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Supporting Information

Non-traditional thermal behavior of Co(II) coordination networks showing slow magnetic relaxation

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Compounds under study

1, $[Co(5,6\text{-}(Me)_2\text{–}bzim)_2(dca)_2]_n$, $C_{22}H_{20}N_{10}Co$ (M = 483.41 g mol^{-1}), CCDC 2085569

2, $[Co(5\text{-}Mebzim)_2(dca)_2]_n$, $C_{20}H_{22}N_{10}Co$ (M = 461.40 g mol^{-1}), CCDC 2085570

3, $[Co(2\text{-}Mebzim)(dca)_2]_n$, $C_{20}H_{16}N_{10}Co$ (M = 455.36 g mol^{-1}), CCDC 2085571

1. Synthesis and characterization

Materials. The reagents used to the synthesis were commercially available and they were used without further purification.

Preparation of the complexes. $NaN(CN)_2$ (0.075 g, 0.84 mmol) dissolved in water (5 cm^3) was added to a deep pink methanolic solution of $CoCl_2 \cdot 6H_2O$ (0.10 g, 0.42 mmol) and suitable benzimidazole derivatives (0.84 mmol). The resulting mixture was filtered and allowed to evaporate at room temperature. X–ray quality pink crystals of **1**–**3** were grown after few days and they were collected by filtration and air-dried.

$[Co(5,6\text{-}(Me)_2\text{–}bzim)_2(dca)_2]_n$ (1): Yield 80%. IR (KBr, cm^{-1}): 3203(m) ν(N–H); 2274(s) ν_{as} + $\nu_s(C{\equiv}N_{dca})$; 2253(s) $\nu_{as}(C{\equiv}N_{dca})$; 2187(vs) $\nu_s(C{\equiv}N_{dca})$; 1507(m), 1399(m) and 1312(s) ν(C=N) and ν(C=C). Anal. calcd for $C_{22}H_{20}N_{10}Co$ (483.41 g/mol) C, 54.66, H, 4.17; N, 28.98; found C, 54.28, H, 4.04; N, 28.81%.

$[Co(5\text{-}Mebzim)_2(dca)_2]_n$ (2) Yield 75%. IR (KBr, cm^{-1}): 3227(m) ν(N–H); 2276(s) ν_{as} + $\nu_s(C{\equiv}N_{dca})$; 2251(s) $\nu_{as}(C{\equiv}N_{dca})$; 2185(vs) $\nu_s(C{\equiv}N_{dca})$; 1503(m), 1408(m) and 1318(s) ν(C=N) and ν(C=C). Anal. calcd for $C_{20}H_{22}N_{10}Co$ (461.40 g/mol) C, 52.06; H, 4.81; N, 30.36 found C, 52.16; H, 4.52; N, 30.76%.

$[Co(2\text{-}Mebzim)(dca)_2]_n$ (3) Yield 75%. IR (KBr, cm^{-1}): 3368(m) ν(N–H); 2277(s) ν_{as} + $\nu_s(C{\equiv}N_{dca})$; 2248(s) $\nu_{as}(C{\equiv}N_{dca})$; 2177(vs) $\nu_s(C{\equiv}N_{dca})$; 1534(m), 1456(s) and 1322(s) ν(C=N) and ν(C=C). Anal. calcd for $C_{20}H_{16}N_{10}Co$ (455.36 g/mol) C, 52.76; H, 3.54; N, 30.76 found C, 52.55; H, 3.47; N, 30.80%.

Physical techniques. The UV-Vis spectra were recorded from solid state samples on Nicolet Evolution 220 and spectrophotometer Nicolet iS50 FT-IR in the ranges 190–1100 nm and 700–1500 nm, respectively (see ESI). IR spectra were recorded on a Nicolet iS5 spectrophotometer in the spectral range 4000–400cm^{-1} with the samples as of KBr pellets. Elemental analysis was registered by Vario EL III apparatus (Elementar, Germany).

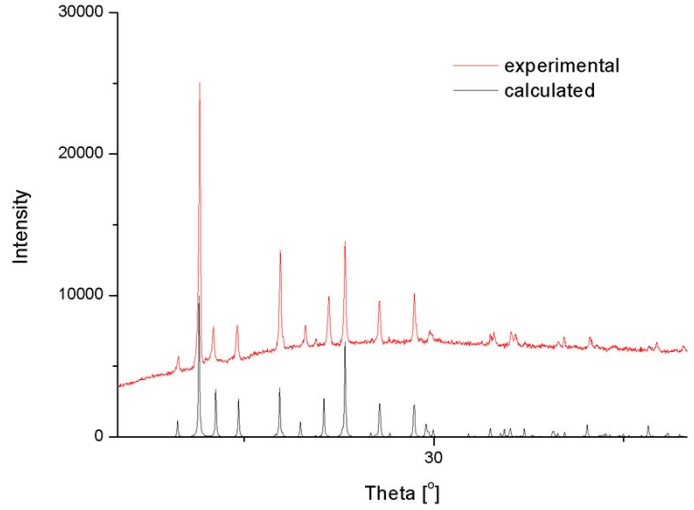

Figure S1. The powder XPRD pattern of **1**.

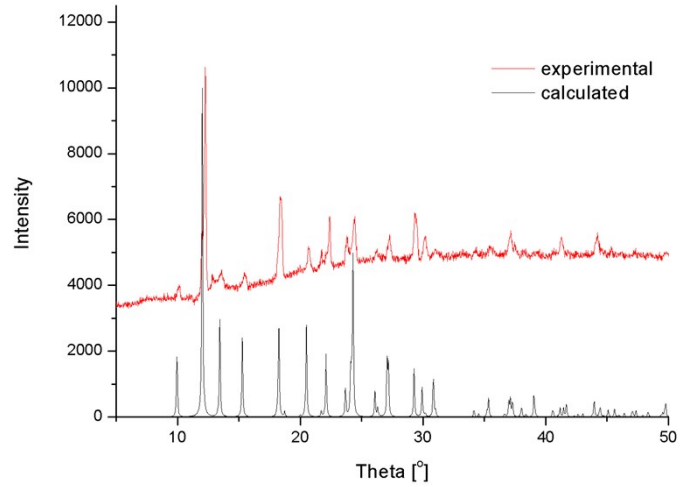

Figure S2. The powder XPRD pattern of **2**.

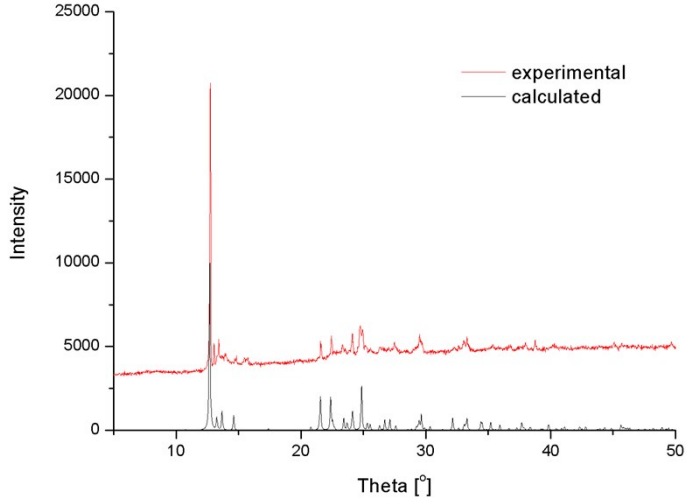

Figure S3. The powder XPRD pattern of **3**.

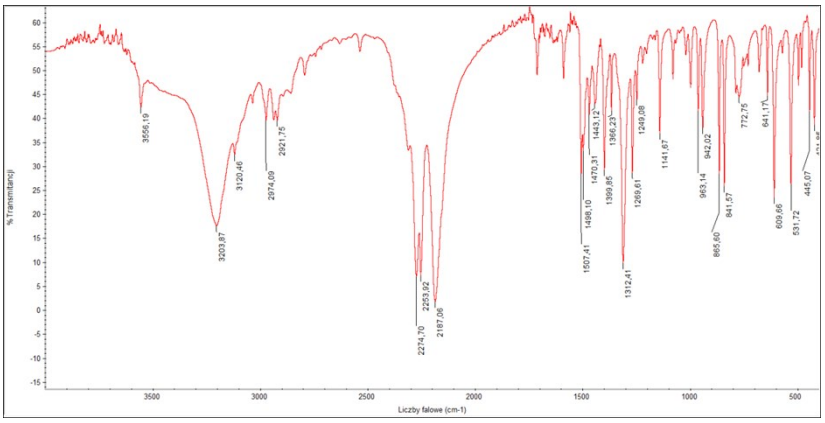

Figure S4. IR spectrum of **1**.

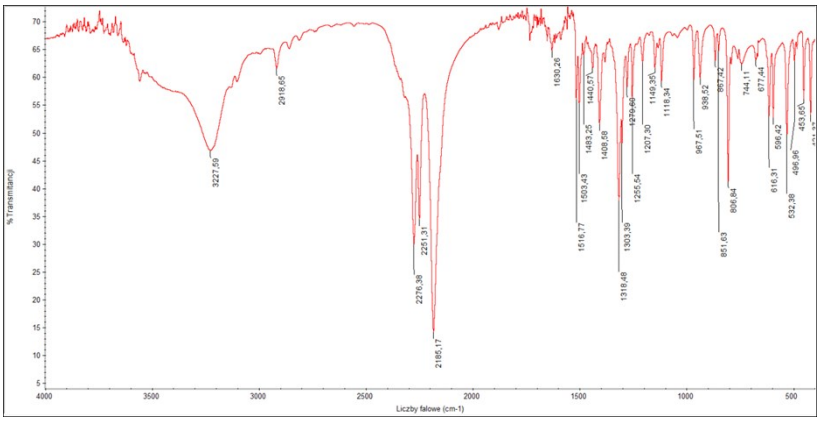

Figure S5. IR spectrum of **2**.

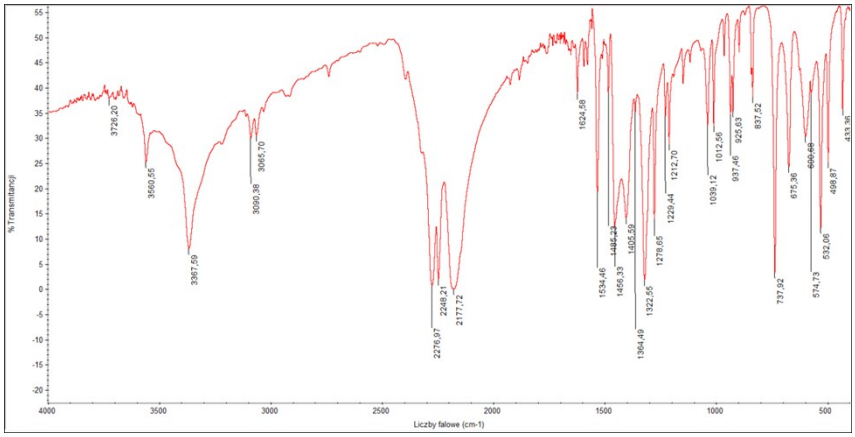

Figure S6. IR spectrum of **3**.

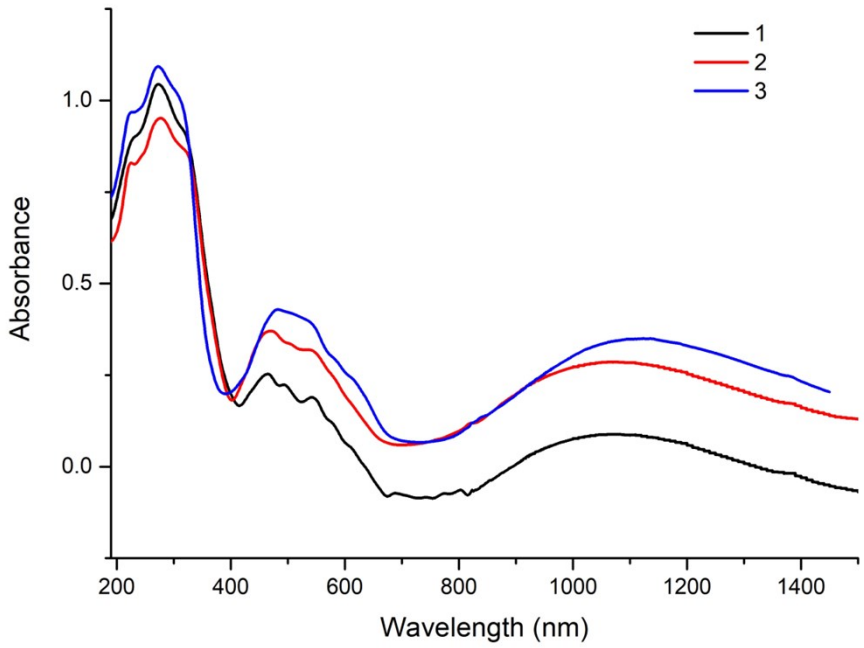

Figure S7. UV/Vis spectra of **1**–**3**.

Table S1. Electronic spectral data for **1**–**3**

Compound	λ_{max}/nm(cm^{-1})	Dq/cm^{-1} [a]	B/cm^{-1} [b]
1	1064 (9398), 546 (18315), 494 (20242), 465 (21505), 314 (31847), 275 (36363), 228 (43859)	892	691
2	1056 (9469), 545 (18348), 499 (20040), 465 (21505), 322 (31055), 279 (35842), 226 (44247)	888	665
3	1079 (9267), 543 (18416), 481 (20790), 307 (32573), 272 (36764), 225 (44445)	915	760

[a] 10Dq – ligand field splitting parameter
[b] B – Racah parameter of the interelectmron repulsion.

2. X-Ray structure data

Table S2. Bond lengths [Å] and angles [°] in **1**

Bond lengths		Bond angles	
Co(1)–N(1)	2.1165(19)	N(1)–Co(1)–N(1)a	180.0
Co(1)–N(1)a	2.1165(19)	N(1)–Co(1)–N(99)a	88.75(5)
Co(1)–N(99)	2.1981(14)	N(1)a–Co(1)–N(99)a	91.25(5)
Co(1)–N(99)a	2.1981(14)	N(1) –Co(1)–N(99)b	91.25(5)
Co(1)–N(99)b	2.1981(14)	N(1)a–Co(1)–N(99)b	88.75(5)
Co(1)–N(99)c	2.1981(14)	N(99)a–Co(1)–N(99)b	86.14(7)
		N(1)–Co(1)–N(99)c	88.75(5)
		N(1)a–Co(1)–N(99)c	91.25(5)
		N(99)a–Co(1)–N(99)c	93.86(7)
		N(99)b–Co(1)–N(99)c	180.00(5)
		N(1)–Co(1)–N(99)	91.25(5)
		N(1)a–Co(1)–N(99)	88.75(5)
		N(99)a–Co(1)–N(99)	180.0
		N(99)b–Co(1)–N(99)	93.86(7)
		N(99)c–Co(1)–N(99)	86.14(7)
		C(99)–N(99)–Co(1)	161.49(12)
		C(99)–N(98)–C(99)b	120.20(18)
		N(99)–C(99)–N(98)	175.43(15)
		N(99)–C(99)–N(98)	175.1(2)

Symmetry codes: (a): 1-*x*,*y*,1-*z*; (b): 1-*x*,1-*y*,1-*z*; (c): *x*,1-*y*,*z*

Table S3. Bond lengths [Å] and angles [°] in **2**

Bond lengths		Bond angles	
Co(1)–N(1)	2.122(3)	N(1)–Co(1)–N(1)d	180.0
Co(1)–N(1)d	2.122(3)	N(1)–Co(1)–N(99)e	90.30(7)
Co(1)–N(99)	2.141(2)	N(1)d–Co(1)–N(99)d	90.30(7)
Co(1)–N(99)d	2.141(2)	N(1)–Co(1)–N(99)d	89.70(7)
Co(1)–N(99)e	2.141(2)	N(1)d–Co(1)–N(99)e	89.70(7)
Co(1)–N(99)f	2.141(2)	N(99)d–Co(1)–N(99)e	89.69(11)
		N(1)–Co(1)–N(99)f	89.70(7)
		N(1)d–Co(1)–N(99)f	90.30(7)
		N(99)d–Co(1)–N(99)f	90.31(11)
		N(99)e–Co(1)–N(99)f	180.00(11)
		N(1)–Co(1)–N(99)	90.30(7)
		N(1)d–Co(1)–N(99)	89.70(7)
		N(99)d–Co(1)–N(99)	180.0
		N(99)e–Co(1)–N(99)	90.31(11)
		N(99)f–Co(1)–N(99)	89.69(11)
		C(99)–N(99)–Co(1)	160.41(19)
		C(99)e–N(98)–C(99)	117.8(3)

Symmetry codes: (d): -*x*,*y*,-*z*; (e): -*x*,-*y*,-*z*; (f): *x*,-*y*, *z*

Table S4. Bond lengths [Å] and angles [°] in **3**

Bond lengths		Bond angles	
Co(1)–N(1)	2.1513(18)	N(1)–Co(1)–N(1)g	180.0
Co(1)–N(1)g	2.1513(18)	N(1)–Co(1)–N(97)	92.63(7)
Co(1)–N(97)	2.1445(19)	N(1)–Co(1)–N(97)g	87.37(7)
Co(1)–N(97)g	2.1445(19)	N(1)–Co(1)–N(99)	93.25(7)
Co(1)–N(99)	2.1405(19)	N(1)–Co(1)–N(99)g	86.75(7)
Co(1)–N(99)	2.1405(19)	N(1)g–Co(1)–N(99)	86.75(7)
		N(1)g–Co(1)–N(99)g	93.25(7)
		N(1)g–Co(1)–N(97)	87.37(7)
		N(1)g–Co(1)–N(97)g	92.63(7)
		N(99)–Co(1)–N(97)	93.98(7)
		N(99)g–Co(1)–N(97)	86.02(7)
		N(99)–Co(1)–N(97)g	86.02(7)
		N(99)g–Co(1)–N(97)g	93.98(7)
		N(99)–Co(1)–N(99)g	180.0
		N(97)–Co(1)–N(97)g	180.0
		C(98)–N(97)–Co(1)	151.16(18)
		C(99)–N(99)–Co(1)	160.73(19)
		N(99)–C(99)–N(98)	173.2(2)
		N(97)–C(98)–N(98)g	173.4(2)
		C(98)g–N(98)–C(99)	119.7(2)

Symmetry codes: (g): 1-*x*,-*y*,1-*z*

Table S5. Short intra– and intermolecular contacts in the structures.

D—H•••A	**D—H**	**H•••A**	**D•••A [Å]**	**D—H•••A [°]**
		1		
N(2)–H(2)•••N(99)^{h}	0.86	2.13	2.979(3)	169.0
		2		
N(2)–H(2)•••N(98)^{i}	0.86	2.16	2.983(5)	159.0
		3		
N(2)–H(2)•••N(98)^{j}	0.86	2.34	3.104(3)	149.0

Symmetry elements: (h): -1/2+*x*,1/2+*y*, *z*; (i): 1/2-*x*,-1/2+*y*,-*z*; (j): 1/2+*x*,1/2-*y*,-1/2+*z*

Table S6. Magneto-structural relationships in 1D cobalt(II)-dicyanamido complexes

Compound /	**Co–N_L/Co–O**	**Co–N_{dca}**	**Co···Co**	**Magnetic properties**	**Ref.**
single μ-1,5-dca bridge					
$[Co(L^1)_4(dca)]_n(ClO_4)_n \cdot 4n(EtOH) \cdot nH_2O$	2.121(4) 2.121(4)	2.088(8) 2.063(9)	8.6090(5)	C = 3.32 cm^3 mol^{-1} K Θ = –31.8 K weak AF interaction	1
$[Co(hypy)_2(dca)(MeOH)_2]_n$	2.138(3) 2.138(3) Co–O= 2.123(3) Co–O= 2.123(3)	2.103(4) 2.103(4)	8.665	C = 3.123 cm^3 mol^{-1} K, Θ = –16.29 K.	13
$[Co(biim)_2(dca)_2]Cl$	2.1386(18) 2.1593(18) 2.1372(18) 2.1325(18)	2.1133(19) 2.1900(19)	7.286	D = 40.3cm^{-1}, J/kB = 20.05 cm^{-1}	17
$[Co(enbzpy)(dca)]_n(ClO_4)_n$	room temperature 2.102(3) 2.083(3) 2.023(3) 2.028(3) **low temperature** 2.138(8) 2.074(8) 2.089(8) 2.133(8)	room temperature 2.092(3) 2.136(3) **low temperature** 2.141(9) 2.073(8)	8.57	SCO	18
$[Co(enbzpy)(dca)]_n(PF_6)_n$	**room temperature** 2.109(5) 2.045(4) 2.034(9) 2.097(4) **Low temperature** 2.039(6) 1.921(6)	**room temperature** 2.127(5) 2.134(5) **Low temperature** 2.163(7)	**room temperature** 8.699 Å **low temperature** 8.718	SCO	20

	1.916(6) 2.043(7)	2.181(8)			
$[Co(bpym)(dca)_2]\cdot H_2O$	2.151(3) 2.151(3) $Co–O_{H2O}$=2.124(4)	2.092(4) 2.103(5)	8.649	*J*= –1.42 Θ= -5.4 K	21
$[Co(L^5)(dca)]_n$	1.985 (4) 1.951 (3) Co-O=1.965 (3)	1.956 (4) 2.330 (5)	5.949	J = –3.52 cm^{-1}	4
$[Co(L^9)(dca)_2]_n$	2.086(2) 2.240(2) 2.154(2) 2.042(3)	2.164(2) 2.098(2)	8.542	C = 2.8–3.4 cm^3 mol^{-1} K J = –0.21 K	9
$[Co(tpz)(dca)(H_2O)](dca)$	2.213(2) 2.078(2) 2.221(2) $Co- O_{H2O}$= 2.005(2)	2.104(2) 2.096(2)	8,465	θ＝7.97 K *C*＝2.59 cm^3Kmol^{-1}	22
$[Co(L^7)(dca)(ClO_4)_2MeOH]_n$	Co(A) 2.1619(19) 2.0785(19) 2.1011(18) 2.1323(19) Co(B) 2.141(2) 2.1017(19) 2.097(2) 2.1661(19)	Co(A) 2.1828(18) 2.0851(19) Co(B) 2.1013(18) 2.089(2)	8.451 Å 8.532 Å	lack of significant magnetic interactions	6
double μ-1,5-dca bridge					
$[Co(im)_2(dca)_2]_n$	2.095(2) 2.095(2)	2.157(2) 2.157(2) 2.153(2) 2.153(2)	7.359	C = 2.8–3.4 cm^3 mol^{-1} J = –24.8 K	5
$[Co(im)_2(dca)_2]_n$	2.101(2)	2.161(2)	7.395(1)	C = 2.8–3.4 cm^3 K mol^{-1}	11

	2.101(2)	2.161(2) 2.164(3) 2.164(3)		J = –1.0 K	
$[Co(ampy)_2(dca)_2]$	2.193(3) 2.193(3)	2.126(2) 2.126(2) 2.128(2) 2.128(2)		–	2
$[Co(4omp)_2(dca)_2]_n$	2.126(4) 2.126(4)	2.116(4) 2.116(4) 2.124(5) 2.124(5)	7.076(3)	C = 3.58 cm^3 mol^{-1} Θ = –15.5 K	14
$[Co(pyr)_2(dca)_2]_n$	Co-O= 2.097(2) Co-O =2.072(3)	2.084 (3) 2.084 (3) 2.099 (2) 2.099 (2)	7.220	weak antiferromagnetic interaction	15
$[Co(mepy)_2(dca)_2]_n$	2.1229 (18) 2.1229 (18)	2.1385 (17) 2.1385 (17) 2.1385 (17) 2.1385 (17)	7.305(1)		24
$[Co(4\text{-}nic)_2(dca)_2]_n \cdot 2nCH_3OH$	2.157(2) 2.157(2)	2.114(3) 2.114(3) 2.128(2) 2.128(2)	7.353	C = 3.58 $cm^3 \cdot mol–1 \cdot K$, θ = –17.8 K	26
$[Co(dca)_2(H_2O)_2]_n \cdot (hmt)_n$	Co- O_{H2O} =2.082(1)	2.122(2) 2.118(2)	7.362	J = –0.50 cm^{-1}	3
$(Ph_4P)[Co(dca)_4]$	–	2.176(3) 2.091(3) 2.165(3) 2.176(3) 2.091(3) 2.165(3)	7.589(1)	C= 1.394 cm^3 mol^{-1} Θ= +0.1 K very weak ferromagnetic interaction	7

$[Co(phen)(dca)_2(H_2O)\cdot MeOH]_n$	2.210(2) 2.210(2) 2.126(2) 2.112(2) Co- O_{H2O} = 2.127(2)	2.106(2) 2.102(2)	7.3244(5)	–	8
$[Co(bipy)(dca)_2]_n$	2.129(2) 2.129(2)	2.134(2) 2.134(2) 2.102(2) 2.102(2)	7.375(1)	D= 93.7cm^{-1}	12
$[Co(mepypz)_2(dca)_2]_n$	Co-O= 2.109(2) Co-O= 2.109(2)	2.122(3) 2.122(3) 2.102(3) 2.102(3)	7.379(3)	–	16
$[Co(pydz)_2(dca)_2]_n$	2.166(2) 2.166(2)	2.1095(14) 2.1095(14) 2.1095(14) 2.1095(14)	7.3409(5)	weak AF interaction C=3.46 cm^3 K mol^{-1} Θ= -20.46	19
$[Co(L^{21})_2(dca)_2]_n$	2.154(3) 2.154(3)	2.130(3) 2.130(3) 2.122(3) 2.122(3)	7.481(1)	–	23
$\{[Co(bpm)_2(dca)](ClO_4)\}_n$	2.141(4) 2.141(4)	2.103(5) 2.103(5) 2.103(5) 2.103(5)	7.592	-	25
double μ-1,5-dca bridge and N-donor ligand					
$[Co(bpds)(dca)_2]_n$	2.180(5) 2.180(5)	2.143(5) 2.142(5) 2.143(5) 2.142(5)	7.302	J = –0.95 cm^{-1}	3
$[Co_2(tppz)(dca)_4]_n$	2.156(2) 2.156(2)	2.044(2) 2.044(2)	7.377 A	J = –1.10 cm^{-1}	10

	2.114(2) 2.114(2) 2.140(2) 2.140(2)	2.141(2) 2.141(2)			

L^1= 4-(imidazol-1-yl)phenol; **L^2**= anion N-(picolinoyl)biurate; **L^3**= (N,N-diethyl,N'-(pyridin-2-yl)benzylidene)ethane-1,2-diamine; **L^4** = N^4-Schiff base ligand; **ampy**= 2-aminopyridine; **hmt**= hexamethylenetetramine; **bpds**= 4,4'-bipyridyl disulfide;; **im**=imidazole; **phen**=4,7-phenanthroline; **tppz**= tetra-2-pyridylpyrazine; **bipy**= 4,4'-bipyridine; **hypy**= 3-hydroxypyridine; **pyr**=2-pyrrolidone; **mepypz**= 3,5-dimethyl-1-(2-pyridyl)pyrazole; **biim**= 2,2'-biimidazole; **enbzpy**= N,N'-bis(2-pyridinylbenzylide=ne)ethane-1,2-diamine; **pydz** = pyridazine, **bpym**= bipyrimidine; **tpz**= 2,4,6-tri(2-pyridyl)-1,3,5-triazine; **L^5**= 4-picolyl choride); **mepy**= 4-methylpyridine; **bpm**= bis(3,5-dimethyl)pyrazolylmethane; **4omp** = 4-methoxypyridine; **4-nic**= isonicotinamide

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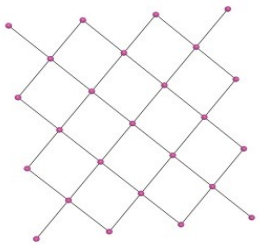
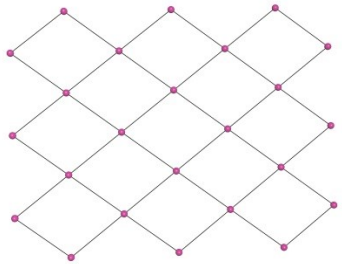
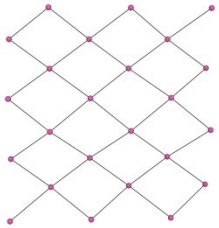
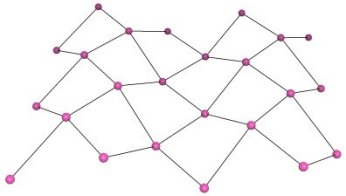
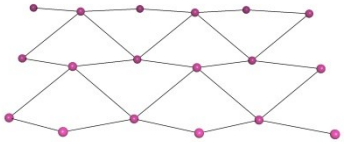
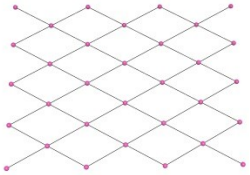
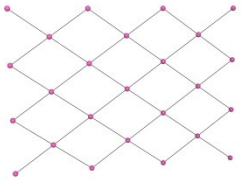
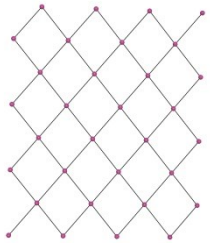
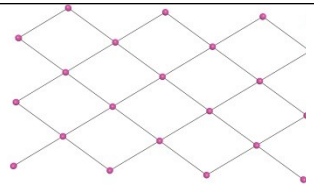
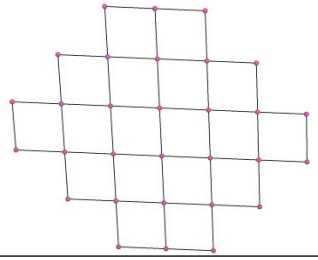
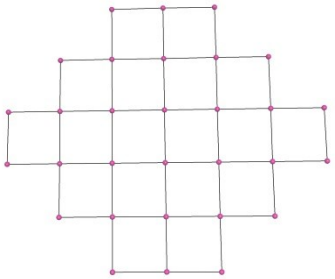
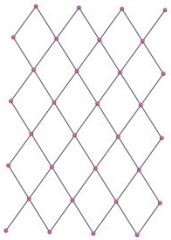
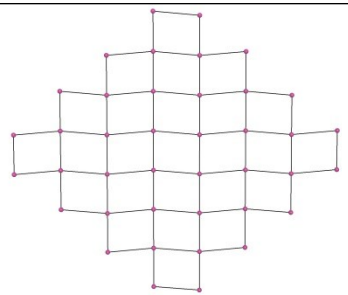
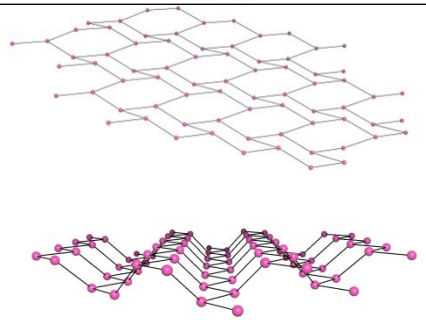
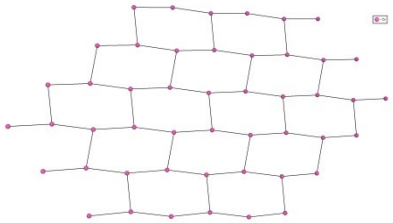
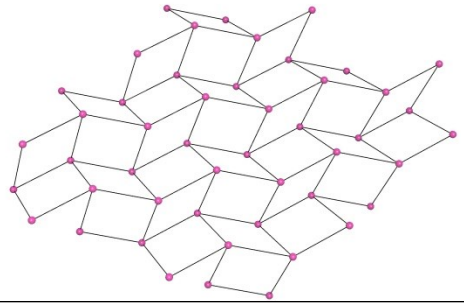
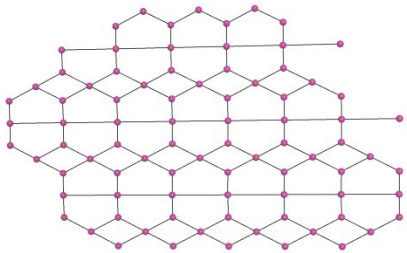
Table S7. Magneto-structural relationships of 2D cobalt(II)-dicyanamido complexes.

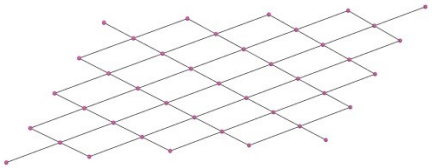
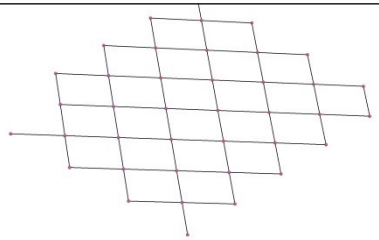
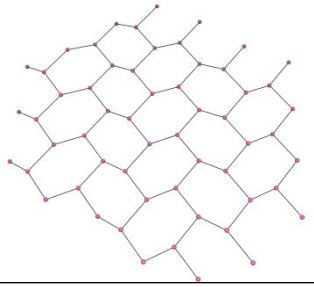
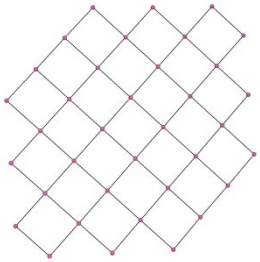
Compound/	**topology**	**Co–N_L/Co–O**	**Co–N_{dca}**	**Co···Co**	**Magnetic properties**	**Ref.**
		single $\mu_{1,5}$-dca				
$[Co(bzim)_2(dca)_2]_n$		2.1492(16) 2.1492(16)	2.1152(17) 2.1152(17) 2.1427(18) 2.1427(18)	7.623	Θ = 17.14 K C = 3.17 $cm^3K\ mol^{-1}$	27
$[Co(pte)_2(dca)_2]_n$		2.169(2) 2.169(2)	2.097(2) 2.097(2) 2.146(2) 2.146(2)	8.5739	C = 3.13 cm^3 K mol^{-1} Θ= –9.1 K weak antiferromagnetic interaction	28
$[Co_2(4\text{-cypy})_4(dca)_4]_n$		Co(1) 2.179(7) 2.156(6) Co(2) 2.149(6) 2.181(6)	2.122(6) 2.079(6)	8.037(3) 7.745(3)	J= –1.14K	30

						
[Co(dmdpy)(dca)$_2$]		2.142(2) 2.142(2)	2.114(2) 2.095(3) 2.114(2) 2.095(3)	8.102(4)	weak magnetic interaction	32
{[Co(ambzim)$_2$(dca)$_4$]}$_n$		2.1171(13) 2.1171(13)	2.1520(13) 2.1520(13) 2.1591(15) 2.1591(15)	8.186 Å	–	33
{[Co(L^6)$_2$(dca)$_2$]$_2$(L^6)}$_n$		Co-Owoda= 2.057(5) Co-Owoda= 2.057(5)	2.124(7) 2.124(7) 2.124(6) 2.124(6)	7.894(1)	–	34
[Co(4NOpy)$_2$(dca)$_2$(CH$_3$CN)]$_n$		2.149, 2.162	2.106, 2.107, 2.110, 2.112	8.13, 8.16	J= −0.8 weak signals for both χmol ′ and χmol	35

$[Co(atz)_2(dca)_2]_n$		2.1677(15) 2.1677(15)	2.0887(17) 2.0968(16) 2.0887(17) 2.0968(16)	8.041	$\tau_0 = 1.7 \cdot 10^{-6}$ s E_a= 5.1 cm^{-1} ***SIM***	38
$[Co(bim)_2(dca)_2]_n$		2.128(3) 2.134(3)	2.190(3) 2.220(3) 2.209(3) 2.219(3)	8.927(2) 8.968(2)	|D| = 74.3 cm^{-1} $\tau_0 = 1.54 \cdot 10{-}6$ s E_a = 5.33 cm^{-1} ***SIM***	39
$[Co(bmim)_2(dca)_2]_n$		2.156(3) 2.163(3)	2.127(3) 2.153(3) 2.152(3) 2.145(3)	8.7110(5) 8.7158(5)	|D| =75.8 cm^{-1} $\tau_0 = 0.63 \times 10^{-6}$ s E_a = 13.81 cm^{-1} ***SIM***	39
$[Co(mepyz)_2(dca)_2]H_2O$		2.1553(12 2.1553(12	2.1210(12) 2.1008(12) 2.1210(12) 2.1008(12)	8.318(6)	μ_{eff} 4.95μ_B	40
double $\mu_{1,5}$-dca + single $\mu_{1,5}$ -dca						

$(Ph_4As)[Co(dca)_3]$		–	2.121 2.121 2.110 2.110 2.140 2.140	7.370 8.650	no long-range magnetic interaction	31
$[Co(phen)(dca)_2]_n$		2.1344(14) 2.1209(13)	2.1346(16) 2.1085(14) 2.2109(16) 2.0845(15)	7.2571(3) 7.6017(3)	J= –0.33 cm^{-1} Θ = –0.017K	46
$[Co(2,9\text{-dmphen})(dca)_2]_n$		2.1707(15) 2.1884(16)	2.1491(17) 2.1097(18) 2.0871(18) 2.1269(18)	7.389(1) 7.718(1)	J= –0.03 cm^{-1} Θ = –0.005K	46
$[Co(dca)_2(pypz)]_n$		2.166(2) 2.130(3)	2.130(2) 2.123(3) 2.107(3) 2.093(3)	8.899 Å	–	16

double $\mu_{1,5}$-dca + double $\mu_{1,3,5}$-dca						
$[Co(dca)_2(H_2O)]\cdot phz$		Co(2)–Owoda = 2.049(2) Co(2)–Owoda = 2.049(2)	Co(1) 2.080(2) 2.086(2) 2.213(2) 2.080(2) 2.086(2) 2.213(2) Co(2) 2.121(2) 2.163(2) 2.121(2) 2.163(2)	7.4110 9.7995	μ_{Co} =4.84μ_B	36
$\mu_{1,5}$-dca + $\mu_{1,3,5}$-dca						
$[Co(pzdo)(dca)_2]$	-	Co-O=2.124(4) Co-O=2.124(4)	Co(1) 2.100(3) 2.100(3) 2.100(3) 2.100(3) Co(2) 2.179(4) 2.179(4)	7.499 Å	Θ=-9.4 K C= 3.17 cm^3 mol^{-1}K	44
$[Co_2(modo)_2(dca)_4]$	-	Co-O=2.122(2) Co-O=2.122(2)	2.065(2) 2.065(2) 2.178(2) 2.089(2)	5.803, 7.877	C = 6.61 cm^3 mol^{-1} K Θ= –33.5 K	44
$[Co(pydz)_2(dca)_2]_n$	-	2.140(3)	2.122(2) 2.088(2) 2.122(2) 2.088(2) 2.231(3) 2.231(3)	7.3474(2) 6.0490(6)	C= 3.50 cm^3 K mol^{-1} Θ = –18.11K μ_{eff} =5.29 μ_B	19

double $\mu_{1,5}$-dca + ligand						
$[Co(bnzd)(dca)_2]_n$		2.1895(16) 2.1895(16)	2.1173(16) 2.1173(16) 2.0996(17) 2.0996(17)	7.293 though dca 12.941 through *bnzd*	J = –3.38 K weak antiferromagnetic interaction	29
$\{[Co(L^7)_2(dca)](OH)(gly)_2\}_n$		2.182 2.163	2.140 2.140 2.163 2.163	8.8 though dca 14.5 though ligand	–	37
$[Co(3bpo)(dca)_2]_n$		2.176(4) 2.160(4)	2.091(4) 2.103(5) 2.136(4) 2.115(4)	7.383(6)	it is impossible to fit the magnetic data of 2-D Co^{II}	41
$[Co(btm)_2(dca)]ClO_4$		2.146(5) 2.140(5) 2.151(5) 2.143(5) Co(2) 2.156(6) 2.156(6) 2.136(6) 2.136(6)	2.084(5) 2.072(5)	8.539(2) 8.910(3)	weak antiferromagnetic interaction	42

L^6= pyridinium-4-olate; **L^7**= bis[3,5-dimethyl-4-(49-pyridyl)pyrazol-1-yl]methane; **bzim** = benzimidazole; **pte** = 1-(2,4-difluorophenyl-2- (1H-1,2,4-triazol-1-yl)ethanone, **bnzd**= benzidine; **4cypy**= 4- cyanopyridine, **dmdpy**= 5,5'-dimethyl-2,2'-dipyridine; **ambzim**= 2-aminobenzimidazole; **4NOpy**= 4-(N-tert-butyloxylamino)pyridine; **pypz**= 3,5-dimethyl-1-(2-pyridyl)pyrazole; **phz**= phenazine; **atz**= 2-amino-

1,3,5-triazine**;** **bim**=1-benzylimidazole, **bmim**= 1-benzyl-2-methylimidazole; **mepyz**= methylpyrazine; **3bpo**= 2,5-bis(3-pyridyl)-1,3,4-oxadiazole; **btrm**= 1,2-bis(1,2,4-triazole-1-yl)methane; **pzdo**= pyrazine dioxide; **modo**= 2,3,5-trimethylpyrazine-dioxide; **phen**= 1,10-phenanthroline; **2,9-dmphen**= 2,9-dimethylphenanthroline

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3. The HFEPR and FIRMS spectra

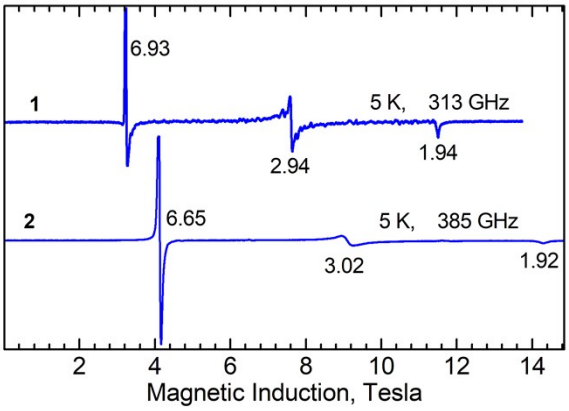

Figure S8. Blue traces: HF EPR spectra of compounds **1** and **2** recorded at similar conditions.

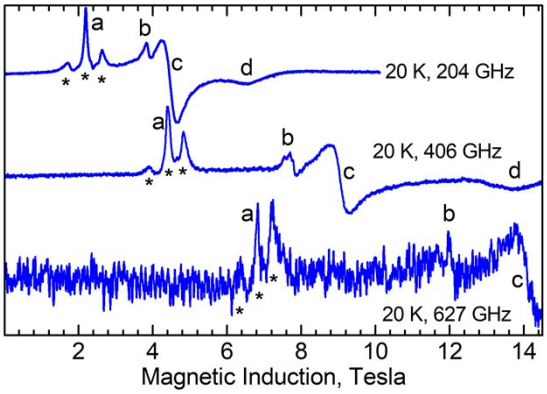

Figure S9. Blue traces: HF EPR spectra of compounds **3**.

4. Selected AC susceptibility data

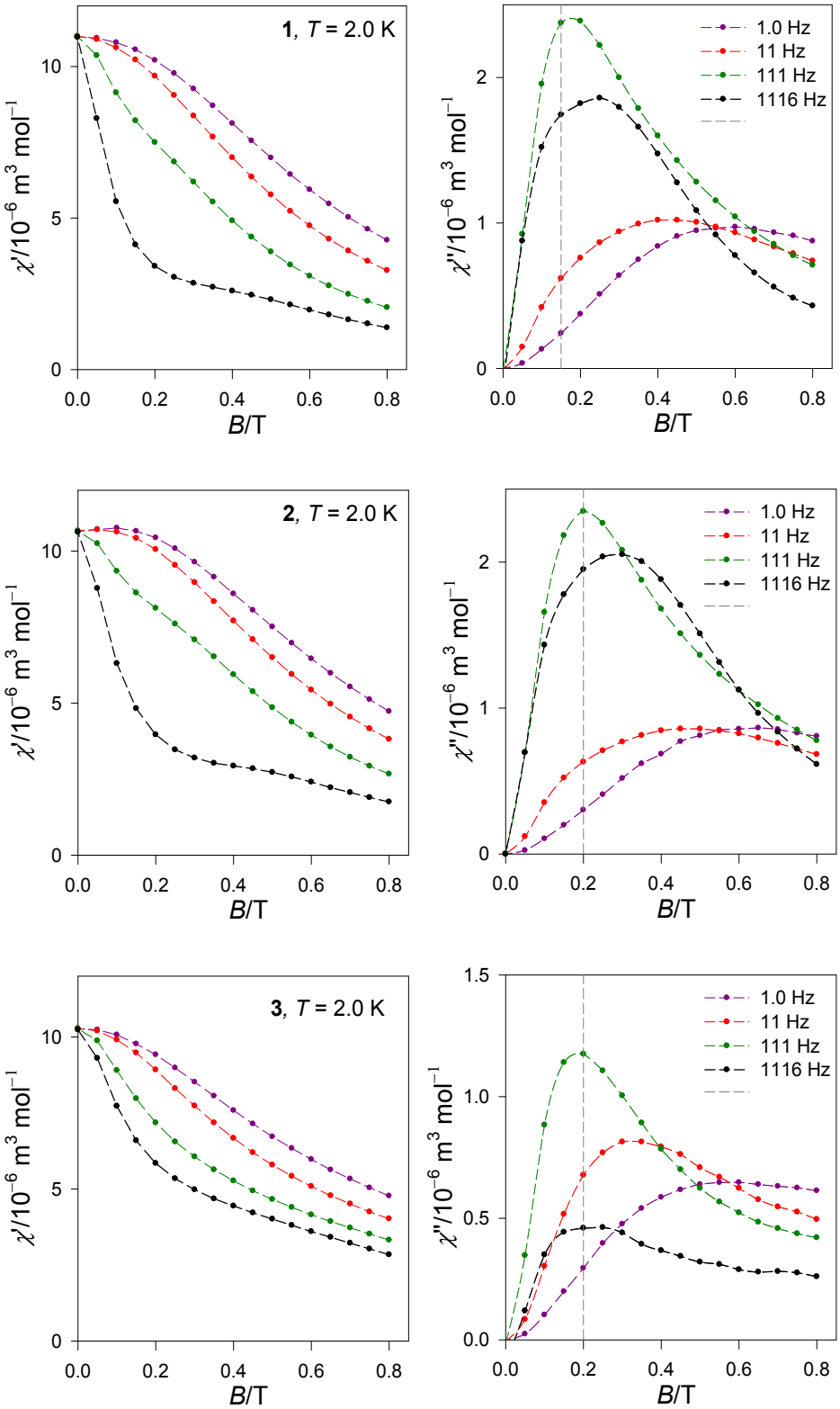

Figure S10. Field dependence of the AC susceptibility for **1** through **3** at $T = 2.0$ K for a set of trial frequencies. Lines – guide for eyes.

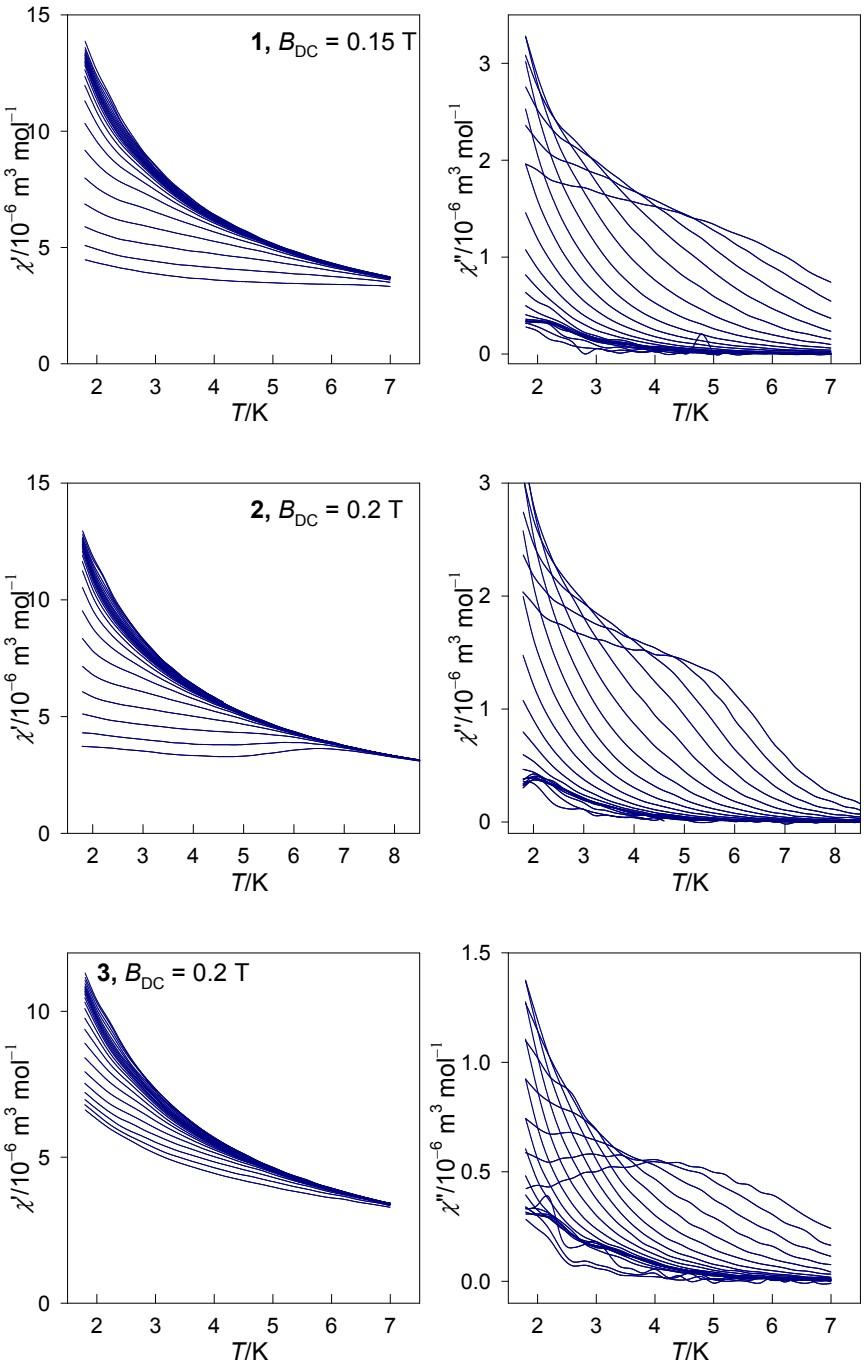

Figure S11. Temperature dependence of the AC susceptibility for **1** through **3** at B_{DC} = 0.2 T for 22 frequencies of the oscillating field.

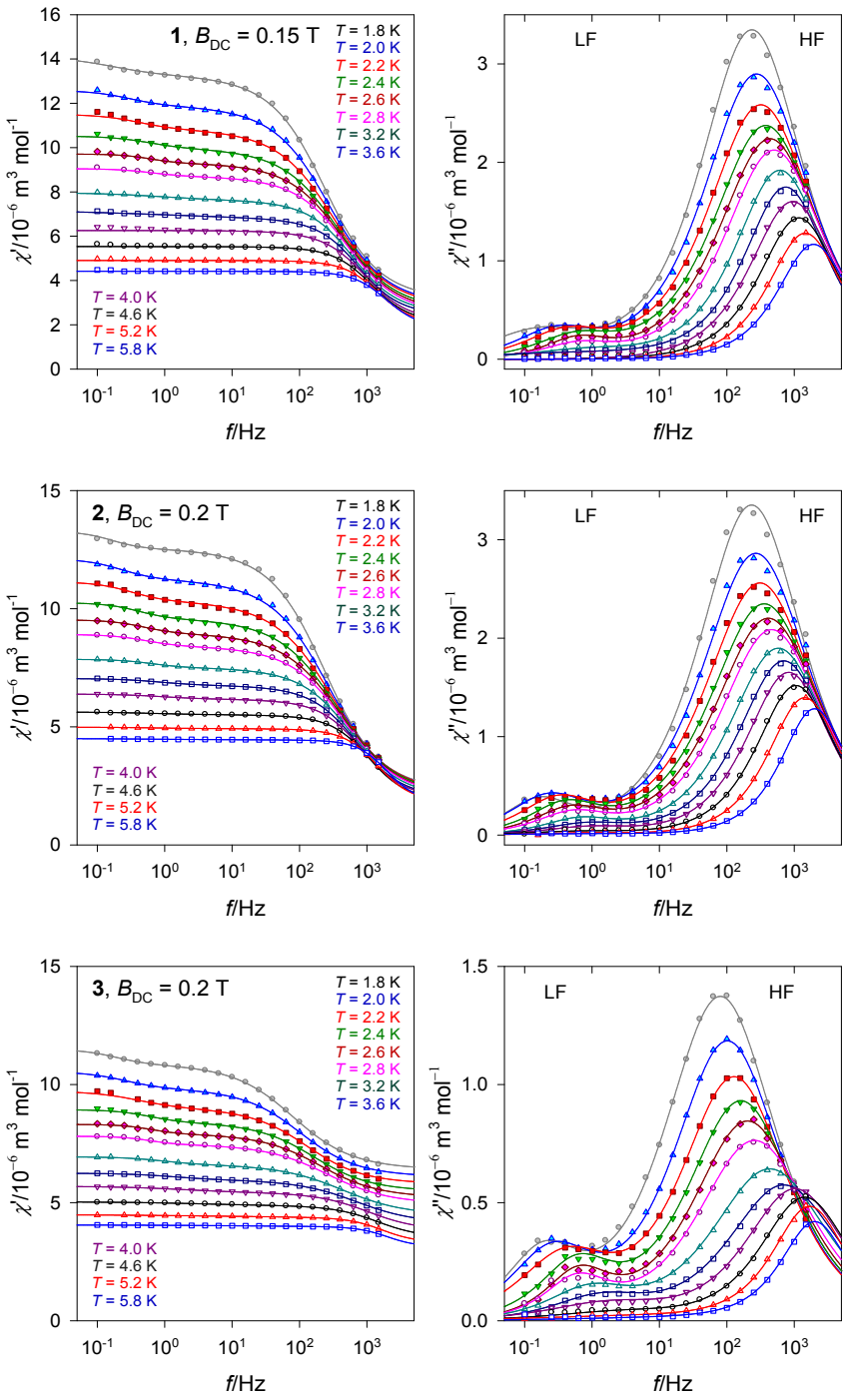

Figure S12. Frequency dependence of the AC susceptibility at B_{DC} = 0.2 T. Lines – fitted, using the two-set Debye model.

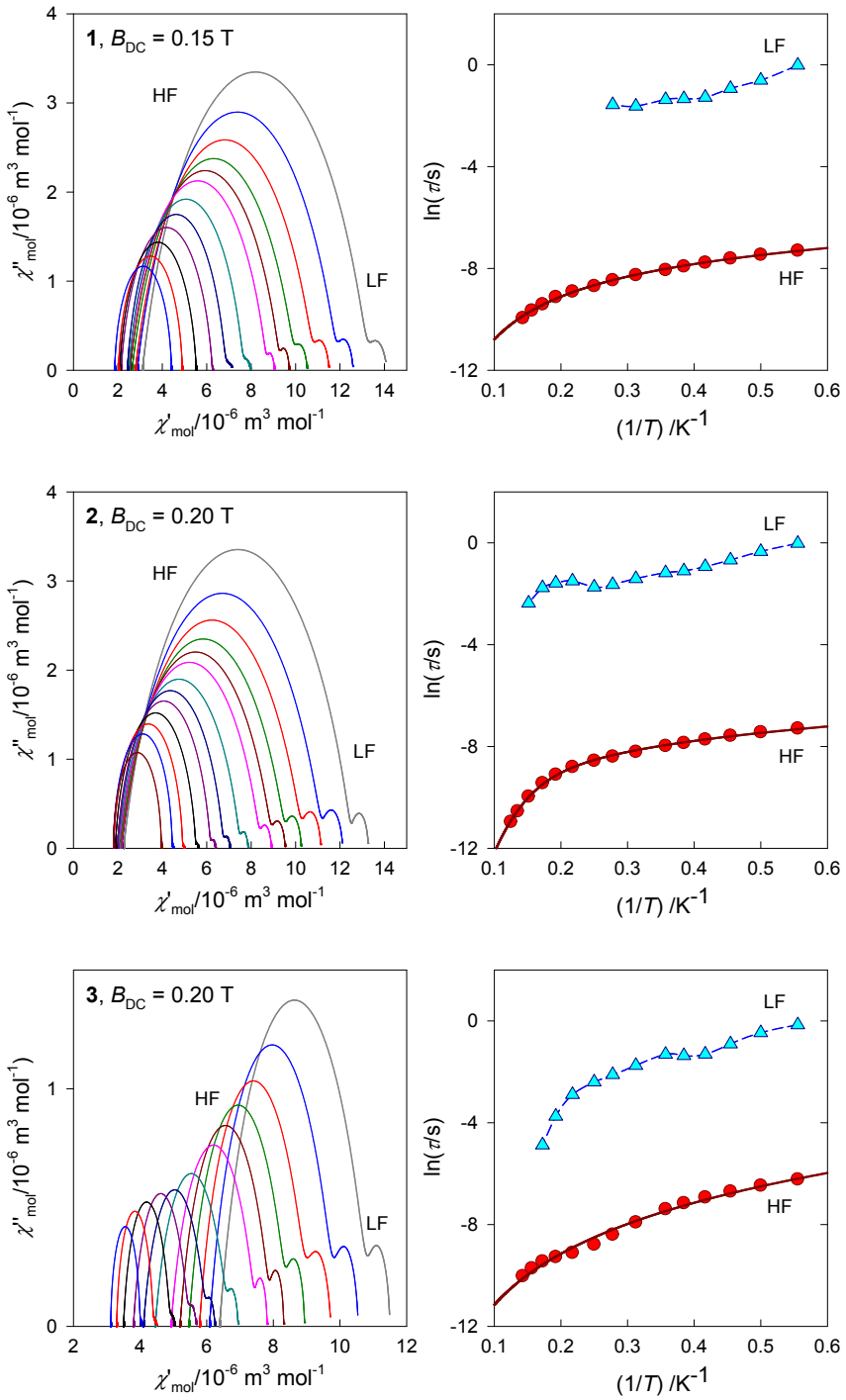

Figure S13. Argand plot (left) and the Arrhenius-like plot (right). Solid line – fitted with Raman-like and phonon-bottleneck terms $\tau^{-1} = CT^n + FT^l$.

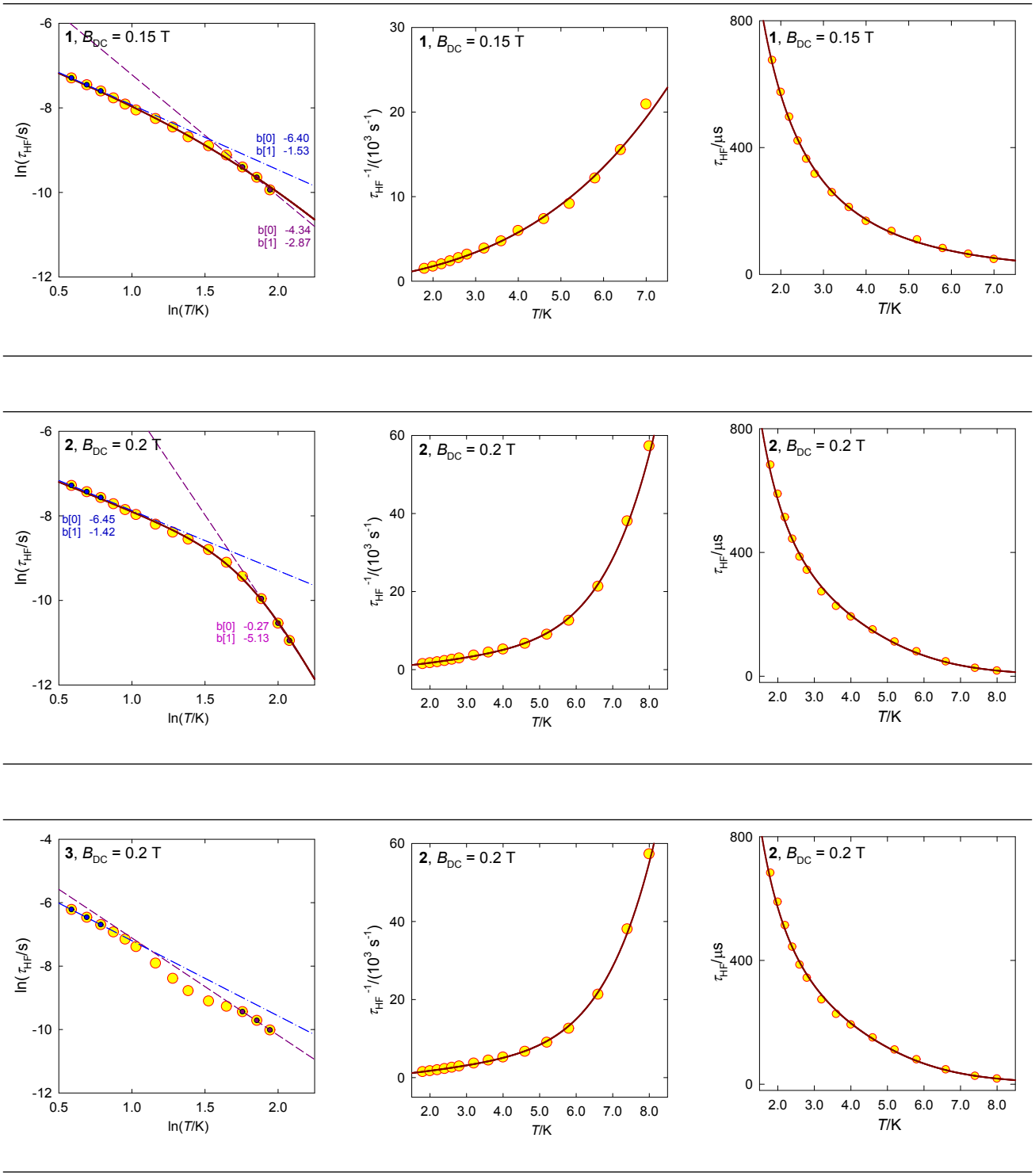

Figure S14. Various dependences of the high-frequency relaxation time. Dashed (dot-dashed) lines – linear fits to the high-temperature (low-temperature) windows. Solid – combined Raman-like and phonon-bottleneck terms.