2.16 ± 0.02	2	0.015 ± 0.016	
		Co-O	2.19 ± 0.02	2	0.015 ± 0.016	

Table S2. List of fit parameters obtained from modeling of the data. R-factor for the fit is 0.02.

	Energy Difference
AFM - FM	-0.0323 eV
AFM - NM	-14.1178 eV
FM - NM	-14.0855 eV

Table S3. DFT+U calculated energy differences between antiferromagnetically (AFM), ferromagnetically (FM) and non-magnetically (NM, i.e. low-spin) coupled systems of **1**.

	Stress at PBE (kbar)	Stress at PBE + U (kbar)
AFM	3.25	7.41
FM	-0.65	7.57
NM	-13.34	-8.09

Table S4. Stress on the unit cell for the three spin states at the experimental lattice constant and PBE relaxed geometry, and for the same geometry with the additional U parameter.

1			3		
Paramater	Value	Error	Paramater	Value	Error
g	1.93	0.04	g	1.90	0.04
J (cm-1)	-4.2	0.96	J (cm-1)	-2.1	1.0
D (cm-1)	10	20	D (cm-1)	20	20

2			4		
Paramater	Value	Error	Paramater	Value	Error
g	2.21	0.09	g	2.34	0.04
J (cm-1)	-0.9	0.2	J (cm-1)	-0.7	0.2
D (cm-1)	60	40	D (cm-1)	60	20

Table S5. Fitting parameters and error from the magnetic data of **1**, **2**, **3** and **4**.

Table S6. Crystal data and structure refinement for **1**.

Identification code	1
Empirical formula	C ₁₂ H ₈ FeN ₂ O ₄
Formula weight	300.05
Temperature/K	100(2)
Crystal system	hexagonal
Space group	<i>P</i> 6/ <i>m</i>
<i>a</i> /Å	24.644(2)
<i>b</i> /Å	24.644(2)
<i>c</i> /Å	7.1068(6)
α /°	90
β /°	90
γ /°	120
Volume/Å ³	3738.0(7)
<i>Z</i>	6
ρ_{calc} /g/cm ³	0.800
μ /mm ⁻¹	0.610
<i>F</i> (000)	912.0
Crystal size/mm ³	0.32 × 0.11 × 0.09
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/°	5.05 to 50.074
Index ranges	-27 ≤ <i>h</i> ≤ 29, -28 ≤ <i>k</i> ≤ 29, -8 ≤ <i>l</i> ≤ 7
Reflections collected	23375
Independent reflections	2407 [<i>R</i> _{int} = 0.1013, <i>R</i> _{sigma} = 0.0529]
Data/restraints/parameters	2407/33/106
Goodness-of-fit on <i>F</i> ²	1.098
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0643, <i>wR</i> ₂ = 0.1645
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0786, <i>wR</i> ₂ = 0.1699
Largest diff. peak/hole / e Å ⁻³	0.70/-1.71

$$R_{\text{int}} = \Sigma |F_o^2 - \langle F_o^2 \rangle| / \Sigma |F_o^2|$$

$$R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$$

$$wR_2 = [\Sigma [w (F_o^2 - F_c^2)^2] / \Sigma [w (F_o^2)^2]]^{1/2}$$

$$\text{Goodness-of-fit} = [\Sigma [w (F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$$

n: number of independent reflections; *p*: number of refined parameters

Table S7. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **1**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	$U(\text{eq})$
Fe1	4104.4(4)	9375.3(4)	10000	17.9(3)
O1	4904.8(18)	9331.7(17)	10000	22.1(9)
O2	5941.5(18)	9810.1(17)	10000	22.5(9)
O3	4796.3(17)	6444.7(18)	10000	23.1(9)
O4	5828.1(17)	6923.5(17)	10000	20.8(8)
N1	4117.2(15)	9390.6(14)	6960(4)	20.6(7)
C1	5404(3)	9320(3)	10000	18.3(12)
C2	5387(3)	8704(2)	10000	19.9(12)
C3	5931(3)	8682(3)	10000	23.8(13)
C4	5921(3)	8113(3)	10000	24.2(13)
C5	5340(3)	7553(3)	10000	24.9(12)
C6	4805(3)	7591(3)	10000	20.7(12)
C7	4804(3)	8148(3)	10000	27.0(14)
C8	5332(3)	6951(3)	10000	21.2(11)
C9	4345(2)	9088.7(19)	5971(6)	30.7(10)
C10	3890.2(19)	9693(2)	5965(6)	28.5(10)

Table S8. Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **1**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe1	21.8(5)	15.8(4)	13.1(4)	0	0	7.1(4)
O1	26(2)	20(2)	24(2)	0	0	14.9(17)
O2	33(2)	20(2)	13.4(19)	0	0	12.1(19)
O3	24(2)	26(2)	24(2)	0	0	16.1(17)
O4	19.3(19)	23(2)	23(2)	0	0	12.9(16)
N1	25.6(17)	15.2(16)	13.8(15)	-1.4(13)	-2.1(14)	4.8(14)
C1	26(3)	28(3)	9(3)	0	0	20(3)
C2	32(3)	15(3)	8(2)	0	0	9(3)
C3	17(3)	34(3)	17(3)	0	0	11(3)
C4	26(3)	28(3)	28(3)	0	0	20(2)
C5	37(3)	21(3)	21(3)	0	0	18(2)
C6	24(3)	20(3)	16(3)	0	0	9(2)
C7	17(3)	36(4)	29(3)	0	0	14(3)
C8	35(3)	24(3)	7(2)	0	0	16(2)
C9	47(3)	33(2)	20(2)	1.0(18)	-0.6(19)	26(2)
C10	31(2)	40(2)	20(2)	0.1(19)	3.1(18)	22(2)

Table S9. Bond Lengths for **1**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Fe1	O1	2.028(4)	N1	C10	1.335(5)
Fe1	O2 ¹	2.066(4)	C1	C2	1.498(8)
Fe1	O3 ²	2.187(4)	C2	C3	1.369(8)
Fe1	O4 ²	2.196(4)	C2	C7	1.405(8)
Fe1	N1 ³	2.161(3)	C3	C4	1.389(8)
Fe1	N1	2.161(3)	C4	C5	1.407(8)
O1	C1	1.246(6)	C5	C6	1.365(8)
O2	C1	1.270(7)	C5	C8	1.476(8)
O3	C8	1.286(7)	C6	C7	1.376(8)
O4	C8	1.256(7)	C9	C9 ⁴	1.380(8)
N1	C9	1.334(5)	C10	C10 ⁴	1.372(8)

¹1-X,2-Y,2-Z; ²1-Y,1+X-Y,+Z; ³+X,+Y,2-Z; ⁴+X,+Y,1-Z

Table S10. Bond Angles for **1**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	Fe1	O2 ¹	125.34(15)	C9	N1	C10	116.2(3)
O1	Fe1	O3 ²	89.78(15)	C10	N1	Fe1	122.2(3)
O1	Fe1	O4 ²	150.16(15)	O1	C1	O2	123.3(5)
O1	Fe1	N1 ³	89.70(9)	O1	C1	C2	119.8(5)
O1	Fe1	N1	89.71(9)	O2	C1	C2	116.9(5)
O2 ¹	Fe1	O3 ²	144.88(16)	C3	C2	C1	120.6(5)
O2 ¹	Fe1	O4 ²	84.50(15)	C3	C2	C7	120.5(5)
O2 ¹	Fe1	N1 ³	89.45(9)	C7	C2	C1	119.0(5)
O2 ¹	Fe1	N1	89.45(9)	C2	C3	C4	121.1(5)
O3 ²	Fe1	O4 ²	60.38(13)	C3	C4	C5	119.0(5)
N1	Fe1	O3 ²	90.88(8)	C4	C5	C8	118.7(5)
N1 ³	Fe1	O3 ²	90.88(8)	C6	C5	C4	118.5(5)
N1 ³	Fe1	O4 ²	90.69(9)	C6	C5	C8	122.7(5)
N1	Fe1	O4 ²	90.69(9)	C5	C6	C7	123.5(5)
N1 ³	Fe1	N1	178.14(18)	C6	C7	C2	117.4(5)
C1	O1	Fe1	178.5(4)	O3	C8	C5	117.7(5)
C1	O2	Fe1 ¹	112.8(3)	O4	C8	O3	120.2(5)
C8	O3	Fe1 ⁴	89.5(3)	O4	C8	C5	122.0(5)
C8	O4	Fe1 ⁴	89.9(3)	N1	C9	C9 ⁵	121.8(2)
C9	N1	Fe1	121.6(3)	N1	C10	C10 ⁵	122.0(2)

¹1-X,2-Y,2-Z; ²1-Y,1+X-Y,+Z; ³+X,+Y,2-Z; ⁴+Y-X,1-X,+Z; ⁵+X,+Y,1-Z

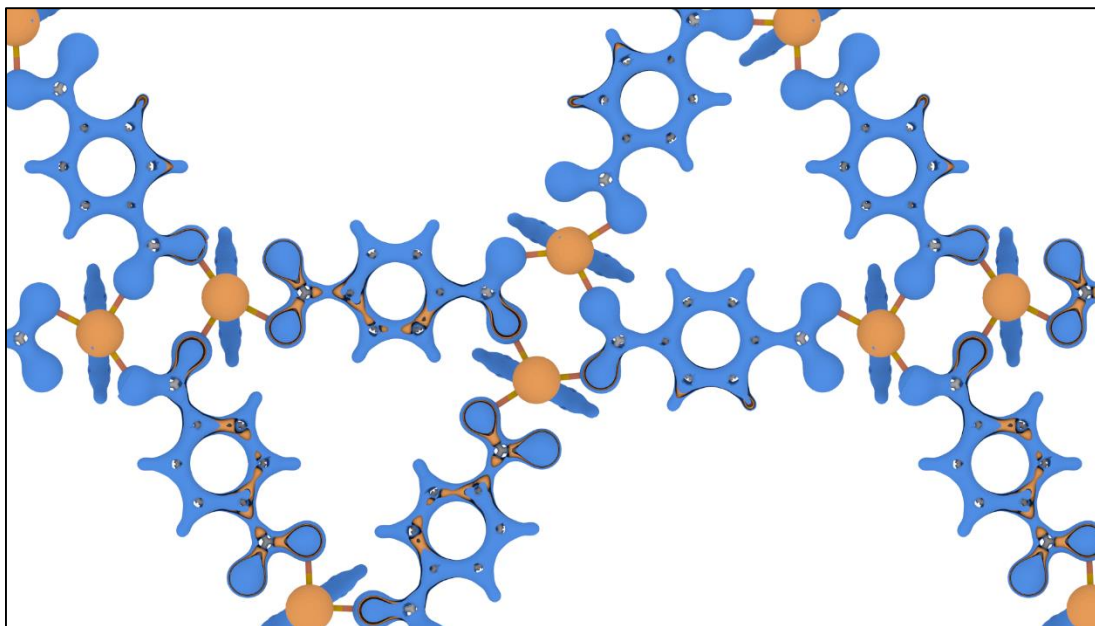


Figure S5. Spin up (orange) and spin down (blue) electron density showing FM ordering for **1**. Isosurfaces are shown at 9% of maximum value.

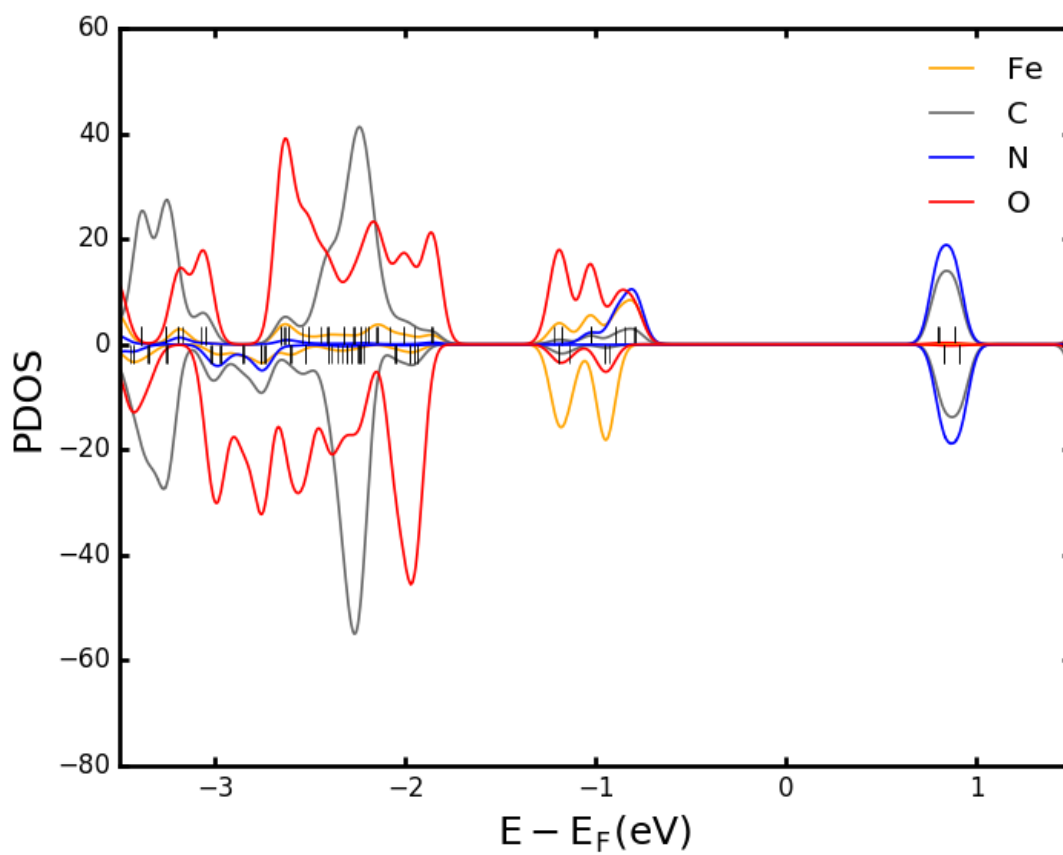


Figure S6. Projected electronic density of states showing FM ordering for **1**.

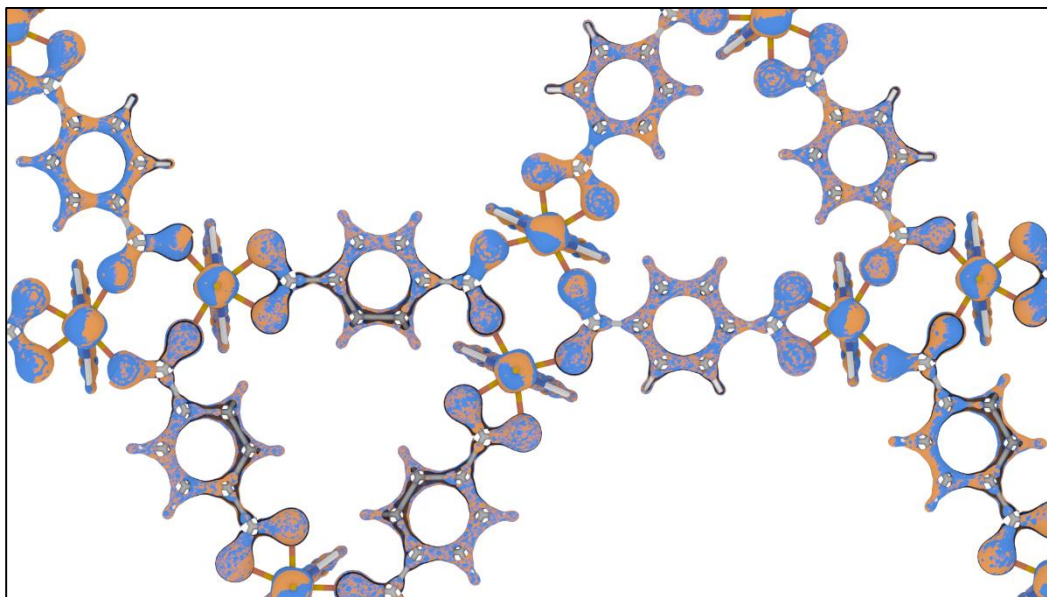


Figure S7. Spin up (orange) and spin down (blue) electron density showing NM (low-spin Fe) ordering for **1**. Isosurfaces are shown at 9% of maximum value.

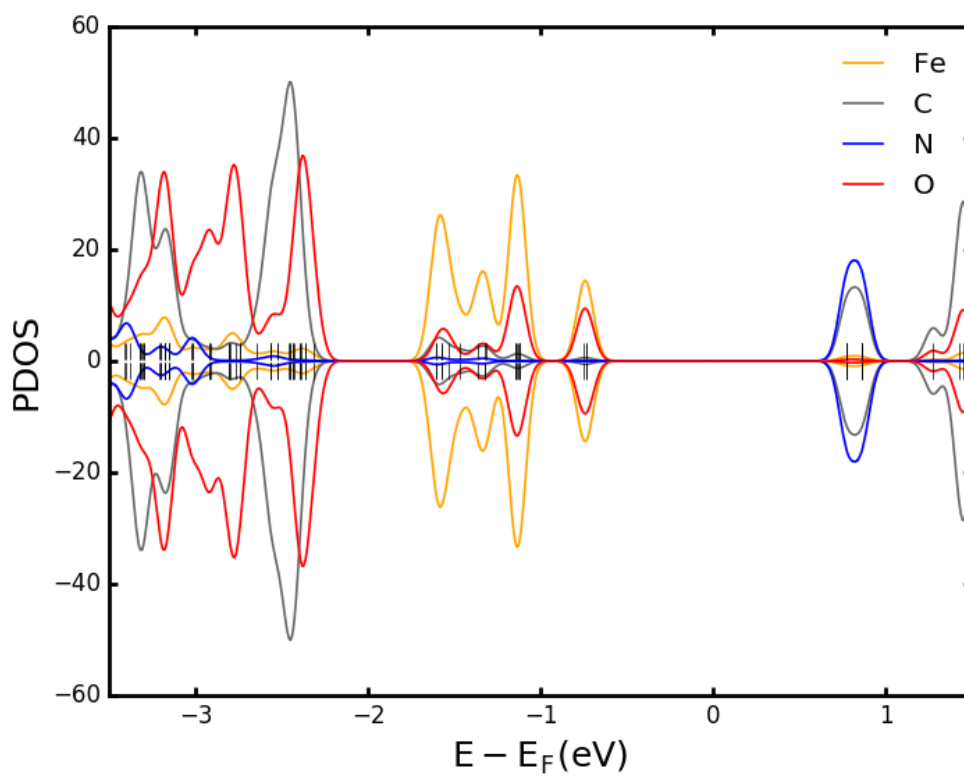


Figure S8. Projected electronic density of states showing NM ordering for **1**.

	Exp. (AFM)	AFM Up (avg)	% difference	AFM Down (avg)	% difference	FM (avg)	% difference	NM (avg)	% difference
Chelated O-Fe-O	60.38(13)°	61.712°	2.18%	61.681°	2.13%	61.757°	2.52%	65.764°	8.53%
Bridging O-Fe-O	125.34(15)°	112.057°	11.2%	112.796°	10.5%	113.522°	9.0%	104.666°	18.0%
N-Fe-N	178.14(18)°	176.992°	0.65%	177.061°	-0.61%	177.369°	0.44%	179.592°	0.81%

Table S11. Comparison of bond angles for the three DFT systems and experimental AFM system

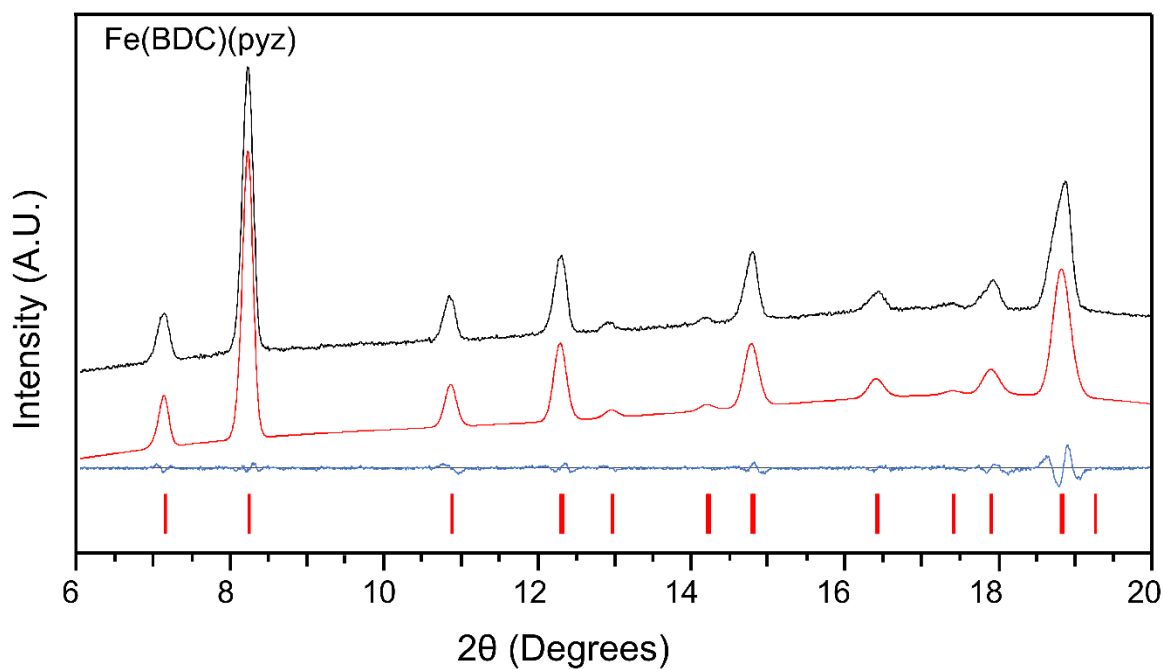


Figure S9. Experimental PXRD pattern (black) for **1** with the Le Bail fit (red) with the residual difference (blue). Theoretical peaks are shown as red lines at the bottom.

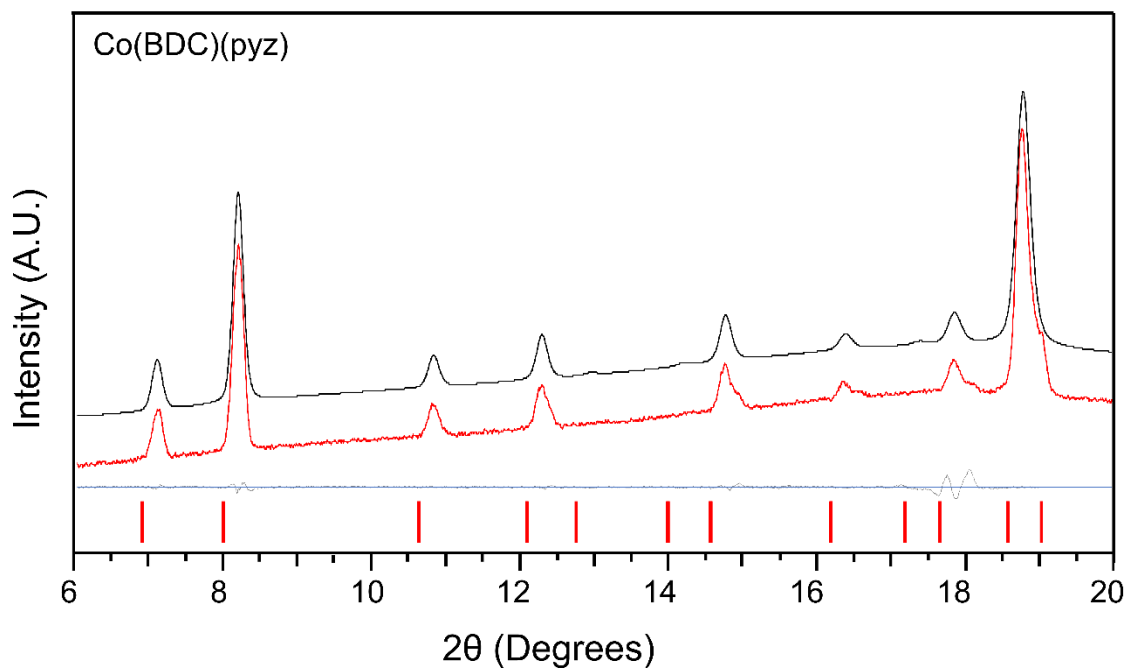


Figure S10. Experimental PXRD pattern (black) for **2** with the Le Bail fit (red) with the residual difference (blue). Theoretical peaks are shown as red lines at the bottom.

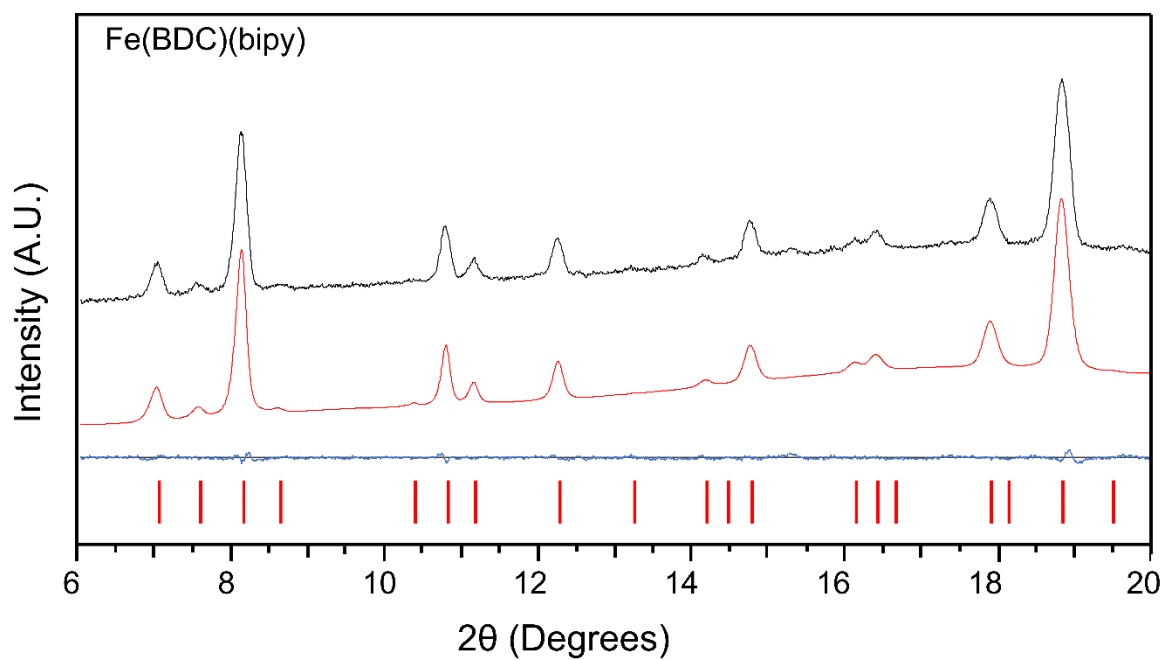


Figure S11. Experimental PXRD pattern (black) for **3** with the Le Bail fit (red) with the residual difference (blue). Theoretical peaks are shown as red lines at the bottom.

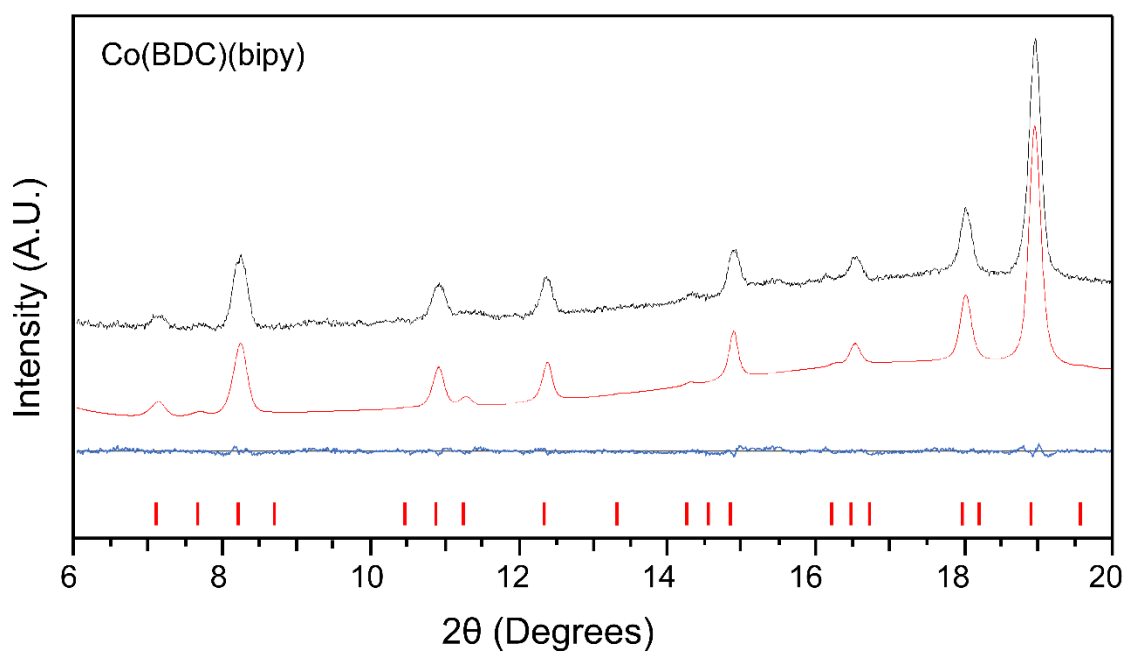


Figure S12. Experimental PXRD pattern (black) for **4** with the Le Bail fit (red) with the residual difference (blue). Theoretical peaks are shown as red lines at the bottom.