Electronic supplementary information

Syntheses, structures and magnetic properties in two isostructural dicyanamide-bridged 2D polymers †

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† Low-dimensional compounds containing cyanido groups. Part XXXVI.

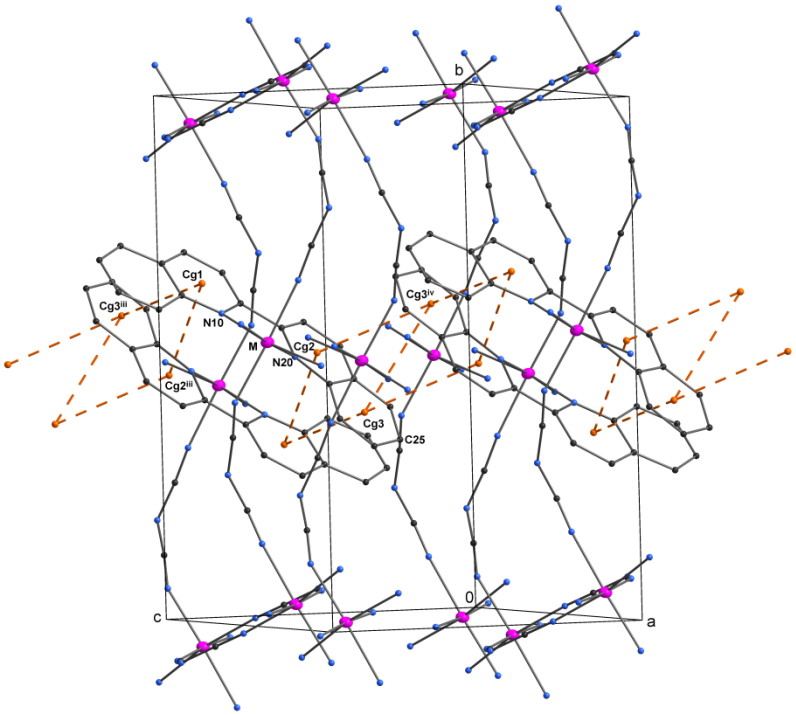


Fig S1 π-π interactions (orange dashed lines) between aromatic rings in **1** and **2**. Hydrogen atoms not involved in hydrogen bonds are omitted for clarity.

Symmetry codes: iii = – *x*, 1 – *y*, 1 – *z*; iv = 1 – *x*, 1 – *y*, 1 – *z*.

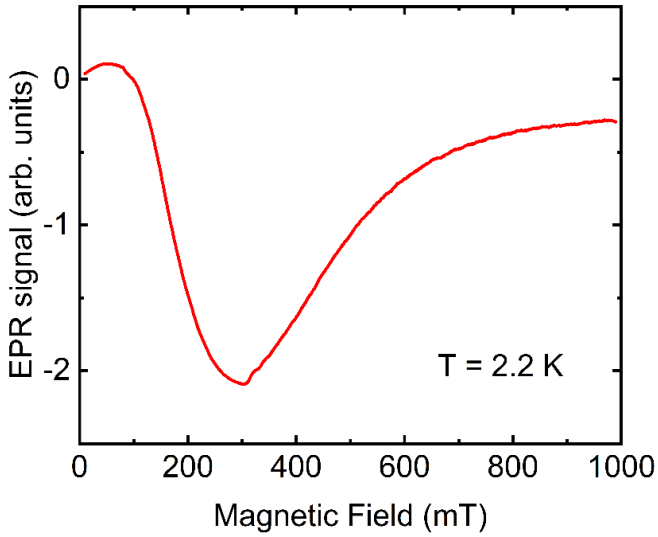


Fig. S2 X-band EPR spectrum of **1** measured at 2.2 K.

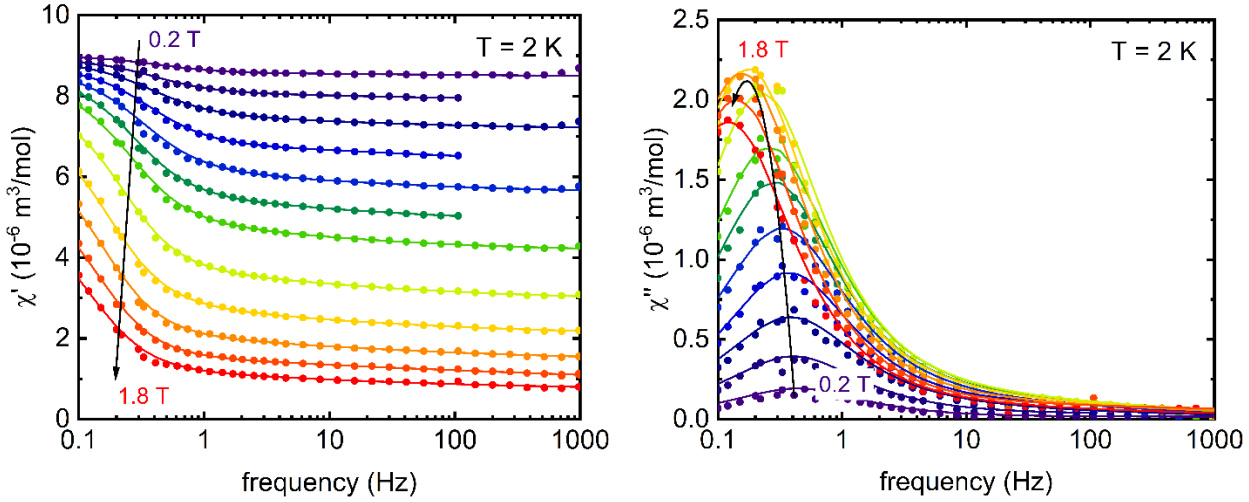


Fig. S3 Frequency dependence of real (left panel) and imaginary (right panel) component of AC susceptibility of **1** measured at different applied DC fields measured at 2 K including the fit of the modified Debye model (an additional Debye function was included to take into account a very small contribution at higher frequencies).

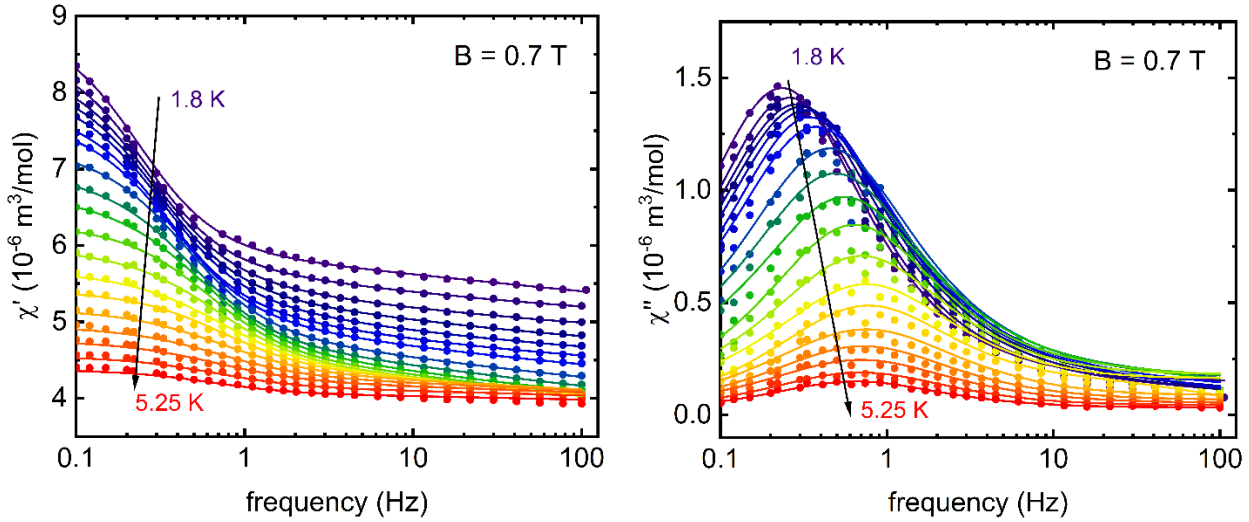


Fig. S4 Frequency dependence of real (left panel) and imaginary (right panel) component of AC susceptibility of **1** measured at an applied DC field 0.7 T in the temperature range 1.8 - 5.25 K including the fit of the modified Debye model (an additional Debye function was included to take into account a very small contribution at higher frequencies).

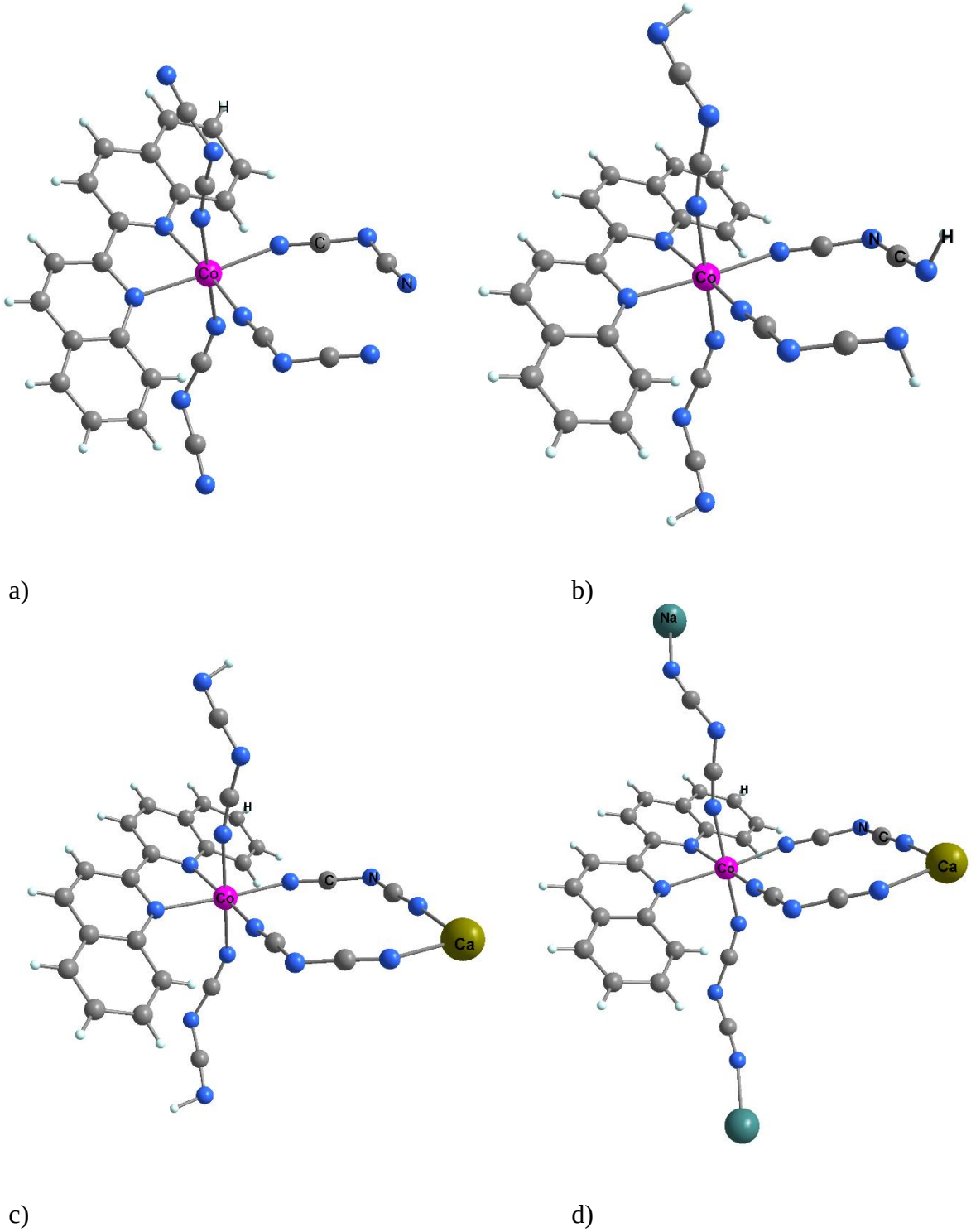


Fig. S5 Structure of all fragments used for the SA-CASSCF/NEVPT2 calculations of ZFS parameters in compound **1**, a) $[Co(biq)(dca)_4]^{2-}$, b) $[Co(biq)(\mu_{1,5}\text{-}dca)_4H_4]^{2+}$, c) $[Co(biq)(\mu_{1,5}\text{-}dca)_4H_2Ca]^{2+}$, d) $[Co(biq)(\mu_{1,5}\text{-}dca)_4Na_2Ca]^{2+}$, the same type of fragments was used for compound **2**.

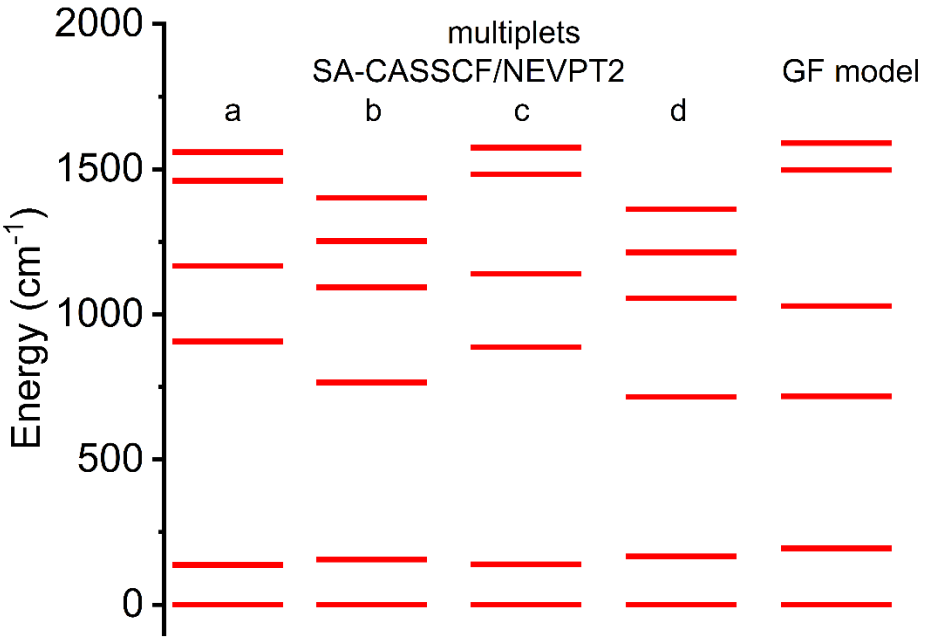
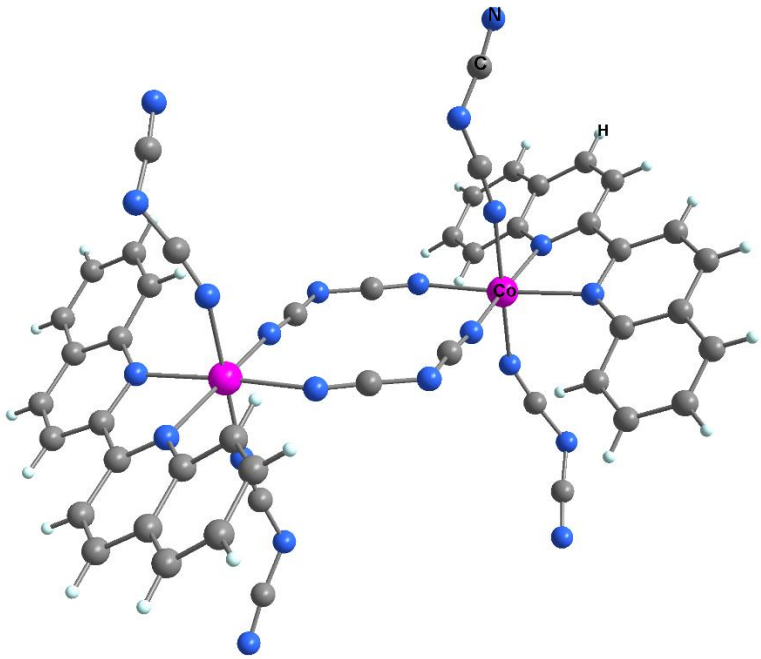
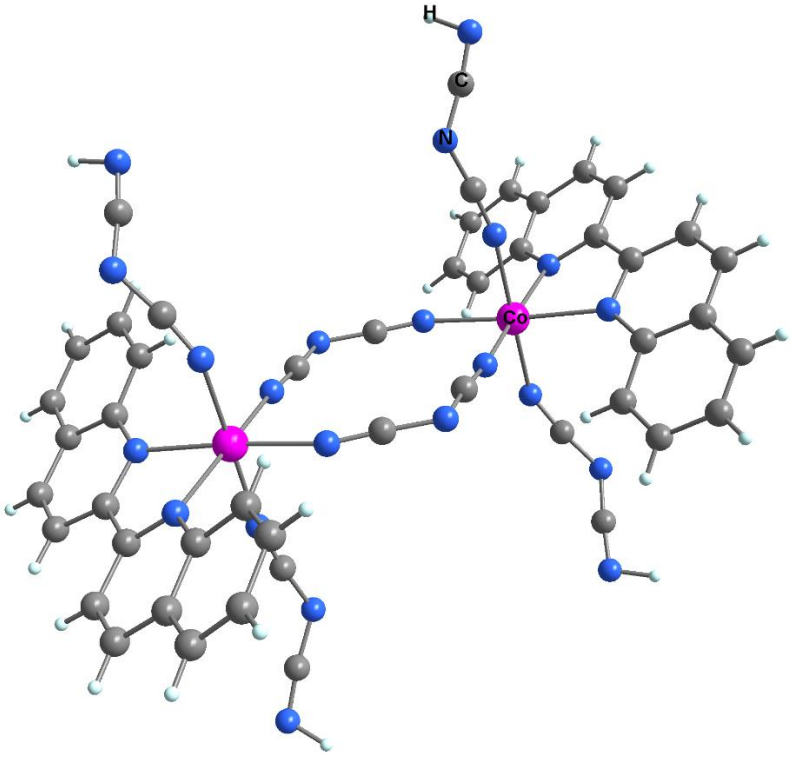


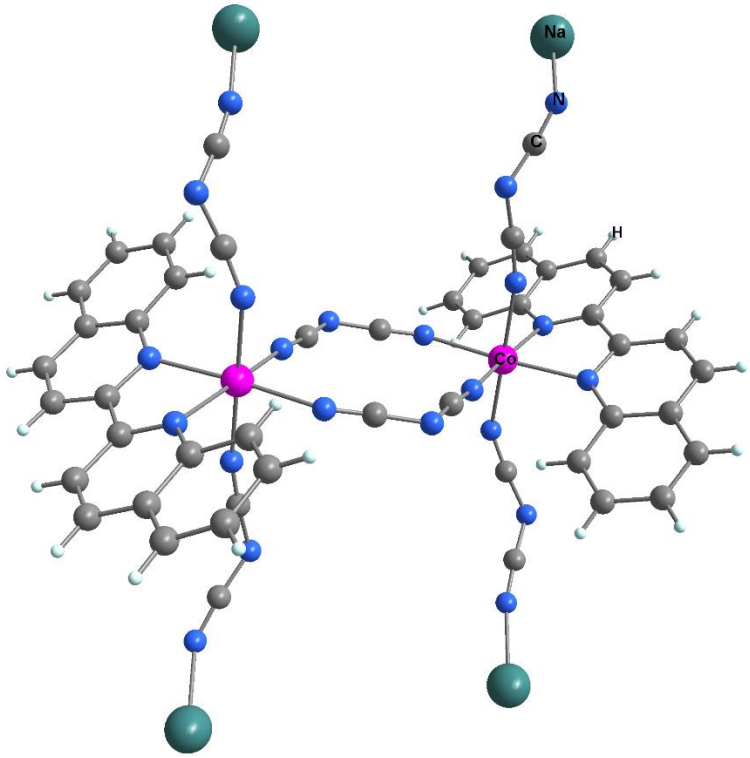
Fig. S6 The energies of 6 lowest multiplets as obtained from SA-CASSCF/NEVPT2 calculations for: a) $[Co(biq)(dca)_4]^{2-}$, b) $[Co(biq)(\mu_{1,5}\text{-}dca)_4H_4]^{2+}$, c) $[Co(biq)(\mu_{1,5}\text{-}dca)_4H_2Ca]^{2+}$, d) $[Co(biq)(\mu_{1,5}\text{-}dca)_4Na_2Ca]^{2+}$. Energies obtained using Griffith-Figgis (GF) Hamiltonian Eq. 3 with the set of the parameters obtained from the fit of $\mu_{eff}(T)$ are included.



a)



b)



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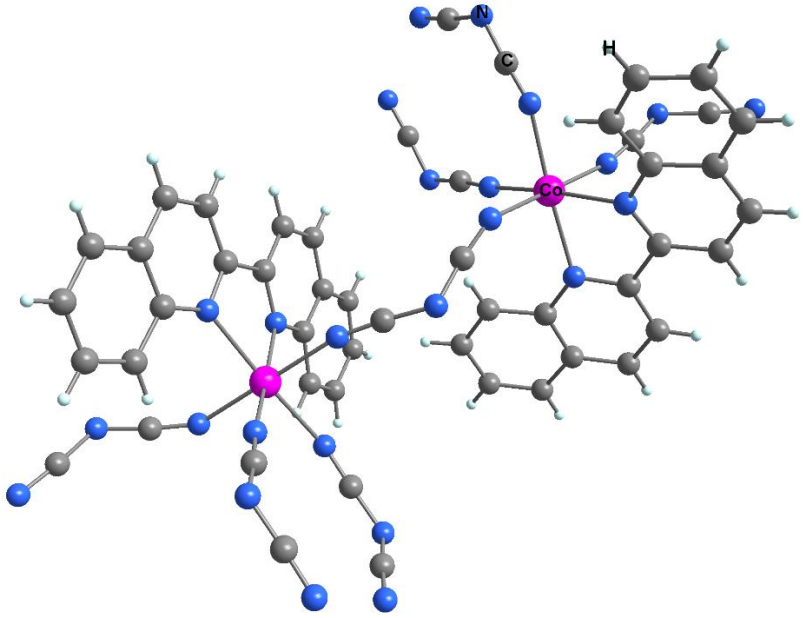

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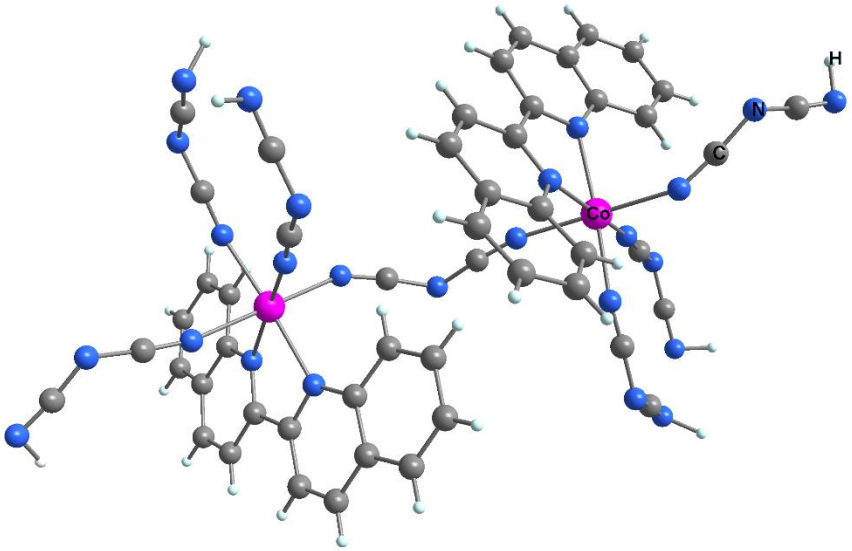
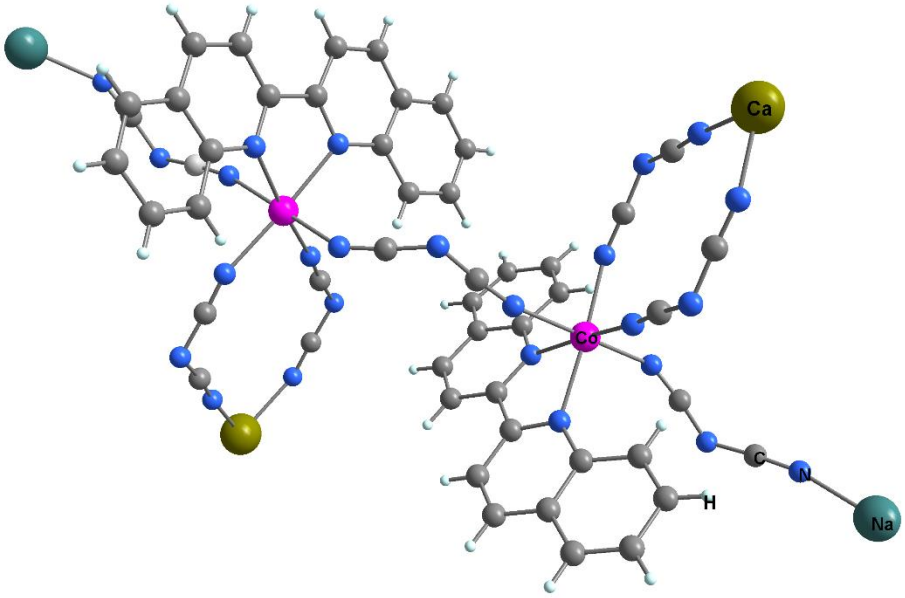


e)



f)

Fig. S7 Structure of all fragments used for the BS DFT calculations of two different exchange paths in compound **1**, a) $[Co(biq)(dca)_2\text{-}(\mu_{1,5}\text{-}dca)_2\text{-}Co(biq)(dca)_2]^{2-}$, b) $[Co(biq)(\mu_{1,5}\text{-}dca)_2H_2\text{-}(\mu_{1,5}\text{-}dca)_2\text{-}Co(biq)(\mu_{1,5}\text{-}dca)_2H_2]^{2+}$, c) $[Co(biq)(\mu_{1,5}\text{-}dca)_2Na_2\text{-}(\mu_{1,5}\text{-}dca)_2\text{-}Co(biq)(\mu_{1,5}\text{-}dca)_2Na_2]^{2+}$, d) $[(dca)\text{-}Co(biq)(dca)_2\text{-}(\mu_{1,5}\text{-}dca)\text{-}Co(biq)(dca)_2\text{-}(dca)]^{3-}$, e) $[H(\mu_{1,5}\text{-}dca)\text{-}Co(biq)(\mu_{1,5}\text{-}dca)_2H_2\text{-}(\mu_{1,5}\text{-}dca)\text{-}Co(biq)(\mu_{1,5}\text{-}dca)_2H_2\text{-}(\mu_{1,5}\text{-}dca)H]^{3+}$, f) $[Na(\mu_{1,5}\text{-}dca)\text{-}Co(biq)(\mu_{1,5}\text{-}dca)_2\ Ca\text{-}(\mu_{1,5}\text{-}dca)\text{-}Co(biq)(\mu_{1,5}\text{-}dca)_2\ Ca\text{-}(\mu_{1,5}\text{-}dca)Na]^{3+}$, the same type of fragments was used for compound **2**.

Table S1 Comparison of magnetic parameters of other dca bridged polymeric complexes showing slow magnetic relaxation.

Compound	**U_{eff} /cm^{-1}** (applied field/T)	**τ_0 / s**	**magnetic interactions**	**Ref.**
$[Co(atz)_2(dca)_2]_n$ easy-axis anisotropy	5.1 (0.1)	1.7×10^{-6}	neglected	Palion-Gazda 2015
$[Co(dca)_2(NH_2pyz)_2]_n\cdot H_2O$ easy-plane anisotropy	24.5 – 28.2 (0.25) 1.62 – 2.37	$1.19 – 2.5\times10^{-7}$ $3.0 – 5.7\times10^{-5}$	neglected	Palion-Gazda 2019
$[Co_3(dca)_6(HOpyz)_5(H_2O)_2]_n$ easy-plane anisotropy	11.6 – 20.1 (0.2) 0.33 – 1.26	$1.73 – 14.1\times10^{-7}$ $1.96 – 4.3\times10^{-5}$	zJ = -0.3 cm^{-1}	Palion-Gazda 2019
$[Co(bim)_2(dca)_2]_n$ easy-axis anisotropy	5.33 (0.1)	1.54×10^{-6}	neglected	Switliczka 2016
$[Co(bmim)_2(dca)_2]_n$ easy-axis anisotropy	13.81 (0.1)	0.63×10^{-6}	Θ = -0.07 cm^{-1}	Switliczka 2016
$[Co(pypz)(dca)(H_2O)]_n\cdot(dca)$ easy-axis anisotropy	103 (0.4)	1.2×10^{-11}	zJ = -0.006 cm^{-1}	Switlicka 2020

atz = 2-amino-1,3,5- triazine; *pyz* = pyrazine; *bim* = 1-benzylimidazole; *bmim* = 1-benzyl-2-methylimidazole; *pypz* = 2,6-bis(pyrazol–1–yl)pyridine

J. Palion-Gazda, T. Klemens, B. Machura, J. Vallejo, F. Lloret and M. Julve, Dalton Trans., 2015, **44**, 2989-2992.

J. Palion-Gazda, K. Choroba, B. Machura, A. Świtlicka, R. Kruszynski, J. Cano, F. Lloret and M. Julve, Dalton Trans., 2019, **48**, 17266-17280.

A. Świtlicka-Olszewska, J. Palion-Gazda, T. Klemens, B. Machura, J. Vallejo, J. Cano, F. Lloret, M. Julve, *Dalton Trans.*, 2016, **45**, 10181–10193.

A. Świtlicka, B. Machura, M. Penkala, A. Bieńko, D. C. Bieńko, J. Titiš, C. Rajnák, R. Boča, A. Ozarowski, Inorg. Chem. Front., 2020, **7**, 2637-2650.

Table S2 The energies (in cm^{-1}) of 6 lowest multiplets as obtained from SA-CASSCF/NEVPT2 calculations for: a) $[Co(biq)(dca)_4]^{2-}$, b) $[Co(biq)(\mu_{1,5}\text{-}dca)_4H_4]^{2+}$, c) $[Co(biq)(\mu_{1,5}\text{-}dca)_4H_2Ca]^{2+}$, d) $[Co(biq)(\mu_{1,5}\text{-}dca)_4Na_2Ca]^{2+}$. Energies obtained using GF Hamiltonian Eq. 3 with the set of the parameters obtained from the fit of the μ_{eff}(T) are included.

multiplet	a	b	c	d	GF model
1	0	0	0	0	0
2	137.5	155.8	166.7	139.4	193.8
3	906.9	765.2	716.1	887.2	717.8
4	1166.9	1093.4	1055.8	1140.0	1028.8
5	1460.2	1252.4	1214.1	1482.8	1497.1
6	1558.9	1401.0	1361.9	1574.4	1590.1

Table S3 Comparison of the exchange coupling J_{BS1} and J_{BS2} in **1** obtained from BS DFT calculations for different binuclear model fragments of the polymeric structure.

	B3LYP	TPSSh	PBE0
		J_{BS1} (cm^{-1})	
[Co(*biq*)(dca)$_2$-($\mu_{1,5}$-dca)$_2$-Co(*biq*)(dca)$_2$]$^{2-}$	-0.44	-0.59	-0.46
[Co(*biq*)($\mu_{1,5}$-dca)$_2$H$_2$-($\mu_{1,5}$-dca)$_2$-Co(*biq*)($\mu_{1,5}$-dca)$_2$H$_2$]$^{2+}$	-0.36	-1.03	-0.41
[Co(*biq*)($\mu_{1,5}$-dca)$_2$Na$_2$-($\mu_{1,5}$-dca)$_2$-Co(*biq*)($\mu_{1,5}$-dca)$_2$Na$_2$]$^{2+}$	-0.60	-1.12	-0.91
		J_{BS2} (cm^{-1})	
[(dca)-Co(*biq*)(dca)$_2$-($\mu_{1,5}$-dca)-Co(*biq*)(dca)$_2$-(dca)]$^{3-}$	-0.34	-0.49	-0.45
[H($\mu_{1,5}$-dca)-Co(*biq*)($\mu_{1,5}$-dca)$_2$H$_2$-($\mu_{1,5}$-dca)-Co(*biq*)($\mu_{1,5}$-dca)$_2$H$_2$-($\mu_{1,5}$-dca)H]$^{3+}$	-0.56	-0.84	-0.40
[Na($\mu_{1,5}$-dca)-Co(*biq*)($\mu_{1,5}$-dca)$_2$ Ca-($\mu_{1,5}$-dca)-Co(*biq*)($\mu_{1,5}$-dca)$_2$ Ca-($\mu_{1,5}$-dca)Na]$^{3+}$	-0.46	-0.71	-0.40

Table S4 Comparison of the exchange coupling J_{BS1} and J_{BS2} in **2** obtained from BS DFT calculations for different binuclear model fragments of the polymeric structure.

	B3LYP	TPSSh	PBE0
		J_{BS1} (cm^{-1})	
[Ni(*biq*)(dca)$_2$-($\mu_{1,5}$-dca)$_2$-Ni(*biq*)(dca)$_2$]$^{2-}$	-0.70	-1.00	0.06
[Ni(*biq*)($\mu_{1,5}$-dca)$_2$H$_2$-($\mu_{1,5}$-dca)$_2$-Ni(*biq*)($\mu_{1,5}$-dca)$_2$H$_2$]$^{2+}$	-0.48	-0.41	0.31
[Ni(*biq*)($\mu_{1,5}$-dca)$_2$Na$_2$-($\mu_{1,5}$-dca)$_2$-Ni(*biq*)($\mu_{1,5}$-dca)$_2$Na$_2$]$^{2+}$	0.15	-0.46	0.33
		J_{BS2} (cm^{-1})	
[(dca)-Ni(*biq*)(dca)$_2$-($\mu_{1,5}$-dca)-Ni(*biq*)(dca)$_2$-(dca)]$^{3-}$	0.36	0.53	1.05
[H($\mu_{1,5}$-dca)-Ni(*biq*)($\mu_{1,5}$-dca)$_2$H$_2$-($\mu_{1,5}$-dca)-Ni(*biq*)($\mu_{1,5}$-dca)$_2$H$_2$-($\mu_{1,5}$-dca)H]$^{3+}$	0.45	0.65	1.11
[Na($\mu_{1,5}$-dca)-Ni(*biq*)($\mu_{1,5}$-dca)$_2$Ca-($\mu_{1,5}$-dca)-Ni(*biq*)($\mu_{1,5}$-dca)$_2$Ca-($\mu_{1,5}$-dca)Na]$^{3+}$	0.38	0.57	1.22