

Supplementary Information for:

Single ion magnet behaviour in a two-dimensional network of dicyanamide-bridged cobalt(II) ions

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Experimental section

Materials and General Methods

All starting chemicals were commercially available (POCh and Aldrich) and were used without further purification. IR spectra were recorded on a *Nicolet Magna 560* spectrometer in the spectral range 4000-400 cm^{-1} with the samples in the form of KBr pellets. The electronic spectra were obtained from solid state samples on Nicolet Evolution 220 (190 – 1100 nm) and on *Nicolet iS50 FT-IR* (700 – 1500 nm) spectrophotometers. Powder X-ray diffraction (PXRD) measurements were carried out on a PANalytical *Empyrean* X-ray diffractometer using Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$), in which the X-ray tube was operated at 40 kV and 30 mA ranging from 5 to 80°.

Crystal structure determination and refinement

The X-ray intensity data of $[\text{Co}(\text{dca})_2(\text{atz})_2]_n$ (**1**) were collected on a Gemini A Ultra diffractometer equipped with Atlas CCD detector and graphite monochromated MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) at room temperature. The unit cell determination and data integration were carried out using the CrysAlis package of Oxford Diffraction.¹ Lorentz, polarization and empirical absorption correction using spherical harmonics implemented in SCALE3 ABSPACK scaling algorithm were applied.² The structures were solved by the direct methods and subsequently completed by the difference Fourier recycling. All the non-hydrogen atoms were refined anisotropically using full-matrix, least-squares technique. The hydrogen atoms were treated as riding on their parent carbon atoms and assigned isotropic temperature factors equal 1.2 times the value of equivalent temperature factor of the parent atom. SHELXS97 and SHELXL97 programs³ were used for all the calculations. Atomic scattering factors were those incorporated in the computer programs. Details concerning crystal data and refinement are given in Table S1. Selected bond lengths and bond angles are listed in Table S2.

Table S1. Crystal data and structure refinement for [Co(dca)₂(atz)₂]_n (**1**).

Empirical formula	C ₁₀ H ₈ CoN ₁₄
Formula weight	383.23
Temperature [K]	293.0(2)
Wavelength [Å]	0.71073
Crystal system	monoclinic
Space group	<i>C2/c</i>
Unit cell dimensions [Å, °]	a = 14.747(2) b = 8.8586(4) c = 13.4233(10) β = 119.302(7)
Volume [Å ³]	1529.2(2)
Z	4
Density (calculated) [Mg/m ³]	1.655
Absorption coefficient [mm ⁻¹]	1.152
<i>F</i> (000)	772
Crystal size [mm]	0.156 x 0.139 x 0.112
θ range for data collection [°]	3.37 to 25.05
Index ranges	-17 ≤ <i>h</i> ≤ 14 -10 ≤ <i>k</i> ≤ 10 -13 ≤ <i>l</i> ≤ 15
Reflections collected	4265
Independent reflections	1348 (<i>R</i> _{int} =0.0270)
Completeness to 2θ = 25.05° [%]	99.8
Max. and min. transmission	0.885 and 1.000
Data / restraints / parameters	1348 / 0 / 115
Goodness-of-fit on <i>F</i> ²	1.041
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0253 <i>wR</i> 2 = 0.0599
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0316 <i>wR</i> 2 = 0.0625
Largest diff. peak and hole [e Å ⁻³]	0.238 and -0.274

Table S2. The selected bond lengths [Å] and angles [°] for [Co(dca)₂(atz)₂]_n^a.

Bond lengths		Bond angles	
Co(1)-N(1)	2.1677(15)	N(1)-Co(1)-N(1)#1	180.00(9)
Co(1)-N(99)	2.0887(17)	N(98)-Co(1)-N(1)	90.39(6)
Co(1)-N(98)	2.0968(16)	N(98)-Co(1)-N(1)#1	89.61(6)
		N(98)#1-Co(1)-N(98)	180.0
		N(99)-Co(1)-N(1)	89.69(6)
		N(99)-Co(1)-N(98)	91.33(7)
		N(99)-Co(1)-N(1)#1	90.31(6)
		N(99)-Co(1)-N(98)#1	88.67(7)
		N(99)-Co(1)-N(99)#1	180.00(7)
		Co(1)-C(98)-N(98)	167.99(17)
		Co(1)-C(99)-N(99)	176.40(16)
		C(98)-N(97)-C(99)#2	121.29(17)
		N(98)-C(98)-N(97)	172.5(2)
		N(99)-C(99)-N(97)#3	172.9(2)

^aSymmetry transformations used to generate equivalent atoms: (#1) = -x+1/2, -y-1/2, -z+1; (#2) = x, -y, z+1/2; (#3) = x, -y, z-1/2.

Table S3. Selected magneto-structural data for dca-bridged Co(II) complexes

L.p	Compound ^b	Dimensionality	Co-dca-Co distance	Co-N _L [Å]	Co-N _{dca} [Å]	Magnetic properties	Ref.
1	[Co(μ _{1,5} -dca) ₂ (imz) ₂] _n	1D	7.395	2.141(4)	2.161(2) 2.164(2)	AF (J = -0.7cm ⁻¹) ^d	4
2	[Co(enbzipy)(μ _{1,5} -dca)] _n (ClO ₄) _n	1D	8.569(8)	2.023(3) 2.028(3) 2.083(3) 2.102(3)	2.092(3) 2.136(3)	SCO	5
3	{[Co(bpm) ₂ (μ _{1,5} -dca)](ClO ₄) _n }	1D	7.999	2.141(4)	2.103(5)	c	6
4	[Co(dmpzm)(μ _{1,5} -dca) ₂] _n	2D	7.4900(8) 8.7527(8)	2.167(3) 2.182(3)	2.134(3) 2.129(3) 2.099(2) 2.129(3)	magnetically isolated cations	7
5	[Co(μ _{1,5} -dca) ₂ (4,4'-bipy)] _n · 0.5nH ₂ O · 0.5nMeOH	2D	7.349(3)	2.138(2)	2.111(1) 2.118(1)	c	8
6	[Co ₂ (μ _{1,5} -dca) ₄ (4-cypy) ₄] _n	2D	7.745(3) 8.037(3) 8.349(2) 8.404(2)	2.149(6) 2.156(6) 2.179(7) 2.181(6)	2.066(6) 2.079(6) 2.113(7) 2.119(6) 2.120(7) 2.122(6) 2.124(6) 2.139(6)	AF (J = -0.80 cm ⁻¹)	9
7	[Co(μ _{1,5} -dca) ₂ (3-cypy) ₂] _n	2D	8.194(1)	2.147(2)	2.125(2) 2.126(2)	AF (J = -1.18 cm ⁻¹)	9
8	[Co(btrm) ₂ (μ _{1,5} -dca)]ClO ₄	2D	8.539(2)	2.136(6) 2.156(6) 2.151(5) 2.143(5) 2.146(5) 2.140(5)	2.072(5) 2.081(6) 2.084(5)	AF ^e	10
9	[Co(μ _{1,5} -dca) ₂ (dmdpy)] _n	2D	8.102(4)	2.142(2)	2.114(2) 2.095(3)	AF (J = -0.08 cm ⁻¹)	11
10	[Co(μ _{1,5} -dca) ₂ (4,4'-bipy)] _n	3D	8.476(2) 8.539(1)	2.131(8) 2.164(8) 2.152(7) 2.153(8)	2.111(6) 2.121(8) 2.122(6) 2.108(6) 2.107(8) 2.080(7) 2.096(6) 2.119(7)	AF ^e	8
11	[Co(μ _{1,5} -dca) ₂ (dbtp)] _n	3D	7.675(1) 7.918(2)	2.136(7) 2.195(7)	2.087(7) 2.109(7) 2.153(7)	AF ^e	12

^a Only six-coordinate Co(II) complexes with CoN₆ chromophore were considered.

^b Abbreviation for the ligands: dmpzm = bis(3,5-dimethylpyrazolyl)methane, 4,4'-bipy = 4,4'-bipyridine, dbtp = 1,3-di(benzotriazol-1-yl)propane, cypy = cyanopyridine, bpm = bis(pyrazolyl)methane, imz = imidazole, enbzipy = N,N'-bis(2-pyridinylbenzylidene)ethane-1,2-diamine, btrm = 1,2-bis(1,2,4-triazole-1-yl)methane.

^c not measured

^d $H = -JS_1S_2$

^e J value not given

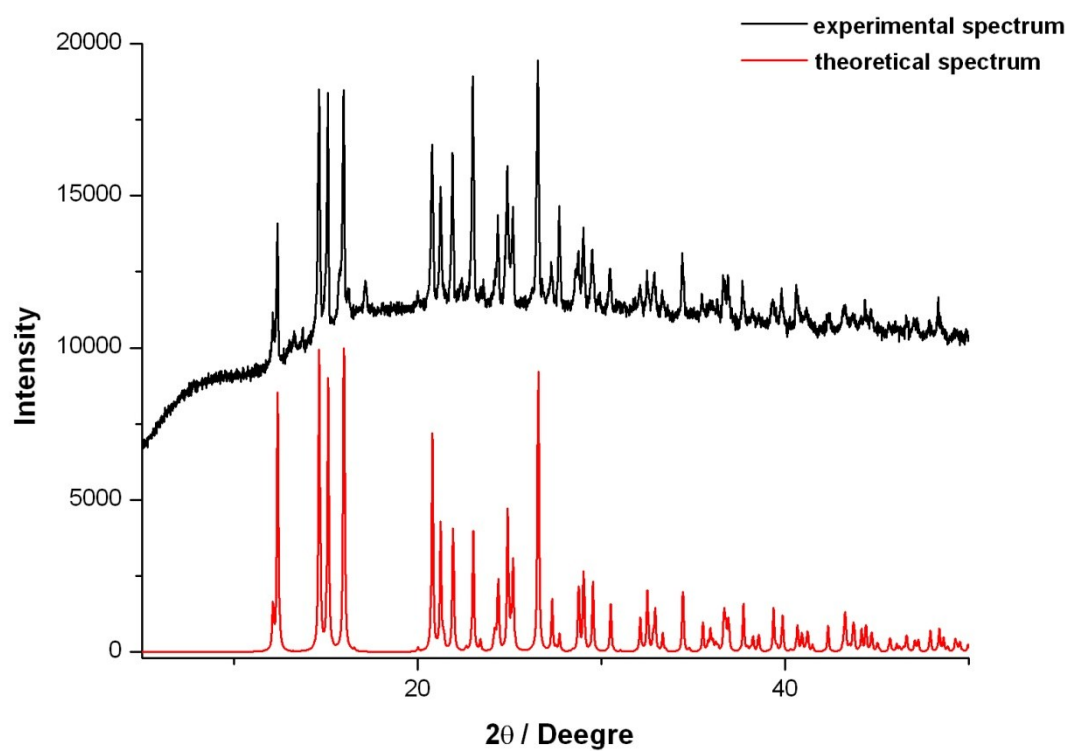


Figure S1. X-ray powder diffraction pattern of $[\text{Co}(\text{dca})_2(\text{atz})_2]_n$ (**1**) at room temperature, together with the calculated pattern from the single crystal data.

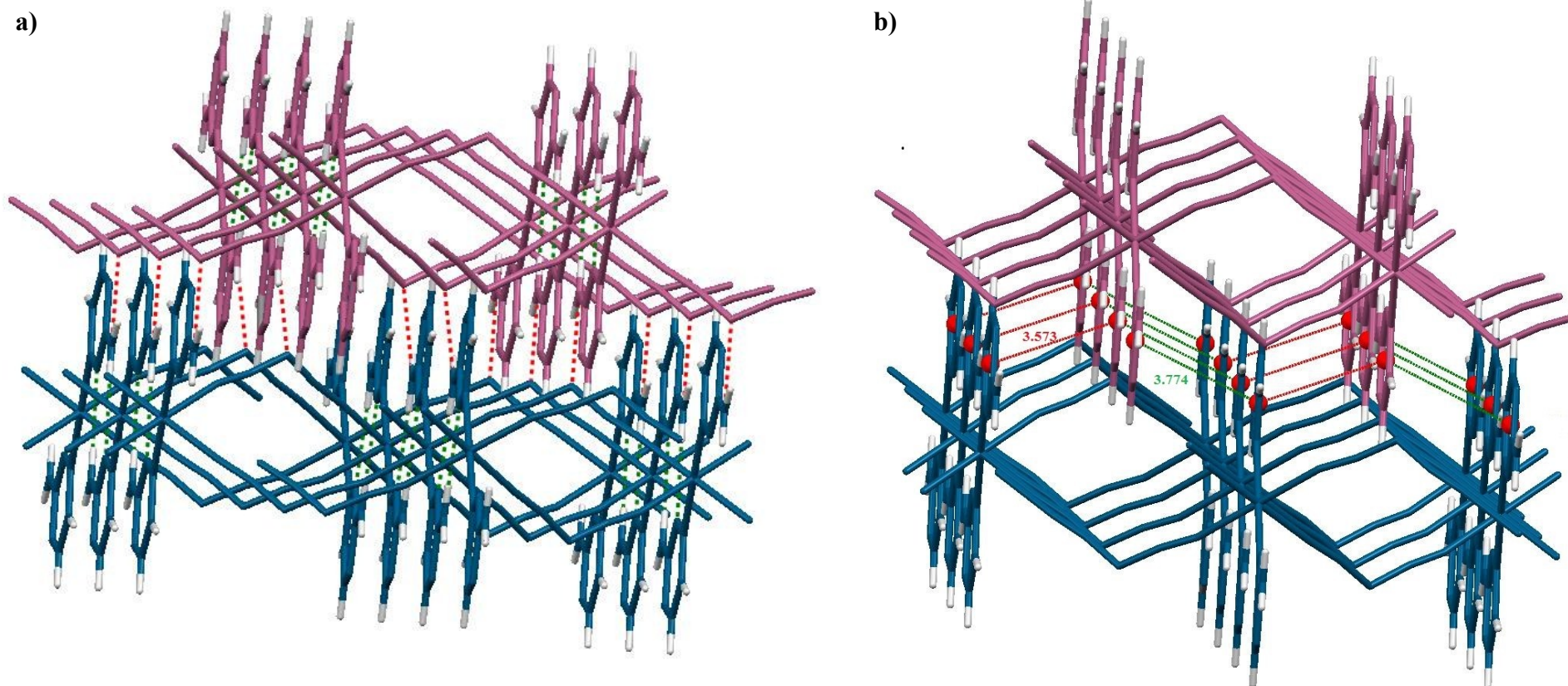


Figure S2. Supramolecular three-dimensional network of **1** constructed by (a) hydrogen-bonding and (b) π -stacking interactions between the neutral 2D framework based on single $\mu_{1,5}$ -dca bridges.

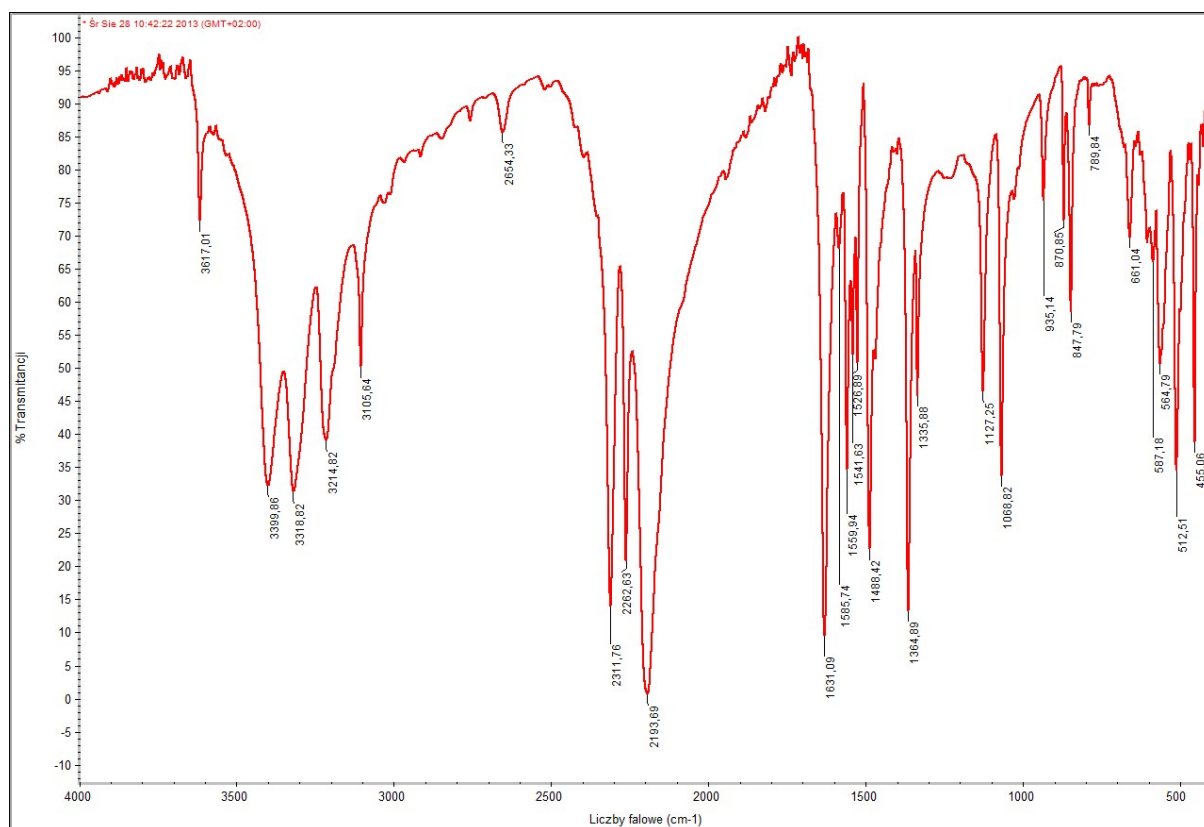


Figure S3. IR spectrum of **1**.

The solid UV-Vis spectrum of **1** shows weak d–d transitions in the visible and NIR regions centered at 9802 cm⁻¹, 19353 cm⁻¹, and 23408 cm⁻¹, which can be assigned to the spin allowed electronic transitions in a d⁷ high-spin octahedral ligand field ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, ${}^4T_{1g} \rightarrow {}^4A_{2g}(F)$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ ¹³. The high energy absorptions (at 28248 cm⁻¹, 33112 cm⁻¹ and 46082 cm⁻¹) were attributed to n (non-bonding) $\rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of the organic ligand.

The ligand field parameters were calculated from the energy data of the d–d transitions through the equations $Dq = \frac{1}{10}(v_2 - v_1)$ and $B = \frac{1}{15}(v_3 + v_2 - 3v_1)$. This assignment gives rise to the values $B = 890 \text{ cm}^{-1}$ i $Dq = 955 \text{ cm}^{-1}$, which are typical of Co(II) octahedrally surrounded by six nitrogen atoms¹⁴. The extent of the covalence in the metal–ligand has been evaluated by the quotient $\beta = B/B_0 = 0.80$ (considering $B_0 = 1117 \text{ cm}^{-1}$).

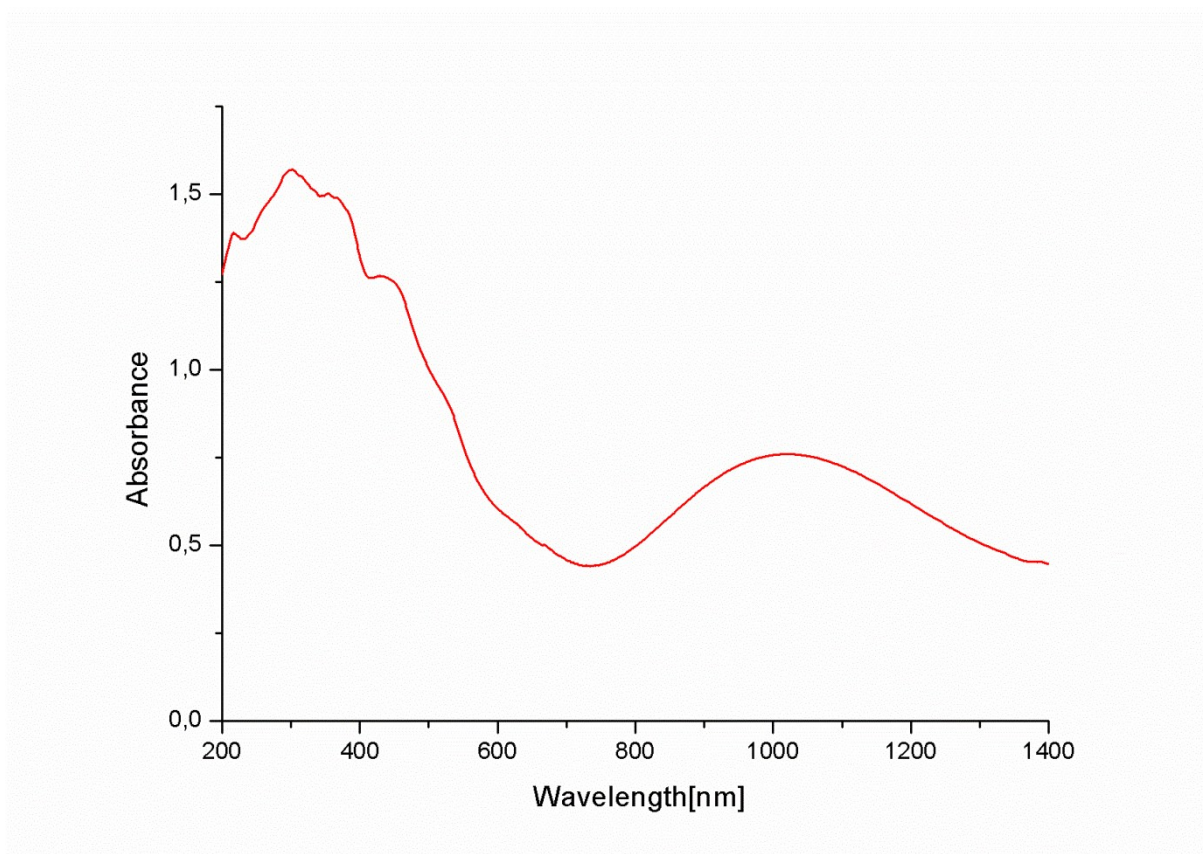


Figure S4. UV-Vis-NIR spectrum of **1**.

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