Supplementary Information

Magnetodielectric coupling in a non-perovskite metal-organic-framework

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1. Properties of CFA-12:

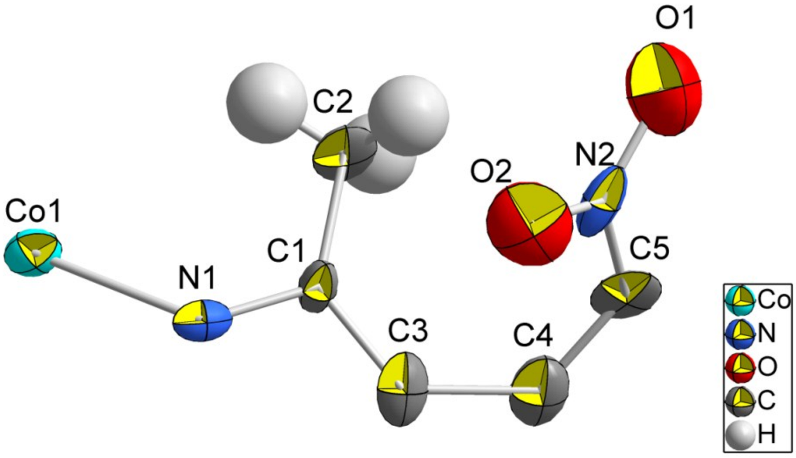

Figure S1: Ortep-style plot of the asymmetric unit of **CFA-12**. Thermal ellipsoids probability: 50 %.

A. Sample synthesis

Commercially available reagents of analytical grade were used as received without further purification.

Synthesis of 4,4'-(2-nitrobenzene-1,4-diyl)bis(3,5-dimethyl-1H-pyrazol) (NO_2-H_2-bdpb):
4,4'-(benzene-1,4-diyl)bis(3,5-dimethyl-1*H*-pyrazole) (5.00 g, 18.8 mmol) was added in small portions at 0°C to 50 ml of concentrated sulfuric acid. Nitric acid (65%, 1.1 ml, 20.6 mmol) was added dropwise and the resulting solution was stirred for one hour at ambient temperature. Then the mixture was poured on ice (100 g) and neutralized by adding a solution of sodium hydroxide (75 g) in water (800 ml). The resulting precipitate was collected by filtration, washed with water and dried at 65°C to give the product (5.40 g, 17.4 mmol, 92 %) as a light yellow solid. M.p. 293-295 °C; IR: $\tilde{\nu}$ = 410w, 454w, 482w, 567m, 597w, 665w, 702w, 753s, 763s, 873m, 897w, 976w, 1008s, 1043s, 1112w, 1154m, 1245w, 1274m, 1308m, 1337s, 1359s, 1413s, 1437m, 1524vs, 1554s, 1585s, 2922m, 3022m, 3142m cm^{-1}; ^{1}H-NMR (400 MHz, DMSO-d_6, 25°C): δ = 12.46 (s_{br}, 1 H, -NH), 12.40 (s_{br}, 1 H, -NH), 7.81 (d, 1 H, ^4J = 1.8 Hz), 7.62 (dd, 1 H, ^3J = 8.0 Hz, ^4J = 1.8 Hz), 7.41 (d, 1 H, ^3J = 8.0 Hz), 2.27 (s_{br}, 3 H),

2.24 (s_{br}, 3 H), 2.05 (s_{br}, 3 H), 1.96 (s_{br}, 3 H) ppm; ^{1}H-NMR (400 MHz, DMSO-d_6, 80°C): δ = 12.21 (s_{br}, 2 H, -NH), 7.78 (s, 1 H), 7.60 (d, 1 H, ^3J = 8.0 Hz), 7.39 (d, 1 H, ^3J = 8.0 Hz), 2.26 (s_{br}, 6 H), 2.02 (s_{br}, 6 H) ppm; ^{1}H-NMR (400 MHz, methanol-d_4, 25°C): δ = 7.82 (d, 1 H, ^4J = 1.8 Hz), 7.63 (dd, 1 H, ^3J = 8.0 Hz, ^4J = 1.8 Hz), 7.42 (d, 1 H, ^3J = 8.0 Hz), 2.32 (s_{br}, 6 H), 2.10 (s_{br}, 6 H) ppm; ^{13}C-NMR (100 MHz, DMSO-d_6, 80°C) δ = 151.0 (q), 135.0 (t), 133.75 (q), 133.73 (q), 132.68 (q), 132.66 (q), 132.0 (q), 129.1 (t), 125.3 (t), 123.43 (q), 123.39 (q), 11.8 (p), 11.1 (p) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$ /methanol-d_4 9:1) δ = 150.2 (q), 142.5 (q), 142.0 (q), 134.5 (t), 133.5 (q), 133.4 (q), 132.7 (q), 132.6 (q), 129.1 (t), 125.4 (t), 124.2 (q), 124.1 (q), 11.29 (p), 11.23 (p), 10.77 (p), 10.74 (p) ppm; MS (ESI) : m/z (%) = 312.15 $(M + H)^+$; elemental analysis: calc. (%) for $C_{16}H_{17}N_5O_2$ (311.3): C 61.72, H 8.63, N 22.49; found: C 61.59, H 8.78, N 22.39. ^{1}H- and ^{13}C-NMR are presented in figures S2-6.

Synthesis of CFA-12 (microwave irradiation method):

In a pyrex sample tube (35 mL), NO_2-H_2-bdpb (228 mg, 733 µmol) and $Co(NO_3)_2 \cdot 6H_2O$ (208 mg, 720 µmol) were dissolved at ambient temperature in DMF (4 mL). The tube was sealed and heated for 8 min at 120°C by a microwave synthesizer (CEM Discover S) at 300W. After cooling down to 20°C the product was filtered, washed with DMF (3x 20 mL) and CH_2Cl_2 (3x 10mL). Afterwards, the resulting solid was suspended three times in CH_2Cl_2 (3 mL) for 24 h (followed by centrifugation and decantation each time), and was subsequently dried in vacuum for 6 h at 25°C prior to further investigations to give phase pure CFA-12 (235 mg, 639 mmol, 87% based on NO_2-H_2-bdpb). Elemental analysis calc. (%) for $Co(C_{16}H_{15}N_5O_2)$: C 52.2, H 4.1, N 19.0; found: C 51.7, H 4.4, N 19.2. The IR spectrum of CFA-12 is shown in figure S7.

Synthesis of CFA-12 (solvothermal method):

The crystals of CFA-12 suitable for single crystal X-ray analysis were synthesized by solvothermal synthesis: NO_2-H_2-bdpb (17.4 mg, 56 µmol) was dissolved in DMF (4 mL). To the solution $Co(NO_3)_2 \cdot 6H_2O$ (100 mg, 344 µmol) was added and dissolved. The resulting solution was placed in a heating tube (10 mL) which was closed with cap and heated at a constant rate of 0.10°C min^{-1} to 120°C and then for 24 h at 120°C. The solution was subsequently cooled to 25°C and the violet crystals were taken for the single-crystal measurements.

B. Physical Methods

Fourier transform infrared (FTIR) spectra were recorded with an attenuated total reflectance (ATR) unit in the range 4000–400 cm^{-1} on a Bruker Equinox 55 FT-IR spectrometer. The following indicators are used to characterize absorption bands: very strong (vs), strong (s), medium (m), weak (w). Molecular mass was determined with a Q-Tof Ultima mass spectrometer (Micromass) equipped with an ESI source. Elemental analysis was performed on a Vario EL III, Elementar-Analysensysteme GmbH. Thermogravimetric analysis (TGA) was performed with a TGA Q500 analyzer in the temperature range of 25–800 °C in flowing nitrogen at a heating rate of 10 K min^{-1}. Ar adsorption/desorption isotherms were measured with a Quantachrome I instrument. Adsorbed gas amounts are given in cm^3 g^{-1} [STP], where STP = 100 kPa and 273.15 K. Prior to the measurement, the sample was heated at 180 °C for

5 h in high vacuum in order to remove occluded solvent molecules. Ambient temperature X-ray powder diffraction (XRPD) pattern was measured with a Seifert XRD 3003 TT diffractometer equipped with a Meteor 1D detector operated at 40 kV, 40 mA, CuK$_{\alpha}$ (λ = 1.54247 Å) with a scan speed of 3 s per step and a step size of 0.02° in 2θ. The variable temperature XRPD (VTXRPD) data were collected in the 2θ range of 4-60° with 0.02° steps, with a Empyrean (PANalytical) diffractometer equipped with Bragg-Brentano^{HD} mirror, PIXcel^{3D} 2x2 detector and XRK 900 Reactor chamber (Anton Paar). The patterns were recorded in a temperature range from 25°C to 500°C. Temperature program between measurements: heating rate (0.5°C s^{-1}), then 10 min isothermal.

C. Single-crystal X-ray diffraction

The crystals of CFA-12 ·1.2(C_3H_7NO) were taken from mother liquor and mounted on a MiTeGen MicroMounts. Several crystals were tested on the diffractometer. Unfortunately, most of the crystals scattered only up to ca. 32° 2θ (1.3 Å resolution). The best recorded data were obtained for a single crystal of CFA-12 ·1.2(C_3H_7NO) of approx. dimensions 35 × 20 × 18 μm^3. X-ray data for the single crystal structure determinations of CFA-12 ·1.2(C_3H_7NO) were collected on a Bruker D8 Venture diffractometer. Intensity measurements were performed using monochromated (doubly curved silicon crystal) MoK$_{\alpha}$ radiation (0.71073 Å) from a sealed microfocus tube. Generator settings were 50 kV, 1 mA. Data collection temperature was -173°C. APEX3 software was used for preliminary determination of the unit cell.[1] Determination of integrated intensities and unit cell refinement were performed using SAINT.[2] The structure was solved and refined using the Bruker SHELXTL Software Package.[3] Selected crystal data and details of structure refinement for CFA-12 ·1.2(C_3H_7NO) are provided in table S1. Complete crystallographic data for the structure reported in this paper have been deposited in the CIF format with the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB21EZ, UK as supplementary publication no. CCDC 1513619. Copies of the data can be obtained free of charge on quoting the depository numbers. (FAX: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http//www.ccdc.cam.ac.uk).

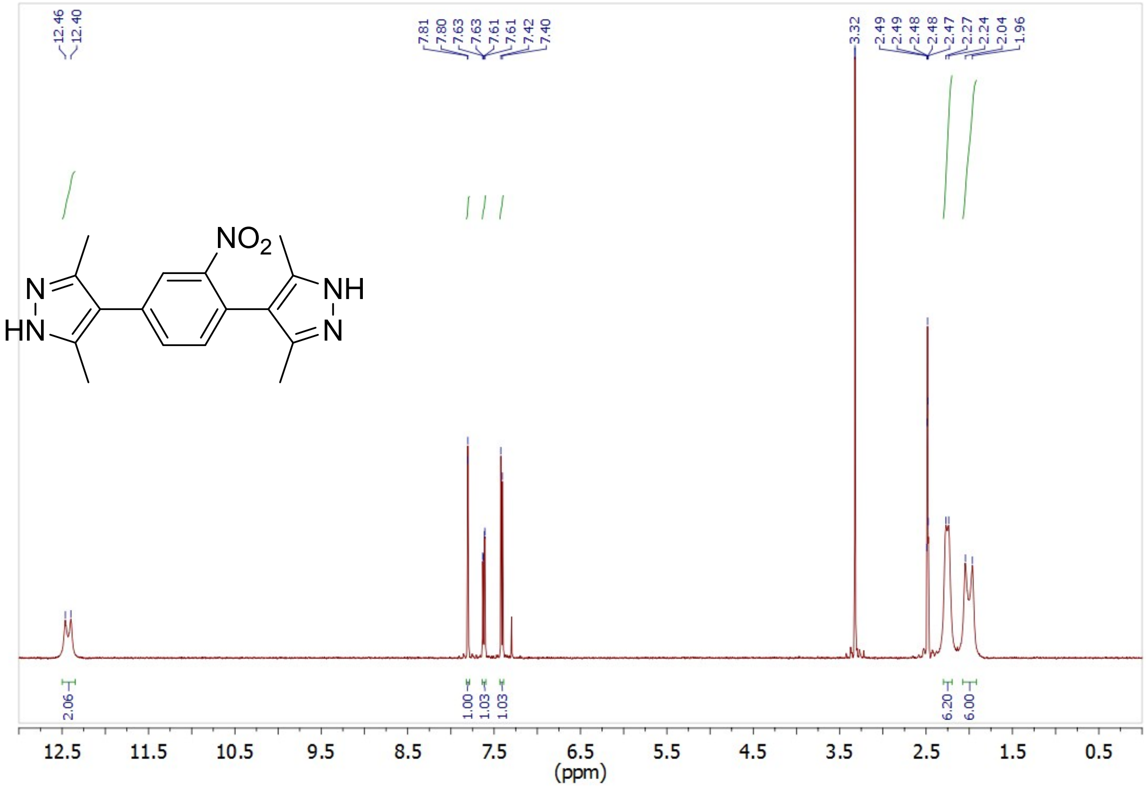

Figure S2: ^1H NMR spectrum (400 MHz, DMSO-d_6, 25°C) for 4,4'-(2-nitrobenzene-1,4-diyl)bis(3,5-dimethyl-1*H*-pyrazole) (NO_2-H_2-bdpb).

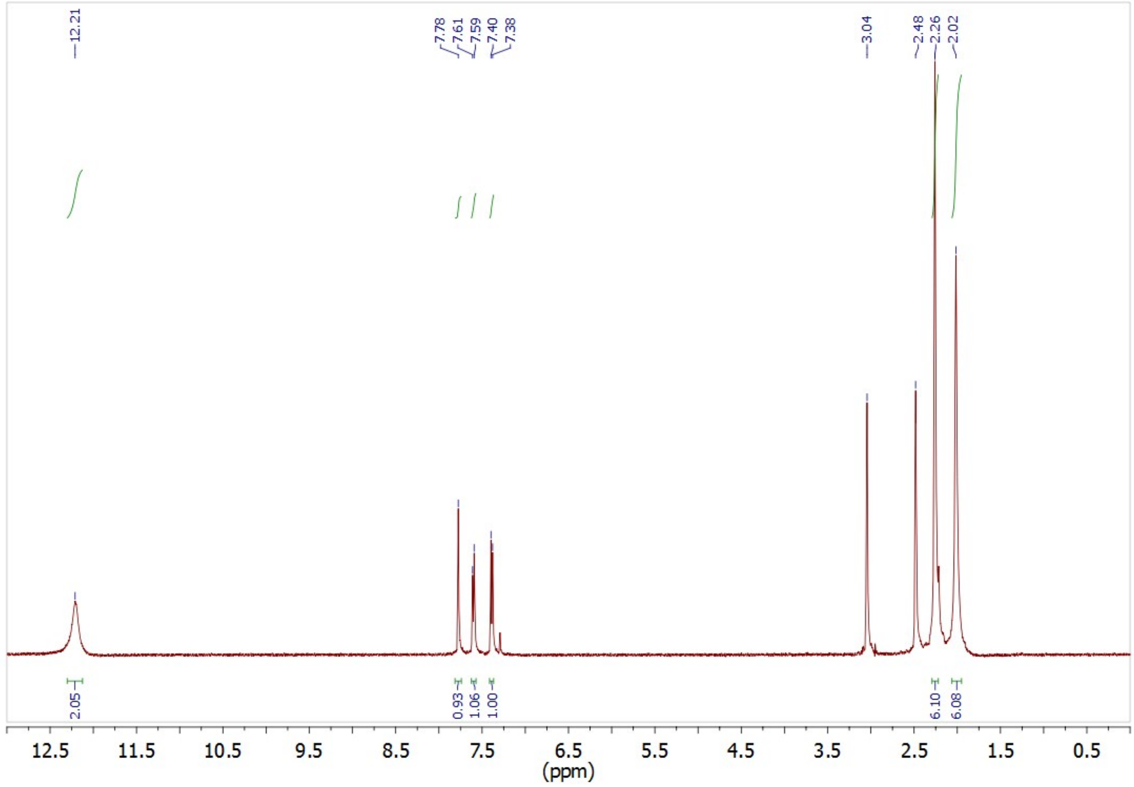

Figure S3: ^1H NMR spectrum (400 MHz, DMSO-d_6, 80°C) for 4,4'-(2-nitrobenzene-1,4-diyl)bis(3,5-dimethyl-1*H*-pyrazole) (NO_2-H_2-bdpb).

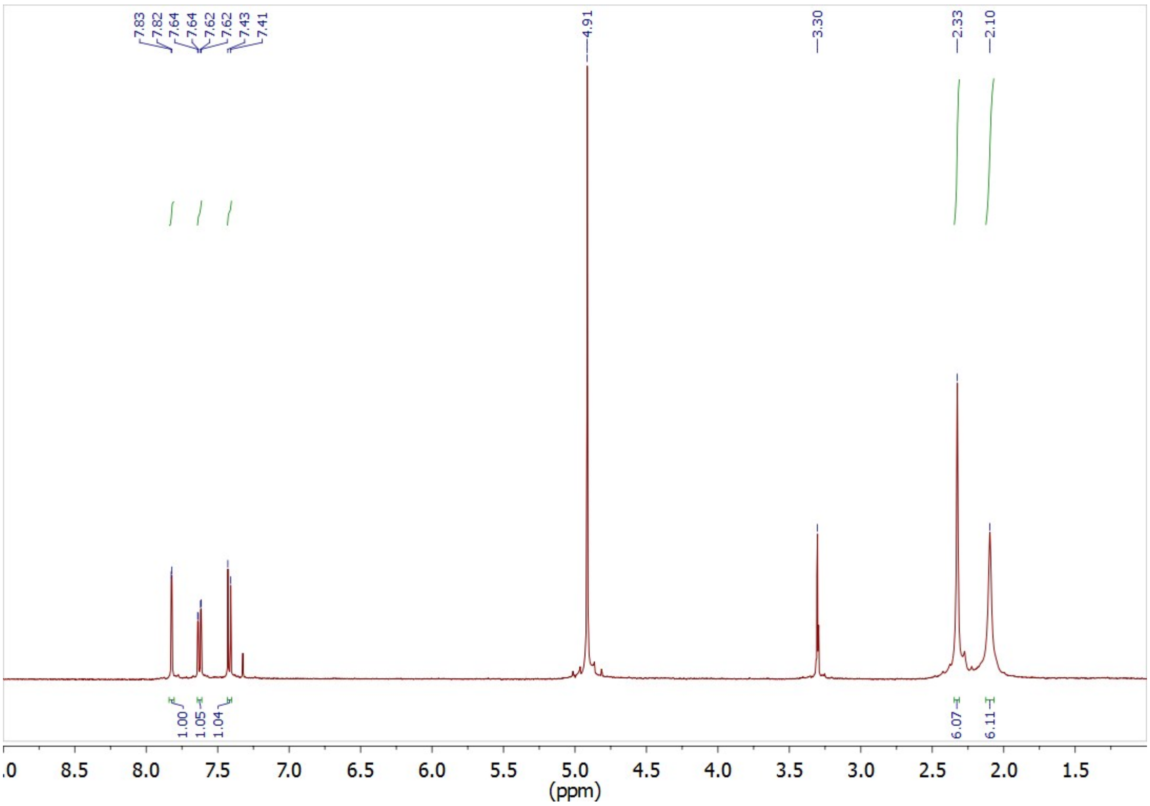

Figure S4: ^{1}H NMR spectrum (400 MHz, methanol-d$_4$, 25°C) for 4,4'-(2-nitrobenzene-1,4-diyl)bis(3,5-dimethyl-1*H*-pyrazole) (NO$_2$-H$_2$-bdpb).

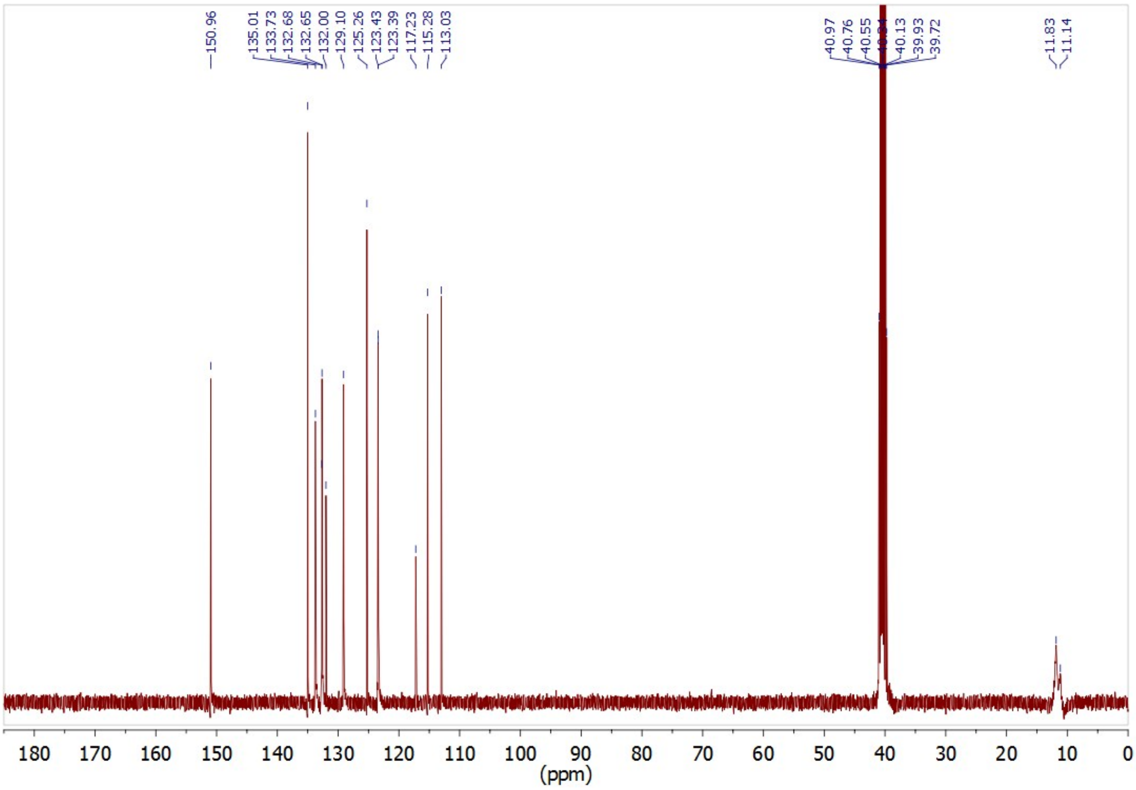

Figure S5: ^{13}C-NMR spectrum (100 MHz, DMSO-d$_6$, 80°C) for 4,4'-(2-nitrobenzene-1,4-diyl)bis(3,5-dimethyl-1*H*-pyrazole) (NO$_2$-H$_2$-bdpb).

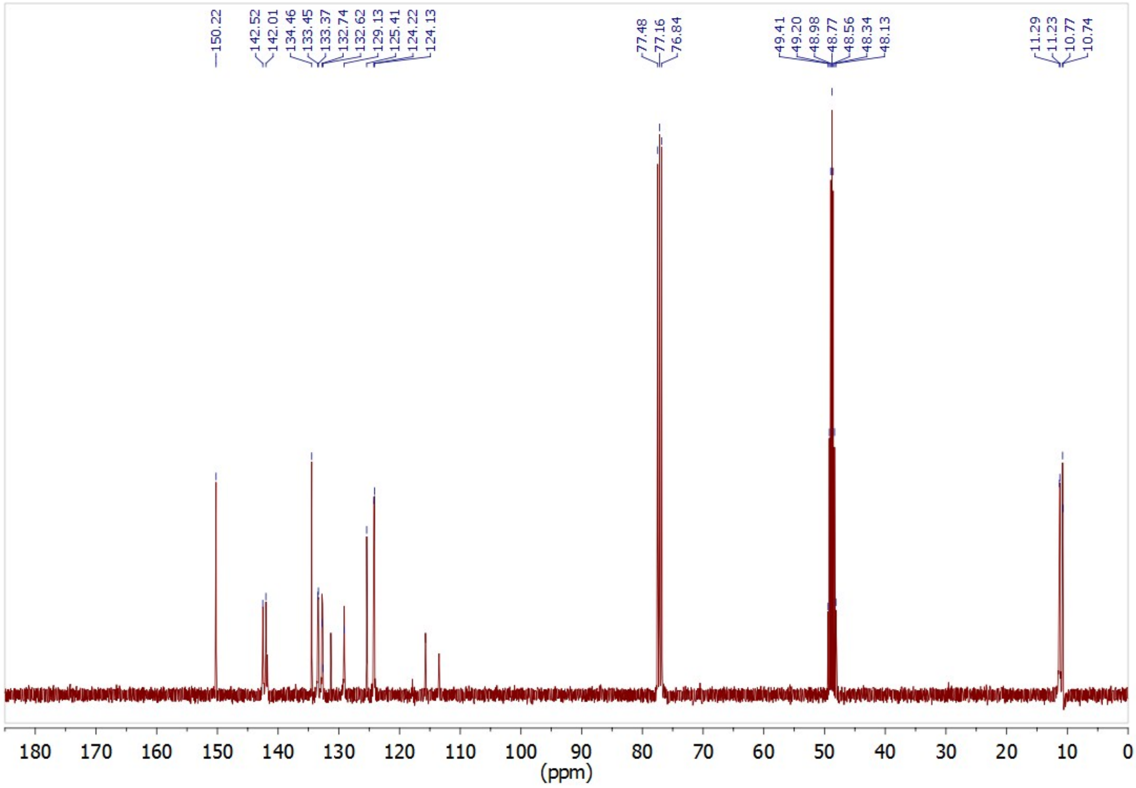

Figure S6: ^{13}C-NMR spectrum (100 MHz, $CDCl_3$/methanol-d_4 9:1, 25°C) for 4,4'-(2-nitrobenzene-1,4-diyl)bis(3,5-dimethyl-1*H*-pyrazole) (NO_2-H_2-bdpb).

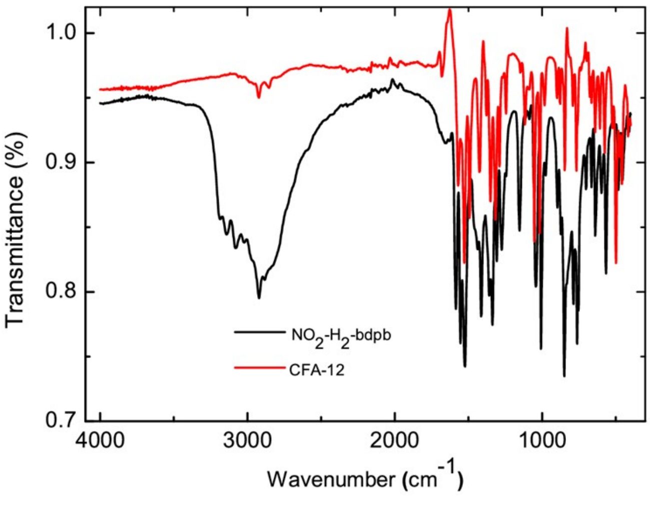

Figure S7: IR-spectra of 4,4'-(2-nitrobenzene-1,4-diyl)bis(3,5-dimethyl-1*H*-pyrazole) (NO_2-H_2-bdpb) and CFA-12.

Table S1 Crystal data and structure refinement of CFA-12 $\cdot 1.2(C_3H_7NO)$

Compound	**CFA-12**
Empirical formula	$C_{19.6}H_{23.4}CoN_{6.2}O_{3.2}$
Formula	$C_{16}H_{15}N_5CoO_2 \cdot 1.2(C_3H_7NO)$
M_r/g mol^{-1}	455.98
T/K	100(2)
Wavelength/Å	0.71073
Crystal system	Tetragonal
Space group	$P4_2/ncm$ (no. 138)
a/Å	18.576(4)
c/Å	7.3728(18)
V/Å^3	2544.0(10)
Z	4
D_c/g cm^{-3}	1.191
μ/mm^{-1}	0.704
F(000)	948
θ Range/°	3.10 to 26.03
Refls. collected	51515
Refls. unique	1280
R(int)	0.2147
GooF	1.206
R_1 (I>2σ(I)]^a	0.1652
wR_2 (all data)^b	0.3729
Largest diff. peak and hole/Å^{-3}	1.691 and -0.447

$^aR_1 = \Sigma||F_0|-|F_c||/\Sigma|F_0|$; $^bwR_2 = \Sigma[w(F_0^2-Fc^2)2]/\Sigma[w(F_0^2)2]^{1/2}$.

D. Pore size distribution of CFA-12

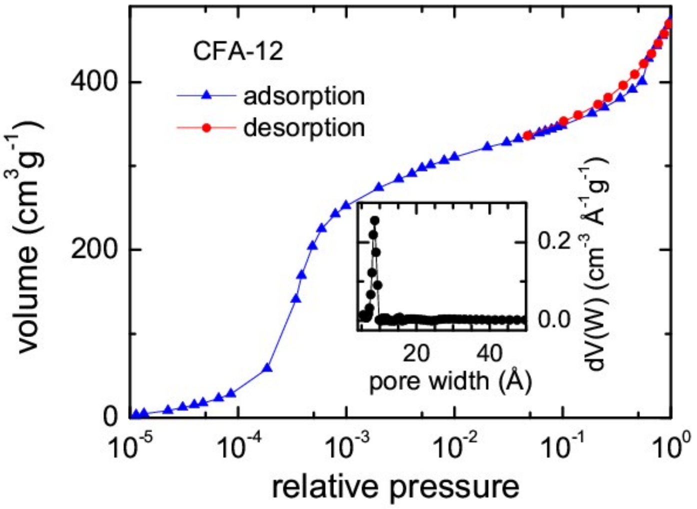

Figure S8: Ar adsorption/desorption isotherms for CFA-12 at 77 K; Inset: Pore size distribution for CFA-12.

The argon adsorption/desorption isotherm for CFA-12 at 77 K, presented in the inset of figure S8, is typical for microporous solids and reveals the Brunauer–Emmett–Teller (BET)[4] surface area of 1190 m^2 g^{-1} and a total pore volume of 0.58 cm^3 g^{-1}. The slight hysteresis observed in the relative pressure range from 0.05-0.6 could be due to the flexibility of the framework (rotation of phenyl rings). The pore size distribution was calculated by using a non-local density functional theory (NLDFT),[5] implementing a carbon equilibrium transition kernel for argon adsorption at 77 K and based on a slit-pore model,[6] reveals a clear maximum at 8.6 Å (inset of figure S8), which is in good agreement with the crystallographic data (8.27 Å).

E. Dielectric properties CFA-12

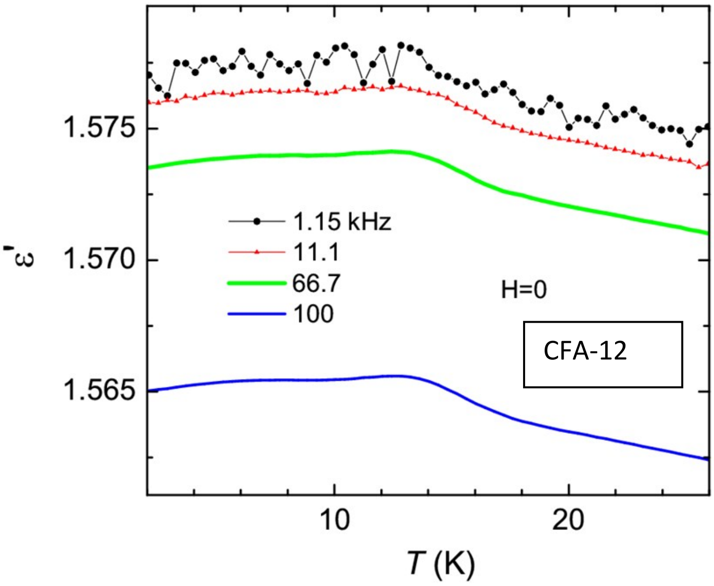

Figure S9: Magnified view of real part of dielectric constant as a function of temperature from 2-26 K for different frequencies between 1 and 100 kHz and for zero external magnetic field for the compound CFA-12.

2. Properties of MFU-2 ($Co[C_{16}H_{16}N_4]$):

A. Magnetic properties of MFU-2:

The magnetic and dielectric investigation is performed on isostructural MFU-2. The dc susceptibility ($\chi = M/H$) as a function of temperature as measured at a field of 5 kOe is shown in figure S10. The compound shows similar magnetic behavior like CFA-12. The compound exhibits FM-like ordering below 20 K. The Curie-Weiss fit of the inverse susceptibility for $T > 150$ K yields an effective moment of $\mu_{eff} = 4.5\ \mu_B$ and a Curie-Weiss temperature of $\Theta_W = -37$ K, which is nearly same as CFA-12, indicating AFM exchange interactions also in this compound. The ZFC-FC bifurcation is observed by application of low external magnetic fields (see left inset of figure S10), similar to bifurcation effects observed in CFA-12. We have also performed isothermal *M(H)* measurements at selected temperatures. The hysteresis at 2 K clearly confirms the FM nature of this compound. However, *M(H)* does not saturate at high fields, rather linearly varies with increasing magnetic field, which confirms the presence of AFM exchange also in this compound. The higher value of Θ_{CW} also manifests the short-range magnetic correlations arising from spin-chains of Co. Finally, we conclude, competing FM-AFM interaction is a common characteristic of this family, which is present in both systems, namely in MFU-2 and CFA-12.

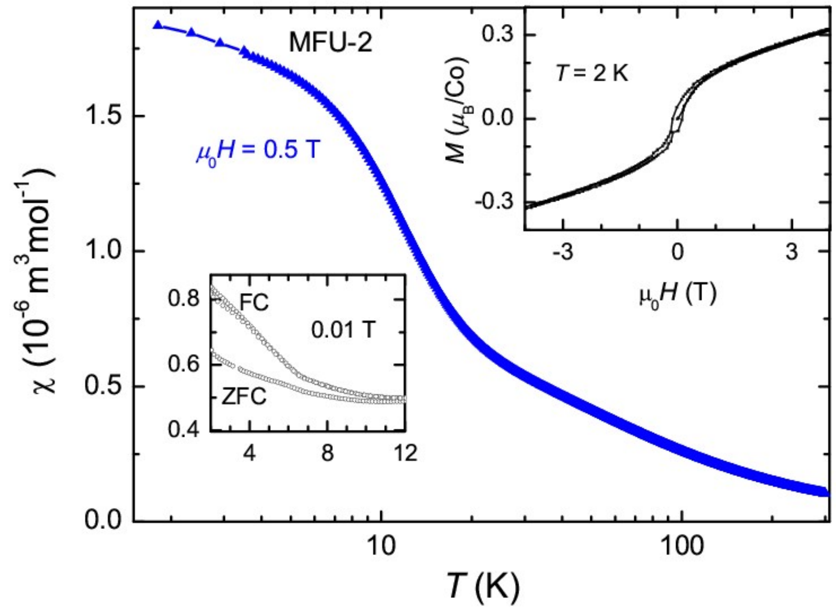

Figure S10: *dc* magnetization divided by magnetic field as a function of temperature for a magnetic field of 0.5 T at temperatures from 2 – 300 K; the left lower inset shows measurements at zero-field-cooled and field-cooled conditions for 0.01 T in the temperature range 2 – 13 K; the upper right inset documents the isothermal magnetization as a function of magnetic field at 2 K.

B. Dielectric and magnetodielectric properties of MFU-2:

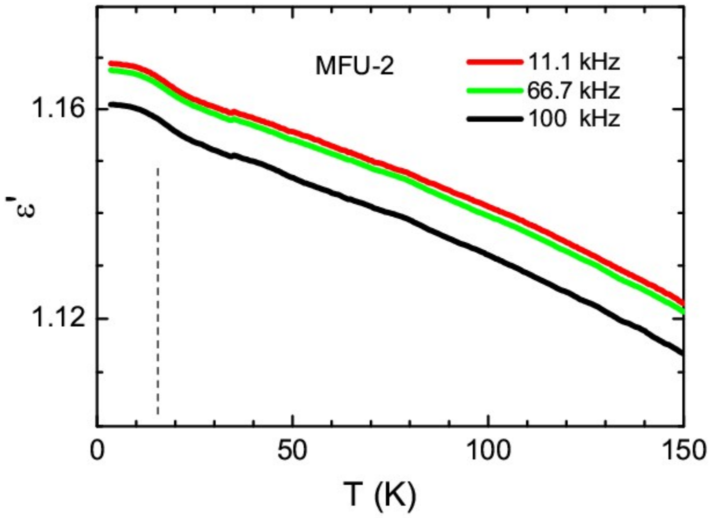

Figure S11: Real part of dielectric constant as a function of temperature from 2 – 150 K for some selective frequencies for the compound MFU-2. Dashed line indicates the magnetic transition.

The dielectric constant ε′ as a function of temperature for the compound MFU-2 is shown in figure S11. No feature is observed at high temperatures. The slow and continuous increase of the dielectric constant with decreasing temperature could be due to volume changes by thermal expansion effects, which in turn decreases the thickness of the capacitor.

Alternatively, it could be a genuine intrinsic temperature change of the dielectric constant. Though, there is no clear feature at the onset of magnetic ordering, a broadened feature is observed around 15 K. While this indicates the possibility of intrinsic magnetodielectric coupling in this compound, we did not observe any appreciable change in dielectric constant in the presence of a magnetic field, which suggest that the coupling strength is very weak in this compound (as shown in the Figure 6 in main article and discussed there). Therefore, the dielectric and magnetodielectric investigation on MFU-2 and CFA-12 clearly demonstrate the role of dipolar NO_2.

References:

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[S5] P. I. Ravikovitch, A. V. Neimark, *Colloids and Surfaces.* **187**, 11 (2001)
[S6] J. Jagiello, M. Thommes, *Carbon* **42**, 1227 (2004)