

A porous cobalt(II)-organic framework exhibiting high room temperature proton conductivity and field-induced slow magnetic relaxation

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EXPERIMENTAL SECTION

Materials. All reagents were commercially available and used as received without further purification. The powder of the starting material 1H-benzimidazole-5-carboxylic acid (**H₂bic**) was directly purchase from Tokyo Chemical Industry (TCI).

Synthesis of {[Co(**Hbic**)(H₂O)]·4H₂O}_n (1)

A mixture of **H₂bic** (0.2 mmol, 32.4 mg) and Co(ClO₄)₂·6H₂O (0.1 mmol, 36.6 mg) was dissolved in 6 ml H₂O. The reaction mixture was stirred at room temperature for several minutes, which was placed in a 15 mL Pyrex glass tube and heated in an oven at 100 °C for three days. Then, the reaction system was cooled to ambient temperature via a programmed cooling process (15 °C per hour). A day later, single-phase orange single crystals were obtained. The product was isolated by filtration, washed with the mother liquor, and air-dried. Yield: 21 mg, ca. 44.6%. Elemental analysis (%) for C₁₆H₂₀CoN₄O₉: C, 40.78; H, 4.28; N, 11.89. Found: C, 40.82, H, 4.41; N, 11.79. IR (KBr, cm⁻¹): 3510-3110 (bs), 2921 (s), 1655 (s), 1614(s), 1600(s), 1554(s), 1464(w), 1424(w), 1392(vs), 1284(s), 967 (w), 786 (m), 761(w), 596 (w) cm⁻¹. Solid-state UV-vis-NIR: 638 nm, 1040 nm (Fig. S13).

Physical measurements

Elemental analyses of C, H, and N were performed at an Elementar Vario MICRO analyzer. Infrared spectra were obtained in the range of 600–4000 cm⁻¹ on a Bruker tensor II spectrometer. Solid-state vis-NIR spectra were obtained on the samples at room temperature using a CARY5000 spectrophotometer equipped with a Harrick Praying Mantis accessory. Variable-temperature powder X-ray diffraction data (PXRD) were recorded on a Bruker D8 Advance diffractometer with Cu K α X-ray source ($\lambda = 1.54056 \text{ \AA}$) operated at 40 kV and 40 mA between 5 and 35° (2 θ). Simulated PXRD patterns were obtained from the Mercury software. Thermal gravimetric analysis (TGA) was carried out on freshly filtered crystals using the Mettler Toledo TGA2 instrument in an insert Ar atmosphere over a temperature range of 27–700 °C with a heating rate of 10 °C/min. Low-pressure volumetric N₂ gas adsorption measurements were

performed on a Quadrasorb automatic volumetric instrument. The samples were activated in dynamic vacuum at 150 °C for 24 h before measurement. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas. Water adsorption/desorption isotherms were measured using a BELSORP max instrument. Proton conductivity measurements were performed using a quasi-four-electrode AC impedance technique with a Solartron 1260 impedance/gain-phase analyzer. The single crystals samples were compressed to 2.5 mm diameter, which were connected to gold wires using silver paste. The sample pellet was measured in the temperature range of 25–50 °C and in the RH range of 40–95%. The conductivity of the samples was deduced from the Debye semicircle in the Nyquist plot.

Magnetic measurements

Direct current (dc) magnetic susceptibility from 2 to 300 K with applied 1000 Oe dc field were performed using a Quantum Design SQUID VSM magnetometer on the crushed single crystals sample of **1**. Alternative current (ac) magnetic susceptibility data were collected in a zero-dc field or an applied 1000 Oe dc fields in the temperature range of 2-10 K, under an ac field of 2 Oe, oscillating at frequencies in the range of 1-1000 Hz. All magnetic data were corrected for the diamagnetic contributions of the sample holder and of core diamagnetism of the sample using Pascal's constants.

X-ray Crystallography

Single crystal X-ray diffraction data were collected on a Bruker D8 QUEST diffractometer with a PHOTON III area detector (Mo-K α radiation, $\lambda = 0.71073 \text{ \AA}$, Bruker *Ius* 3.0) at room temperature. The APEX III program was used to determine the unit cell parameters and for data collection. The data were integrated and corrected for Lorentz and polarization effects using SAINT.^{S1} Absorption corrections were applied with SADABS.^{S2} The structures were solved by direct methods and refined by full-matrix least-squares method on *F*² using the SHELXTL^{S3} crystallographic software package integrated in Olex 2.^{S4} All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the organic ligands were refined as riding on the corresponding non-hydrogen atoms. Additional details of the data collections and structural refinement parameters are provided in Table 1. Selected bond lengths and

angles of **1** were listed in Table S2, S3. CCDC 2208435-2208438 are the supplementary crystallographic data for this paper. They can be obtained freely from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Structural and magnetic parameters of reported 2D SIMs.

Complexes	Geometry	Closest Co-Co distance (Å)	D (cm ⁻¹)	U_{eff} (K)	Ref.
[Co(ppad) ₂] _n	O_h	8.302	+76	16.4	S1
[Co(dca) ₂ (atz) ₂] _n	O_h	8.602	/	7.3	S2
{[Co(bmzbc) ₂ ·2DMF] _n	O_h	8.32	+62.6	11.8	S3
[Co(L) ₂ (SCN) ₂ ·2(CH ₃ CN)·2(dmf)] _n	O_h	13.028	+41.6	36.9	S4
{[Co(3,3'-Hbpt) ₂ (SCN) ₂ ·2H ₂ O] _n	O_h	9.854	+70.1	33.5	S5
[Co(dca) ₂ (bim) ₂] _n	O_h	8.927(2)	+74.3	7.7	S6
[Co(dca) ₂ (bmim) ₂] _n	O_h	8.7110(5)	+75.8	19.9	S6
[Co(bpeb) ₂ (NCS) ₂ ·nG (G= DCB)]	O_h		+64.9(9)	45.1	S7
[Co(bpeb) ₂ (NCS) ₂ ·nG (G= TAN)]	O_h		+67.1(9)	24.6	S7
[Co(bpeb) ₂ (NCS) ₂ ·nG (G= TOL)]	O_h		+84.4(4)	16.56	S7
[Co(bpeb) ₂ (NCS) ₂ ·nG (G= PYR)]	O_h		+70.3(9)	30.24	S7
[Co(bmzbc) ₂ (1,2- <i>etdio</i>)] _n	O_h	8.61	/	16.7	S8
[Co(bmzbc) ₂ (Hbmzbc)] _n	O_h	7.73	/	31.2	S8
{[Co(HL)(bpy)(H ₂ O) ₂ ·DMF] _n	O_h	11.36	-0.071	13.9	S9
{[Co(HL)(bpe)]·0.5bpe] _n	O_h	10.86	-0.076	8.7	S9
[Co(μ-6ani) ₂ ·H ₂ O]	O_h	7.099	+28	18.7	S10
{[Co ^{II} (TPT) _{2/3} (H ₂ O) ₄][CH ₃ COO] ₂ ·(H ₂ O) ₄] _n	O_h	8.293	+47.7	6.912	S11
[Co ^{III} (CN) ₆] ₂ [Co ^{II} (TODA)] ₃ ·9H ₂ O	D_{5h}	7.58	+29.9	16	S12
[Co(bpg) ₂ (SCN) ₂ ·3MeOH]	O_h	9.110	+64.2	5.0	S13
[Co(bpg) ₂ (SCN) ₂ ·2DMF]	O_h	8.544	+67.5	15.3	S13
[Co(1,4-bimb) _{0.5} (5- <i>aip</i>)(H ₂ O)] _n	O_h	5.7874	/	4.9	S14
[Co(dps) ₂ Cl ₂] _n	O_h	7.500	27.2	12.4	S15
[Co(dps) ₂ Br ₂] _n	O_h	8.992	28.0	27.1	S15
[Co(dps) ₂ (H ₂ O) ₂ ·I ₂ ·(H ₂ O) ₄] _n	O_h	7.534	9.5	28.8	S15
{Co(DMSO) ₂ [Au(CN) ₂] ₂] _n	O_h	10.344	+68	22.1	S16
{Co(DMF) ₂ [Au(CN) ₂] ₂] _n	O_h	7.557	+90	18.5	S16
{Co(PY) ₂ [Au(CN) ₂] ₂] _n	O_h	7.135	+75	22.0	S16
{Co(PyPhCO) ₂ [Au(CN) ₂] ₂] _n	O_h	7.436	+80	15.9	S16
[Co(m-NPy3)(TPA)0.5Cl·CH ₃ OH] _n	O_h	9.89	/	9.89	S17
{[Co(IPEH) ₂ (SCN) ₂ ·H ₂ O] _n	O_h	8.397	89.3	6.5	S18
[Co(Hbic) ₂] _α	T_d	7.912	-20.4	24.9	S19
[Co(Hbic) ₂] _β	T_d	7.487	-14.6	4.3	S19
{Co ₂ (DCIQ) ₄ (tpb)] _n	O_h	9.064	-46.0	23.5	S20

Ppad, N3-(3-pyridoyl)-3-pyridinecarboxamidrazone; **dca**, dicyanamide; **atz**, 2-amino1,3,5-triazine; **bmzbc**⁻, 4-(benzimidazole-1-yl)benzoate; **L** = 4'-4-(4-methoxyphenyl)-4,2':6',4''-terpyridine; **3,3'-Hbpt**, 1H-3-(3-pyridyl)-5-(30-pyridyl)-1,2,4-triazole; **dca**, dicyanamide; **bim** = 1-benzylimidazole; **bmim** = 1-benzyl-2-methylimidazole; **6ani**, 6-aminonicotinate; **TPT**, 2,4,6-Tris(4-pyridyl)-1,3,5-triazine; **bpg** = meso-α,β-bi(4-pyridyl) glycol; **1,2-*etdio***, 1,2-ethanediol; **Hbmzbc**, 4-(benzimidazole-1-yl)benzoic acid; **6ani**, 6-aminonicotinate; **TPT**, 2,4,6-Tris(4-pyridyl)-1,3,5-triazine; **bpg**, meso-α,β-bi(4-pyridyl) glycol; **dps**, 4,4'-dipyridyl sulfide; **PyPhCO**, benzoylpyridine; **TPA** = bidentate terephthalic acid; **m-NPy3**, tris(4-(pyridine-3-yl)phenyl)amine ligand; **IPEH**, (((1E,2E)-1,2-bis(1-(4-(1H-imidazol-1-yl)phenyl)ethylidene)hydrazine; **tpb** = 1,2,4,5-tetra(4-pyridyl)benzene; **DCIQ** = (5,7-dichloro-8-hydroxyquinoline).

Table S2. Crystallographic data and structure refinement parameters for **1** at different measured temperature.

Complex	1			
Empirical formula	C ₁₆ H ₂₀ CoN ₄ O ₉			
Formula weight	471.29			
<i>T</i> / K	123	193	293	323
Crystal system	triclinic			
Space group	<i>P</i> $\bar{1}$			
<i>a</i> /Å	8.8988(6)	8.8963(7)	8.8974(6)	8.8812(14)
<i>b</i> /Å	9.8033(6)	9.8095(8)	9.8135(6)	9.8009(15)
<i>c</i> /Å	11.4213(7)	11.4439(9)	11.4695(7)	11.4837(17)
α /°	90.342(2)	90.451(3)	90.505(2)	91.074(4)
β /°	103.096(2)	102.942(3)	102.776(2)	102.543(4)
γ /°	104.310(2)	103.990(3)	103.451(2)	103.688(5)
Volume/Å ³	938.31(10)	942.42(13)	947.95(10)	945.4(3)
<i>Z</i>	2	2	2	2
$\rho_{\text{calc}}/\text{cm}^3$	1.668	1.661	1.651	1.656
μ/mm^{-1}	0.976	0.971	0.966	0.968
F(000)	486	486	486	486
2 Θ range for data collection/°	4.298 to 51.422	4.288 to 51.49	4.276 to 52.858	4.29 to 53.118
Reflections collected	36302	30488	37643	42636
Independent reflections	3572	3587	3889	3944
$R_{\text{int}} / R_{\text{sigma}}$	0.1123 / 0.0516	0.0518/0.0251	0.0987/0.0480	0.1446/0.0690
Goodness-of-fit on F^2	1.056	1.036	1.030	1.022
R_1^a / wR_2^b ($I > 2\sigma(I)$)	0.0654 / 0.1655	0.0589/ 0.1537	0.0620/0.1666	0.643/0.1598
R_1 / wR_2 (all data)	0.0899 /0.1823	0.0666/ 0.1606	0.0821/0.1848	0.1094/0.1850
Max/min [$e \text{ \AA}^{-3}$]	1.01 / -0.95	1.16 / -0.88	0.89/-0.89	0.64/-0.59
$^a R_1 = \sum F_o - F_c / \sum F_o $ $^b wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$				

Table S3. Selected bond lengths (Å) and angles [°] in **1**.

Parameter	Value / Å, °			
T / K	123	193	293	323
Co1-O1	2.054(3)	2.050(3)	2.047(3)	2.045(3)
Co1-O3	2.138(3)	2.140(3)	2.140(3)	2.153(3)
Co1-O4 ¹	2.230(3)	2.230(3)	2.236(3)	2.238(3)
Co1-O5 ¹	2.173(4)	2.174(3)	2.179(3)	2.178(4)
Co1-N ¹	2.113(4)	2.115(3)	2.114(4)	2.114(4)
Co1-N4 ²	2.102(4)	2.100(3)	2.103(4)	2.095(4)
O1-Co1-O3	90.40(13)	90.40(11)	90.61(12)	90.69(13)
O1-Co1-O4 ¹	151.36(14)	151.09(12)	150.85(13)	150.79(14)
O1-Co1-O5 ¹	91.93(14)	91.82(11)	91.76(12)	91.54(14)
O1-Co1-N1	103.08(15)	103.19(12)	103.13(13)	103.80(15)
O3-Co1-N4 ¹	84.21(13)	84.23(11)	84.03(12)	84.22(13)
O5 ¹ -Co1-O4 ¹	59.73(13)	59.58(11)	59.41(11)	59.52(13)
N1-Co1-O3	92.65(14)	92.18(12)	92.04(13)	92.25(14)
N4 ² -Co1-O3	174.62(15)	174.87(13)	174.98(13)	175.07(15)
N4 ² -Co1-N1	91.48(16)	91.63(13)	91.48(14)	91.41(16)
Symmetry operation: ¹ +X, -1 + Y, + Z; ² 1 + X, + Y, + Z				

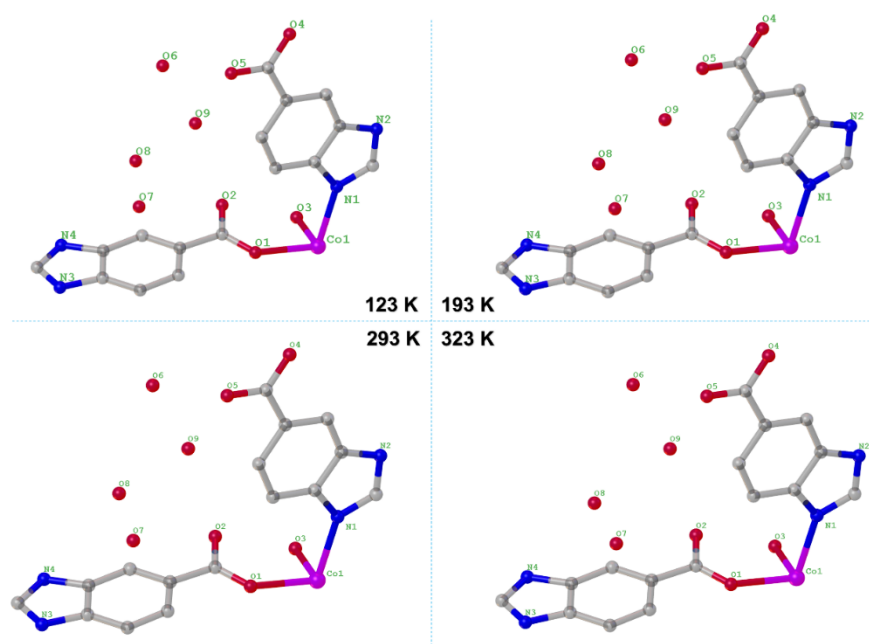


Figure S1. The asymmetric units of **1** measured at different temperatures.

Table S4. Continuous Shape Measure (CSM) analysis for six-coordinated Co(II) in **1**.

Compound, Metal center	T / K	CSM parameters*					Determined coordination geometry
		six-coordinated coordination sphere					
		HP-6	PPY-6	OC-6	TPR-6	JPPY-6	
Co1	123	30.837	23.083	2.104	13.672	26.934	OC-6
	193	30.764	22.959	2.138	13.624	26.787	
	293	30.649	22.790	2.171	13.584	26.596	
	323	30.794	22.951	2.161	13.478	26.753	

*CSM^{S2} parameters for six-coordinated complexes:

HP-6 - the parameter related to the hexagon (D_{6h})

PPY-6 - the parameter related to the pentagonal pyramid (C_{5v})

OC-6 - the parameter related to the octahedron (O_h)

TPR-6 - the parameter related to the trigonal prism (D_{3h})

JPPY-6 - the parameter related to the Johnson pentagonal pyramid (C_{5v})

Table S5. The possible hydrogen bonds in **1** at 123 K calculated by PLATON.

D-H...A	d(D- H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(2)...O(9)	0.86	2.01	2.8358	160
N(3)-H(3)...O(6)	0.86	2.04	2.8791	165
O(3)-H(3A)...O(2)	0.87	1.85	2.6072	147
O(3)-H(3B)...O(4)	0.85	1.87	2.7053	164
O(6)-H(6A)...O(9)	0.84	2.10	2.8596	149
O(6)-H(6B)...O(3)	0.85	2.46	3.2114	148
O(7)-H(7A)...O(8)	0.85	1.86	2.6617	157
O(7)-H(7A)...O(7)	0.85	2.22	2.5903	107
O(7)-H(7B)...N(3)	0.85	2.49	3.2815	156
O(9)-H(9B)...O(2)	0.84	1.98	2.7547	153

Table S6. The possible hydrogen bonds in **1** at 193 K calculated by PLATON.

D-H...A	d(D- H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(2)...O(9)	0.86	2.02	2.8423	159
N(3)-H(3)...O(6)	0.86	2.05	2.8905	164
O(3)-H(3A)...O(2)	0.87	1.85	2.6091	145
O(3)-H(3B)...O(4)	0.85	1.87	2.7081	163
O(6)-H(6A)...O(9)	0.84	2.11	2.8811	150
O(6)-H(6B)...O(3)	0.85	2.47	3.2155	148
O(7)-H(7A)...O(8)	0.85	1.74	2.5016	148
O(7)-H(7B)...N(3)	0.85	2.55	3.3672	162
O(9)-H(9B)...O(2)	0.84	1.98	2.7607	154

Table S7. The possible hydrogen bonds in **1** at 293 K calculated by PLATON.

D-H...A	d(D- H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(2)...O(9)	0.86	2.03	2.8358	160
N(3)-H(3)...O(6)	0.86	2.06	2.8791	165
O(3)-H(3A)...O(2)	0.87	1.87	2.6072	143
O(3)-H(3B)...O(4)	0.87	1.87	2.7053	163
O(6)-H(6A)...O(9)	0.85	2.16	2.8596	152
O(6)-H(6B)...O(3)	0.85	2.49	3.2114	147
O(7)-H(7A)...O(8)	0.85	1.54	2.6617	138
O(7)-H(7B)...N(3)	0.85	2.54	3.2815	159
O(9)-H(9A)...N(2)	0.84	2.51	2.8505	105
O(9)-H(9B)...O(2)	0.85	2.00	2.7682	150

Table S8. The possible hydrogen bonds in **1** at 323 K calculated by PLATON.

D-H...A	d(D- H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(2)...O(9)	0.86	2.05	2.8683	160
N(3)-H(3)...O(5)	0.86	2.53	3.0468	120
N(3)-H(3)...O(6)	0.86	2.11	2.9411	162
O(3)-H(3A)...O(2)	0.87	1.86	2.6080	143
O(3)-H(3B)...O(4)	0.87	1.87	2.7146	165
O(6)-H(6A)...O(9)	0.85	2.52	2.9046	108
O(6)-H(6B)...O(3)	0.85	2.49	3.1975	141
O(8)-H(8A)...N(3)	0.85	2.46	3.2134	148
O(9)-H(9A)...N(2)	0.85	2.28	2.8683	126
O(9)-H(9B)...O(2)	0.85	2.01	2.7737	149

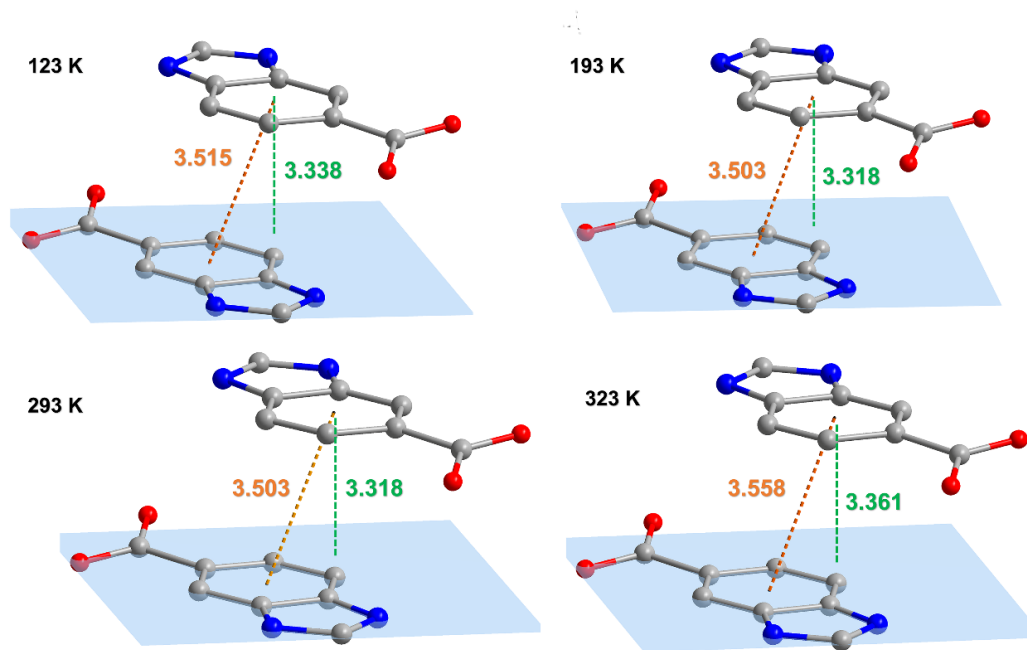


Figure S2. Intermolecular $\pi \cdots \pi$ distances between benzimidazole molecules **1**.

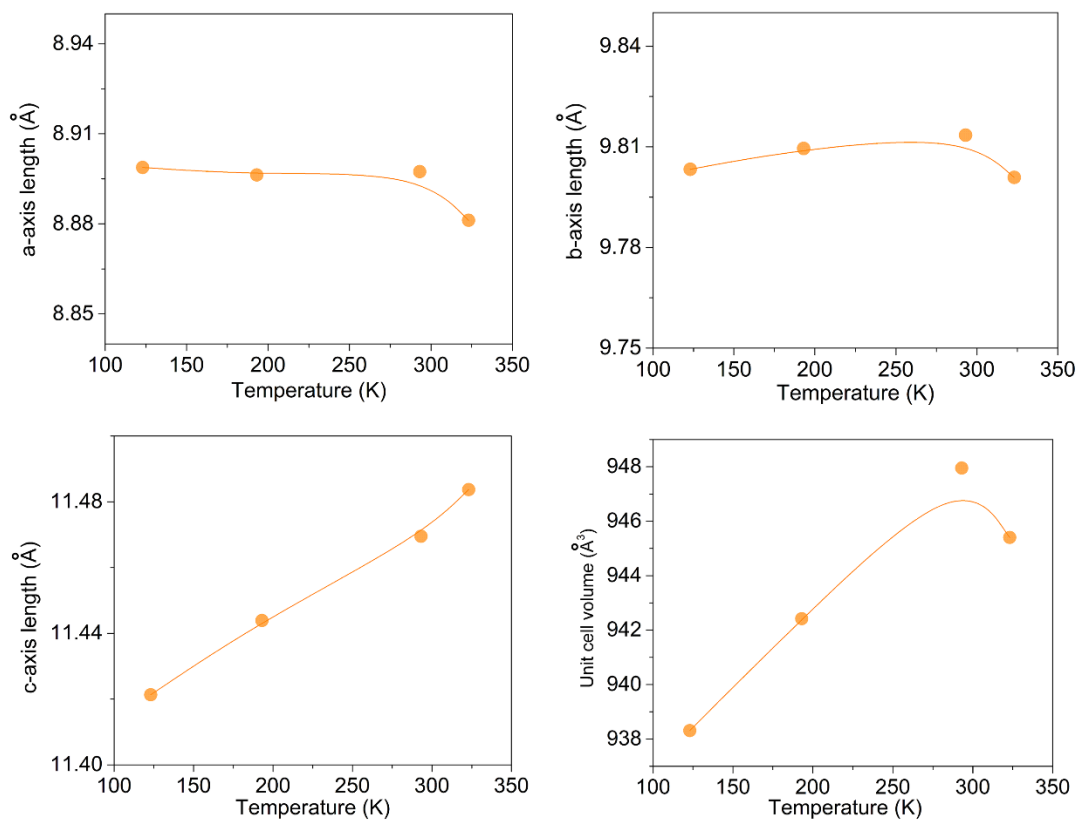


Figure S3. The anisotropic thermomechanical behavior of **1**.

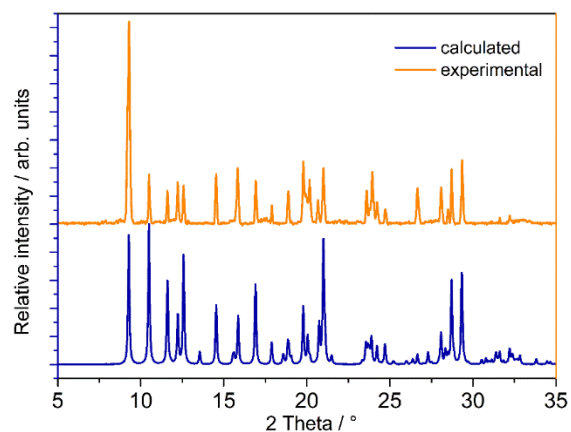


Figure S4. Comparison of the experimental PXRD pattern at room temperature of **1** with the simulated pattern from single crystal structure at 293 K.

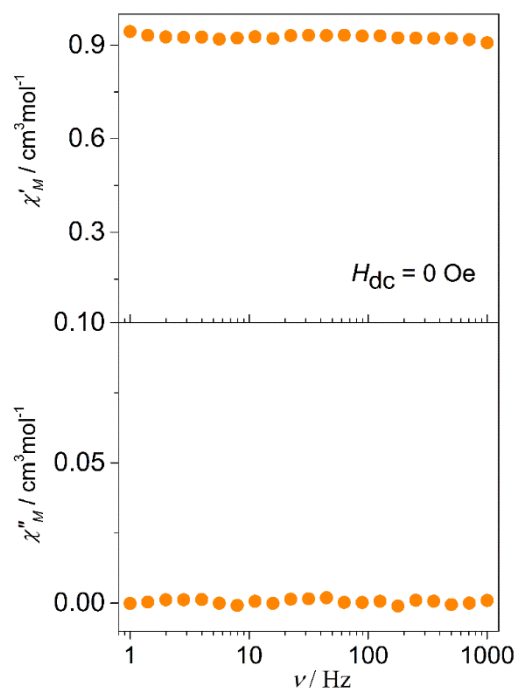


Figure S5. Frequency dependence of the ac susceptibilities measured under zero dc field at 2.0 K for **1**.

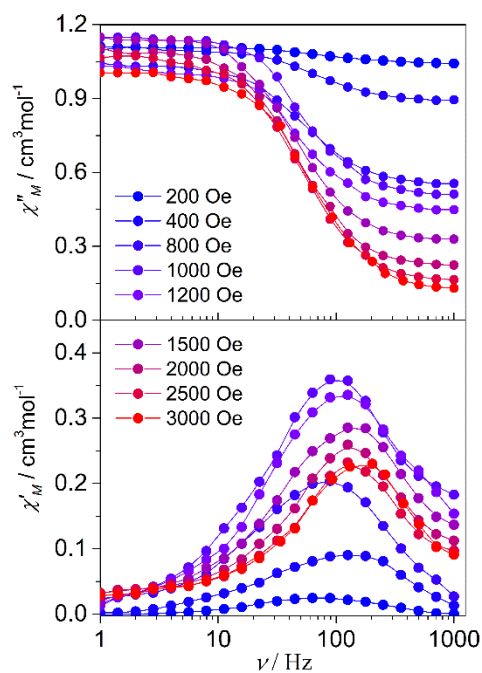


Figure S6. Frequency dependence of the in-phase (χ') and out-of-phase (χ'') magnetic susceptibility of **1** measured at 1.8 K in various applied fields from 0 to 3000 Oe.

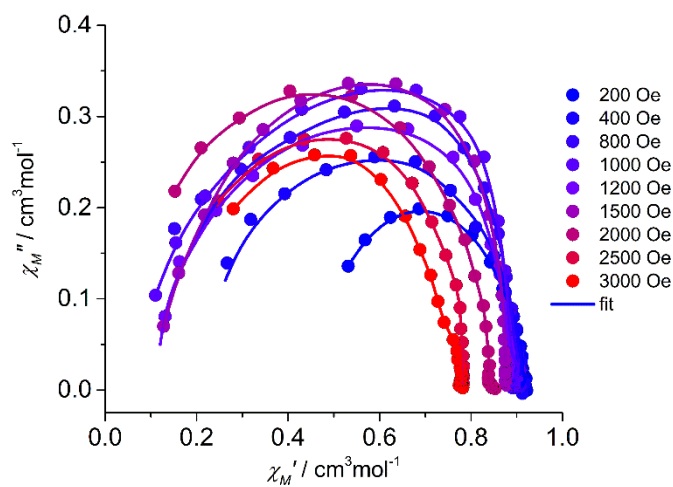


Figure S7. Cole–Cole plots of χ' vs. χ'' of **1** at 2.0 K under various applied dc fields. The solid lines represent the best fit of the experimental results with the generalized Debye model.

Table S9. Relaxation fitting parameters at 2.0 K under different fields from the least-square fitting of the Cole-Cole plots of **1** according to the generalized Debye model.

H / Oe	$\chi_S / \text{cm}^3\text{mol}^{-1}\text{K}$	$\chi_T / \text{cm}^3\text{mol}^{-1}\text{K}$	τ / s	α
200	0.54433	0.91216	4.5E-4	0.11021
400	0.23783	0.92901	5.7E-4	0.0819
800	0.20008	0.90461	7.1E-4	0.08204
1000	0.07203	0.91261	6.4E-4	0.11467
1200	0.09686	0.88107	6.6E-4	0.02572
1500	0.11278	0.93018	9.1E-4	0.10531
2000	0.10157	0.82412	4.2E-4	0.05941
2500	0.15103	0.78419	3.7E-4	0.02231
3000	0.18047	0.76184	3.5E-4	0.03081

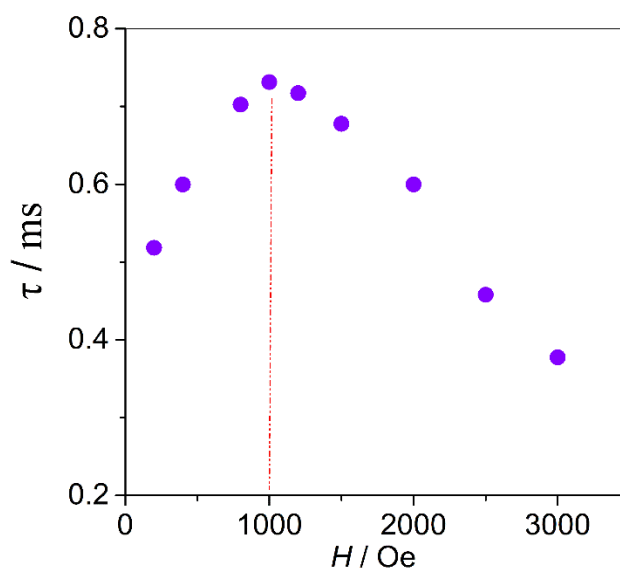


Figure S8. Field dependence of the magnetic relaxation time at 2.0 K for **1**.

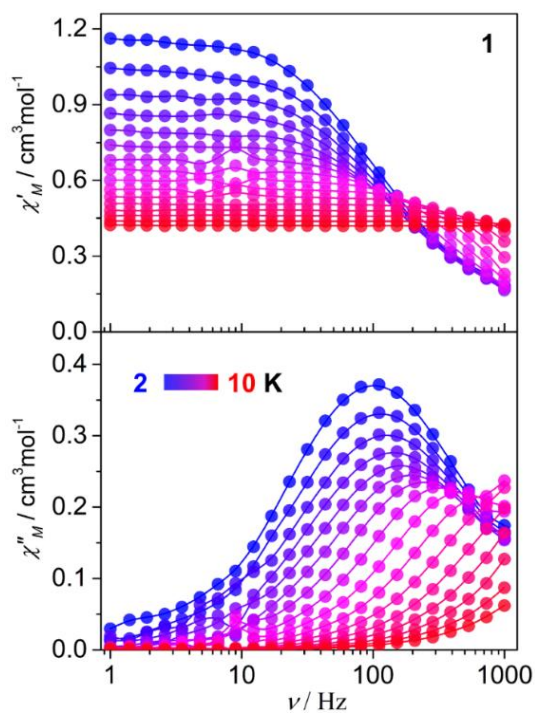


Figure S9. Frequency dependence of the in-phase (χ') and out-of-phase (χ'') ac susceptibilities measured under 1 kOe dc field in the temperature range of 2.0 – 10 K for **1**.

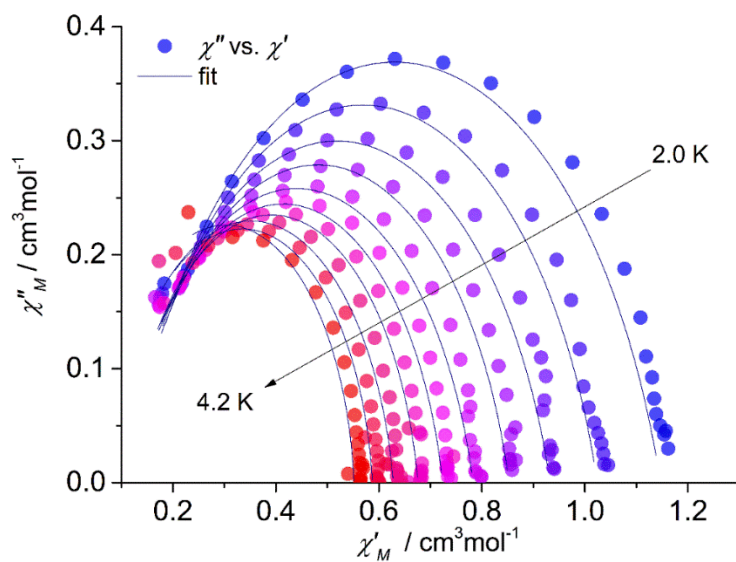


Figure S10. Cole-Cole plots of **1** obtained from 1 kOe dc field. The solid lines represent the best fits according to the generalized Debye model.

Table S10. Relaxation fitting parameters from the least-square fitting of the Cole-Cole plots of 1 under 1 kOe dc field according to the generalized Debye model.

T / K	τ / s	χ_S / cm ³ mol ⁻¹ K	χ_T / cm ³ mol ⁻¹ K	α
1.99996	0.00147	0.11446	1.14691	0.20983
2.25002	0.0013	0.11349	1.02411	0.19896
2.50005	0.00116	0.10502	0.9327	0.20182
2.75	0.00104	0.11063	0.8527	0.17932
2.99994	8.83193E-4	0.09775	0.78312	0.17811
3.24993	7.58355E-4	0.10465	0.72393	0.14891
3.49996	6.16703E-4	0.10693	0.67591	0.12118
3.74992	4.33585E-4	0.07622	0.62805	0.11632
3.99993	3.23559E-4	0.08242	0.58753	0.07998
4.24991	2.16892E-4	0.0534	0.55167	0.06177

COMPUTATIONAL DETAILS

All calculations were performed using the ORCA 4.2.1^{S25} software suite. We prepared a monomeric model and optimized the position of hydrogens using the BP86 level of theory^{S26, S27} with DKH-def2-SVP^{S28} basis set for all the atoms to extract the zero-field splitting parameters, g-value in complex **1**. The electronic, magnetic, and spin-Hamiltonian parameters (g, D, E) were calculated using the complete active space self-consistent (CASSCF)^{S29} method with an active space of CAS (7, 5), i.e., seven active electrons in the five active d-orbitals of Co. (II). We computed 10 quartets and 40 doublet states using this active space. All calculations were performed using a DKH-def2-TZVPP^{S28} basis set for Co and a DKH-def2-SVP basis set for all other atoms. On the converged CASSCF wavefunction, the second-order N-electron valence perturbation theory (NEVPT2)^{S30, S31} method was used to treat the dynamic correlations. To investigate the nature of ligand field and d-orbital splitting ab-initio based ligand field theory (AILFT) calculations were carried out as implemented in ORCA.

Table S11. CASSCF/NEVPT2 computed 10 spin-free quartet (red) and 40 spin-free doublet (blue) states along the spin-orbit states for Co centre in complex 1a. All the values are reported here in cm^{-1}

Complex 1a							
SPIN-FREE STATES				SPIN-ORBIT STATES			
CASSCF		NEVPT2		CASSCF			
CASSCF		NEVPT2		NEVPT2			
0.0		0.0		0.00	26412.51	0.00	23113.49
265.6		398.7		247.00	26722.98	222.46	24779.11
508.6		608.2		469.26	28804.31	530.37	27099.15
5701.5		7411.4		883.08	29112.14	921.78	27430.42
6131.3		7998.2		1065.40	29371.21	1109.56	28046.89
7147.3		9258.9		1186.93	29443.22	1245.88	28130.29
13499.1		17340.7		6116.17	29711.50	7763.54	28568.47
22834.0		20739.7		6188.25	30202.58	7823.52	29315.15
23250.1		21241.0		6544.04	31705.10	8346.20	30669.73
24002.0		22132.2		6618.40	31872.76	8407.36	30939.89
14499.6	34113.1	9846.4	33136.8	7555.45	34328.01	9601.57	33346.51
15788.5	34187.4	11566.8	33303.7	7650.40	34456.52	9674.77	33580.09
19428.9	34289.2	17023.6	33369.1	13980.36	34635.87	10259.69	33853.82
19953.7	34623.0	17909.0	34374.6	13985.05	35073.53	11955.77	34845.57
20037.6	34698.7	17911.6	34583.0	14913.75	35180.66	17320.72	34981.12
20155.1	34793.9	18096.3	34792.5	16199.51	35327.77	17675.15	35209.04
20586.2	34841.0	18780.0	34963.1	19824.84	35737.02	17814.12	35466.61
20861.8	35120.4	19336.3	34992.9	20144.84	36085.79	18069.51	35891.07
24324.0	46532.3	21950.6	40351.0	20456.30	46868.64	18343.05	40682.22
25657.9	46826.1	22125.7	40827.0	20766.78	47306.15	18651.01	41242.93
25745.8	47124.6	22143.7	41295.2	21141.73	47647.93	19272.41	41754.98
25872.3	47563.0	24292.2	42511.2	21450.50	47996.66	19850.21	42891.99
28439.7	47717.3	26770.2	42715.9	23108.85	48132.46	20843.66	43078.26
28577.8	47962.4	26911.9	42991.4	23146.45	48512.95	20968.74	43482.24
28876.3	48581.5	27600.5	43364.6	23516.92	49064.69	21236.18	43789.58
28906.4	71731.6	27699.9	62767.8	23638.94	72169.83	21509.21	63178.12
29230.3	72024.1	28157.9	63336.2	24219.42	72478.51	21885.45	63716.28
29771.7	72376.7	28942.5	63643.4	24456.71	72799.32	22295.02	64015.58
31199.7	72633.6	30218.2	63897.5	24681.38	73198.93	22887.79	64414.58
31376.3	72863.1	30505.0	64098.3	26145.03	73408.68	23057.28	64602.20

Table S12. CASSCF (7,5)+NEVPT2 computed Spin – Hamiltonian parameter (g, D, |E/D|) along with listed state – by – state contribution to the D. All the values are reported here in cm^{-1}

Parameters	1	
	CASSCF	NEVPT2
	Contribution to D (cm^{-1})	
D	121.15	109.29
E/D	0.11	0.11
g_{xx}	1.850	1.900
g_{yy}	2.336	2.442
g_{zz}	2.961	2.783
KD1		
g_{xx}	3.102	2.782
g_{yy}	3.828	4.008
g_{zz}	6.134	6.065
KD2		
g_{xx}	0.522	0.737
g_{yy}	1.126	0.992
g_{zz}	4.826	5.221

EHA : Effective Hamiltonian approach

Table S13. AILFT derived ligand field parameters computed at NEVPT2 level of theory for model complexes **1**. The values of B, C, ξ and Δ_o parameters are provided in units of cm^{-1} .

Parameter	Free Co(II)	1	% reduction
ξ	530.3	520.4	1.87
B	1040.3	1005.7	3.33
C	4158.1	3909.0	5.99
C/B	3.997	3.887	2.75
Δ_o		7519.8	

Table S14. NEVPT2-AILFT computed d-orbital ordering for model complexes **1**.

Orbital	Energy (cm^{-1})
d_{yz}	0
d_{xz}	329.8
d_{xy}	593.2
$d_{x^2-y^2}$	7012.2
d_{z^2}	8642.7

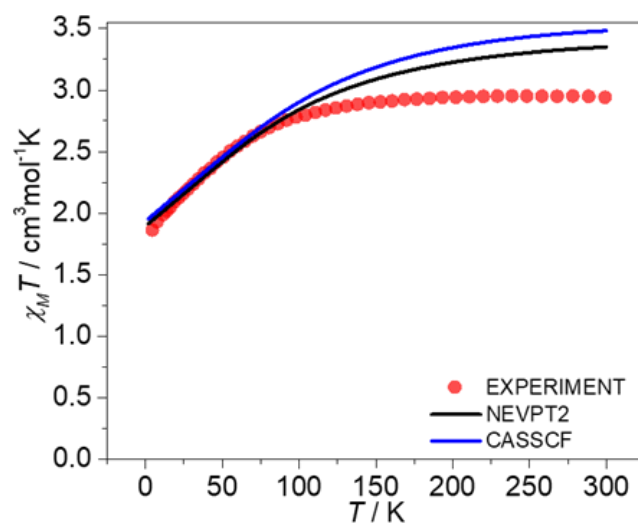


Figure S12. Experimental and ab initio computed molar magnetic susceptibility plots where red circles correspond to the experimental values and the blue and black lines correspond to CASSCF and NEVPT2 computed values respectively.

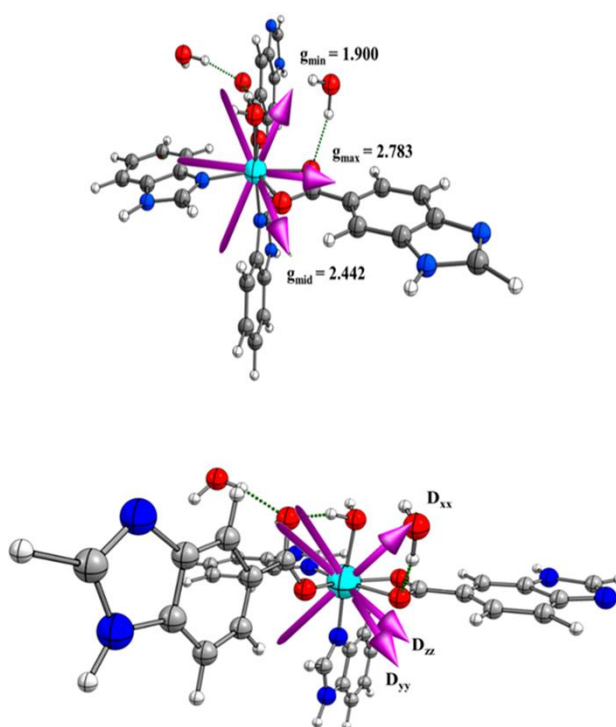


Figure S11. NEVPT2 computed orientation of computed effective g-tensor and D-tensor for complex **1**. Color code: Co(cyan), N (blue), C (grey), O(red), H(white).

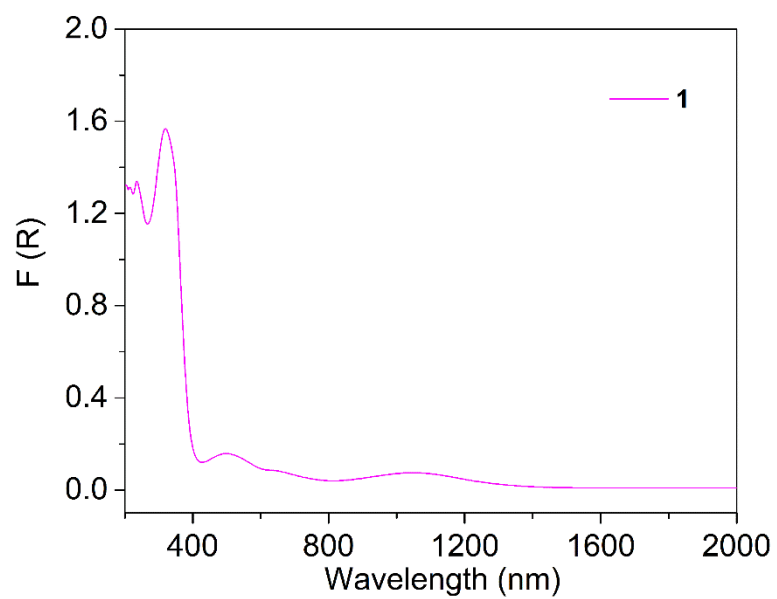


Figure S13. Solid-state UV-vis-NIR of **1**.

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