

**SUPPLEMENTARY INFORMATION**

Rational design of 1D metal organic frameworks based on the novel pyrimidine-4,6-dicarboxylate ligand. New insights into the pyrimidine through magnetic interaction.

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S1. Experimental and simulated XRPD patterns of compounds **6** and **5**, respectively.

S2-S3. Selected bond lengths and angles within the *pmdc* ligand for **1–9**.

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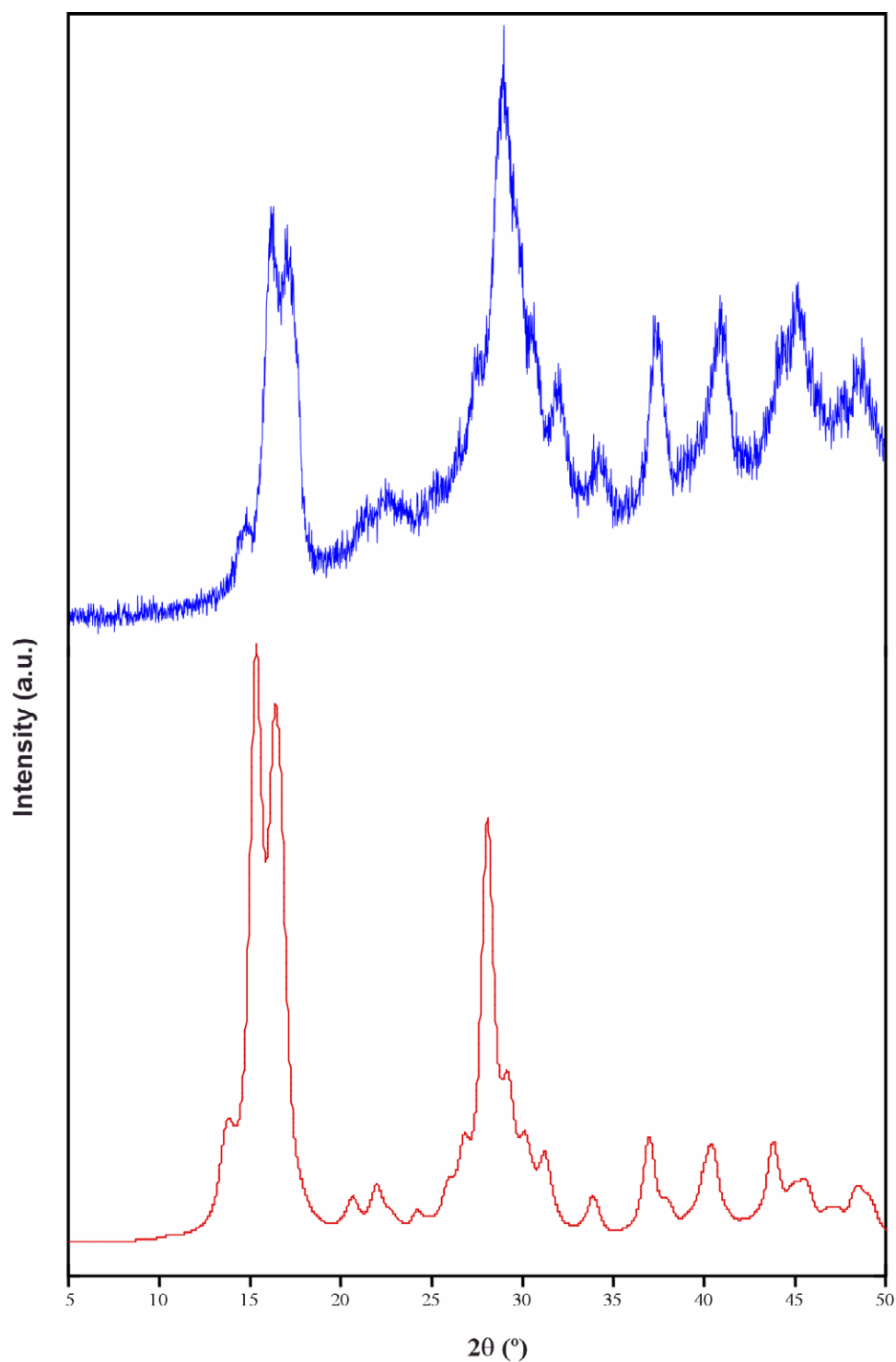
S11.  $\chi_M T$  vs. T plots for compounds **4–6** and **8–12**.

S12. Calculated coupling constants as function of M–N<sub>pym</sub> distance for [(VO)<sub>2</sub>(μ-pym)(H<sub>2</sub>O)<sub>6</sub>]<sup>4+</sup> and [Cr<sub>2</sub>(μ-pym)(H<sub>2</sub>O)<sub>10</sub>]<sup>6+</sup> dimer models.

S13. Calculated coupling constants as function of the metal displacement from the mean plane of the pyrimidine ring for [Cu<sub>2</sub>(μ-pym)(H<sub>2</sub>O)<sub>6</sub>]<sup>4+</sup> and [M<sub>2</sub>(μ-pym)(H<sub>2</sub>O)<sub>10</sub>]<sup>4+</sup> [M(II) = Mn, Fe, Co, Ni] dimer models.

S14. Calculated coupling constants as function of the metal displacement from the mean plane of the pyrimidine ring at different M–N<sub>pym</sub> distances for [Ni<sub>2</sub>(μ-pym)(H<sub>2</sub>O)<sub>10</sub>]<sup>4+</sup> and [Cr<sub>2</sub>(μ-pym)(H<sub>2</sub>O)<sub>10</sub>]<sup>6+</sup> dimer models.

S15. Calculated coupling constants for [Ni<sub>2</sub>(μ-pym)(NH<sub>3</sub>)<sub>10</sub>]<sup>4+</sup>, [Cu<sub>2</sub>(μ-5mpym)(H<sub>2</sub>O)<sub>6</sub>]<sup>4+</sup>, and [Cu<sub>2</sub>(μ-5pymcH)(H<sub>2</sub>O)<sub>6</sub>]<sup>4+</sup> dimer models (*5mpym*: 5-methylpyrimidine; *5pymcH*: 5-pyrimidinecarboxylic acid).



**Figure S1.** Experimental XRPD pattern of compound **6** (up) and the simulated one for compound **5** (down) with a FWHM of 0.5.

**Table S1.** Selected bond lengths (Å) and angles (deg) within the *pmdc* entity for 1–3.<sup>a</sup>

	<b>1</b>	<b>2</b>		<b>3</b>
N1-C2	1.330(2)	1.362(11)	N2-C1	1.333(2)
N1-C6	1.330(2)	1.369(10)	N2-C3	1.340(3)
C2-N3	1.332(2)	1.295(11)	C3-C4	1.381(2)
N3-C4	1.329(2)	1.307(11)	C3-C5	1.531(3)
C4-C5	1.379(2)	1.417(10)	O51-C5	1.247(2)
C4-C7	1.508(2)	1.556(9)	O52-C5	1.236(2)
C5-C6	1.381(2)	1.347(10)	C1-N2-C3	115.9(2)
C6-C8	1.505(2)	1.461(10)	N2-C3-C4	121.0(2)
C7-O71	1.293(2)	1.286(8)	N2-C3-C5	117.5(2)
C7-O72	1.201(2)	1.191(9)	C4-C3-C5	121.4(2)
C8-O81	1.297(2)	1.267(8)	C3-C4-C3a	118.6(2)
C8-O82	1.197(2)	1.257(9)	O52-C5-O51	127.8(2)
C6-N1-C2	116.3(1)	115.1(6)	O52-C5-C3	115.7(2)
N1-C2-N3	126.4(1)	127.6(4)	O51-C5-C3	116.5(2)
C4-N3-C2	116.0(1)	116.6(6)	N2-C1-N2a	127.5(3)
N3-C4-C5	122.5(1)	121.9(6)	$\delta_{C5}$	11.55(1)
N3-C4-C7	118.0(1)	117.9(6)		
C5-C4-C7	119.5(1)	120.1(6)		
C4-C5-C6	116.6(1)	117.9(4)		
N1-C6-C5	122.1(1)	120.7(7)		
N1-C6-C8	118.5(1)	116.5(6)		
C5-C6-C8	119.4(1)	122.7(6)		
O72-C7-O71	125.9(1)	129.2(6)		
O72-C7-C4	120.8(1)	120.3(6)		
O71-C7-C4	113.2(1)	110.5(6)		
O82-C8-O81	125.5(1)	123.3(6)		
O82-C8-C6	121.2(1)	120.4(6)		
O81-C8-C6	113.3(1)	116.4(6)		
$\delta_{C7}$	11.09(1)	6.57(1)		
$\delta_{C8}$	2.14(1)	5.82(1)		

<sup>a</sup> Symmetry code: (a)  $x, -y - 1/2, z$ . <sup>b</sup>  $\delta$ : dihedral angles between pyrimidine ring and carboxylate groups.

**Table S2.** Selected bond lengths (Å) and angles (deg) within the *pmdc* ligand for 4–9.<sup>a</sup>

	4	5	7	9		8
N1-C2	1.326(2)	1.322(3)	1.326(3)	1.325(3)	N1-C2	1.341(4)
N1-C6	1.339(2)	1.340(3)	1.338(4)	1.338(3)	N1-C4	1.325(3)
C2-N3	1.326(2)	1.321(3)	1.323(3)	1.338(3)	C2-C3	1.374(4)
N3-C4	1.337(2)	1.342(3)	1.339(4)	1.333(3)	C2-C5	1.526(4)
C4-C5	1.385(2)	1.379(4)	1.387(4)	1.372(3)	C3-C2a	1.374(4)
C4-C8	1.531(2)	1.525(4)	1.527(4)	1.529(3)	C4-N1a	1.325(3)
C5-C6	1.389(2)	1.388(4)	1.382(4)	1.380(3)	C5-O52	1.225(4)
C6-C7	1.525(2)	1.529(4)	1.532(4)	1.512(3)	C5-O51	1.263(4)
C7-O72	1.231(2)	1.228(3)	1.223(3)	1.222(3)	C4-N1-C2	118.8(3)
C7-O71	1.2637(2)	1.265(3)	1.269(3)	1.278(3)	N1-C2-C3	121.1(3)
C8-O82	1.241(2)	1.236(3)	1.238(3)	1.230(3)	N1-C2-C5	114.7(3)
C8-O81	1.258(4)	1.259(3)	1.268(3)	1.254(3)	C3-C2-C5	124.2(3)
C2-N1-C6	118.1(1)	118.1(2)	118.2(2)	117.1(2)	C2-C3-C2a	117.1(4)
N3-C2-N1	124.5(1)	124.5(3)	124.4(3)	125.9(2)	N1-C4-N1a	123.1(4)
C2-N3-C4	118.0(1)	118.0(2)	118.3(2)	116.3(2)	O52-C5-O51	127.1(3)
N3-C4-C5	121.6(1)	121.5(2)	120.8(2)	122.0(2)	O52-C5-C2	118.4(3)
N3-C4-C8	114.7(1)	114.1(2)	115.2(2)	115.7(2)	O51-C5-C2	114.4(3)
C5-C4-C8	123.8(1)	124.4(3)	123.9(3)	122.3(2)		
C4-C5-C6	116.7(1)	116.6(2)	117.2(3)	117.7(2)		
N1-C6-C5	121.2(1)	121.2(2)	121.0(3)	121.0(2)		
N1-C6-C7	115.4(1)	115.0(2)	115.7(2)	116.5(2)		
C5-C6-C7	123.5(1)	123.9(3)	123.3(3)	122.5(2)		
O72-C7-O71	126.0(1)	126.0(3)	126.3(3)	125.9(2)		
O72-C7-C6	118.2(1)	118.6(3)	117.9(3)	118.0(2)		
O71-C7-C6	115.8(1)	115.4(2)	115.8(3)	116.1(2)		
O82-C8-O81	126.5(1)	126.2(3)	126.2(3)	126.4(2)		
O82-C8-C4	117.32(12)	118.0(3)	117.6(3)	116.8(2)		
O81-C8-C4	116.13(12)	115.8(2)	116.2(2)	116.8(2)		

<sup>a</sup> Symmetry: (a) – x + 2, y, – z + 1/2.

**Table S3.** Hydrogen-bonding contacts ( $\text{\AA}$ ,  $^\circ$ ) in compounds **1** and **2**.<sup>a</sup>

<i>D-H...A</i> <sup>b</sup>	<i>D-H</i>	<i>H...A</i>	<i>D...A</i>	<i>D-H...A</i>
<b>Compound 1</b>				
O81-H81...O1wa	0.87	1.64	2.509(2)	171.7
O71-H71...O2wb	0.86	1.68	2.505(2)	159.6
O1w-H11...N1c	0.87	2.10	2.960(2)	171.7
O1w-H12...O82d	0.86	1.90	2.763(2)	176.5
O2w-H21...N3e	0.99	1.90	2.886(2)	171.9
O2w-H22...O72f	0.83	1.99	2.802(2)	163.8
<b>Compound 2</b>				
O71-H71...O81	0.73	1.71	2.426(8)	171(4)

<sup>a</sup> Symmetry: (a)  $x + 1, y + 1, z$ . (b)  $-x, -y + 1, -z$ . (c)  $-x + 1, -y + 1, -z + 1$ . (d)  $-x + 1, -y + 2, -z + 1$ . (e)  $x + 1, y, z$ . (f)  $x + 1, y - 1, z$ .

<sup>b</sup> D = donor; A = acceptor.

**Table S4.** Hydrogen-bonding contacts (Å, °) in compounds **4**, **5**, **7**, and **8**.<sup>a</sup>

<i>D-H...A</i> <sup>b</sup>	<i>D-H</i>	<i>H...A</i>	<i>D...A</i>	<i>D-H...A</i>
<b>Compound 4</b>				
O1w-H11...O3w	0.76	2.02	2.768(2)	169.2
O1w-H12...O82a	0.70	2.11	2.762(2)	156.5
O2w-H21...O72b	0.74	1.96	2.686(2)	166.0
O2w-H22...O82c	0.74	2.04	2.754(2)	161.8
O3w-H31...O81d	0.77	2.35	3.096(2)	165.8
O3w-H32...O71e	0.89	2.06	2.936(2)	167.2
<b>Compound 5</b>				
O1w-H11...O3w	0.82	2.01	2.800(3)	161.2
O1w-H12...O82a	0.84	1.93	2.763(3)	171.8
O2w-H21...O72b	0.84	1.86	2.695(3)	170.1
O2w-H22...O82c	0.86	2.00	2.823(3)	159.1
O3w-H31...O81d	0.84	2.19	3.026(3)	168.3
O3w-H32...O71e	0.85	2.17	2.936(3)	149.8
<b>Compound 7</b>				
O1w-H11...O3w	0.82	2.00	2.782(3)	160.3
O1w-H12...O82a	0.72	2.07	2.780(3)	172.4
O2w-H21...O72b	0.85	1.87	2.711(3)	170.5
O2w-H22...O82c	0.68	2.12	2.783(3)	163.5
O3w-H31...O81d	0.64	2.43	3.065(3)	170.4
O3w-H32...O71e	0.69	2.26	2.947(3)	171.3
<b>Compound 8</b>				
O1w-H11...O52f	0.82	2.00	2.782(3)	160.3
O1w-H12...O52g	0.72	2.07	2.780(3)	172.4

<sup>a</sup> Symmetry: (a)  $-x + 1, y + 1/2, -z + 3/2$ . (b)  $-x, -y - 1, -z + 1$ . (c)  $-x, y + 1/2, -z + 3/2$ .

(d)  $-x + 1, -y - 1, -z + 2$ . (e)  $-x + 1, -y - 1, -z + 1$  (f)  $x - 1/2, y + 1/2, z$ . (g)  $-x + 3/2, -y - 1/2, -z + 1$ .

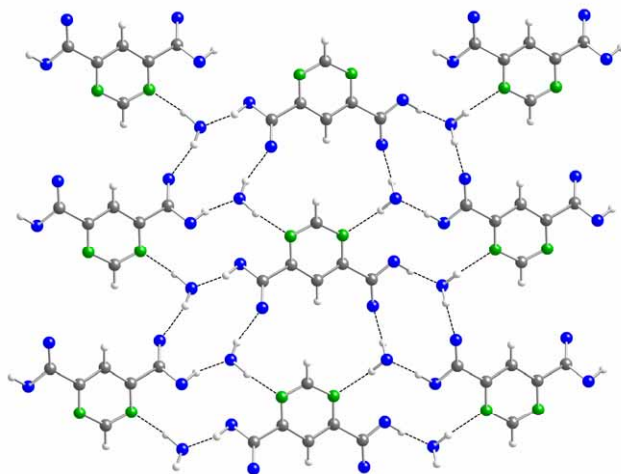
<sup>b</sup> D = donor; A = acceptor.

**Table S5.** Hydrogen-bonding contacts (Å, °) in compound **9**.<sup>a</sup>

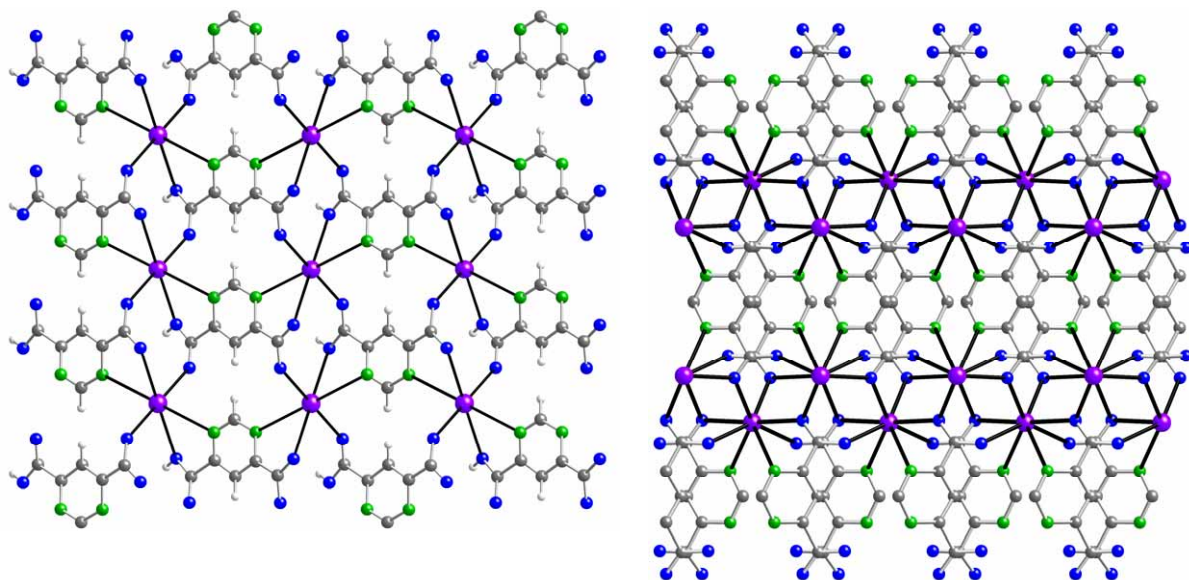
<i>D-H...A</i> <sup>b</sup>	<i>D-H</i>	<i>H...A</i>	<i>D...A</i>	<i>D-H...A</i>
N17-H17...O4wa	0.86	2.01	2.852(2)	165.5
O1w-H12...O82a	0.86	1.94	2.763(3)	159.8
O2w-H21...O1w	0.93	1.96	2.878(3)	172.9
O2w-H22...O72b	0.86	1.97	2.803(3)	162.3
O3w-H31...O2wc	0.82	2.06	2.834(3)	156.6
O3w-H32...O71d	1.00	1.91	2.888(3)	165.2
O4w-H41...O3w	0.89	1.88	2.753(3)	168.5
O4w-H42...O81e	0.85	2.08	2.919(2)	171.0

<sup>a</sup> Symmetry: (a)  $x + 1, y, z$ . (b)  $-x - 1, -y, -z$ . (c)  $-x - 1, y - 1/2, -z + 1/2$ . (d)  $x, -y - 1/2, z + 1/2$ . (e)  $x, -y - 1/2, z - 1/2$ .

<sup>b</sup> D = donor; A = acceptor.

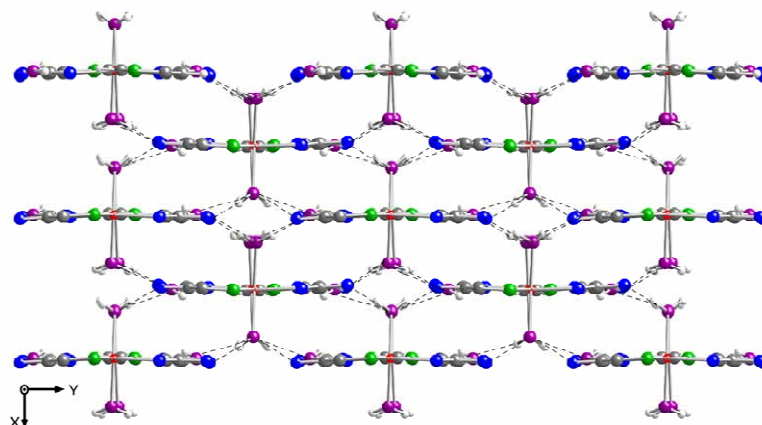


**Figure S2.** A view of the crystal packing of compound **1** along [10-1] crystallographic direction, showing the hydrogen-bonding network.

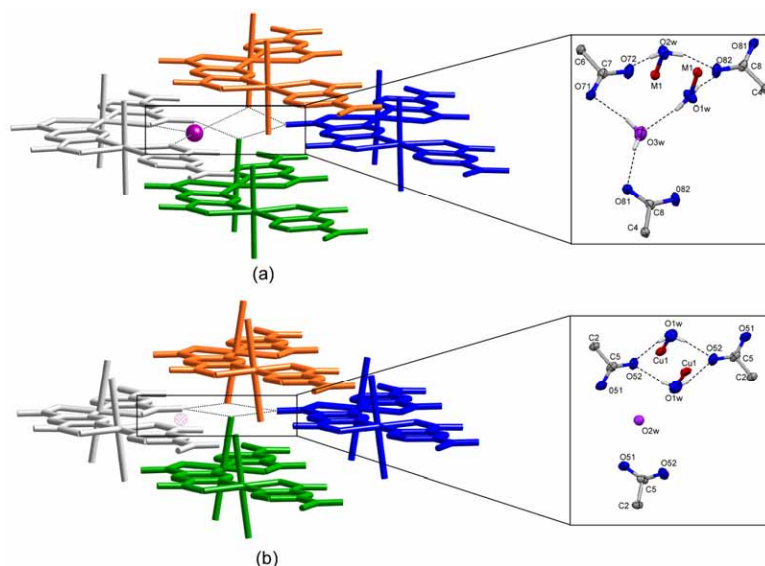


**Figure S3.** Crystal structure of compound **2** and **3** viewed along the [100] crystallographic direction.



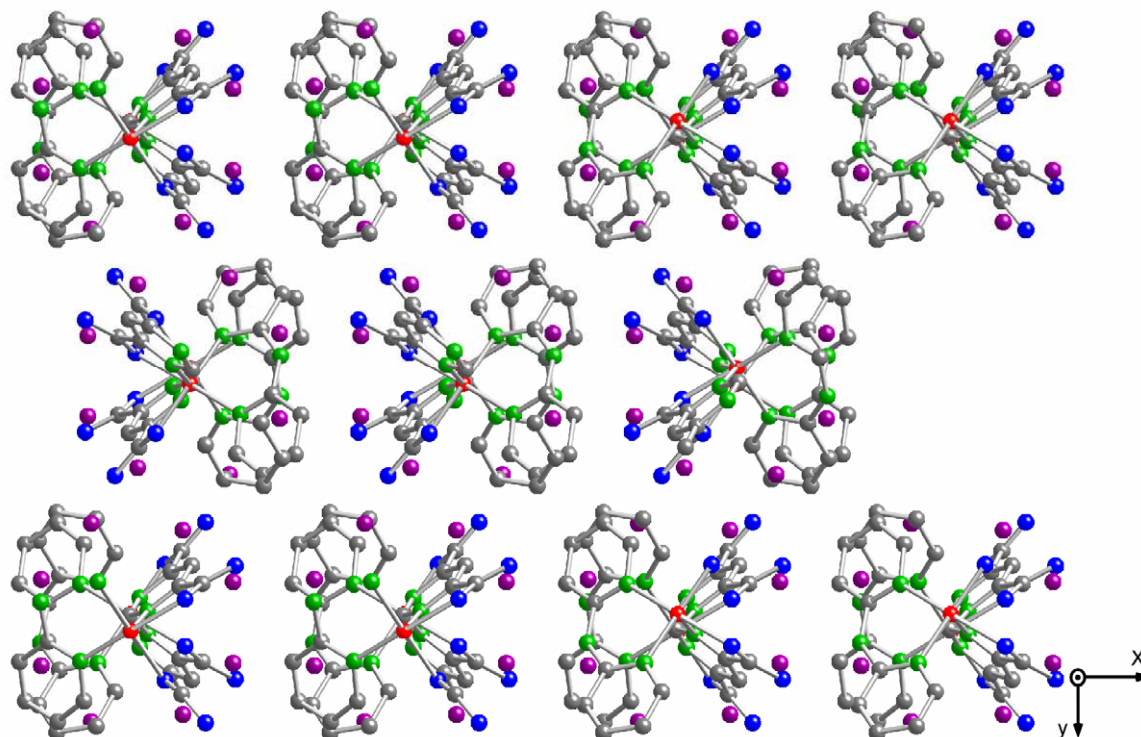


**Figure S4.** Crystal structure of compounds **4–8** viewed along the  $[001]$  direction showing the hydrogen bonding interactions (dashed lines).

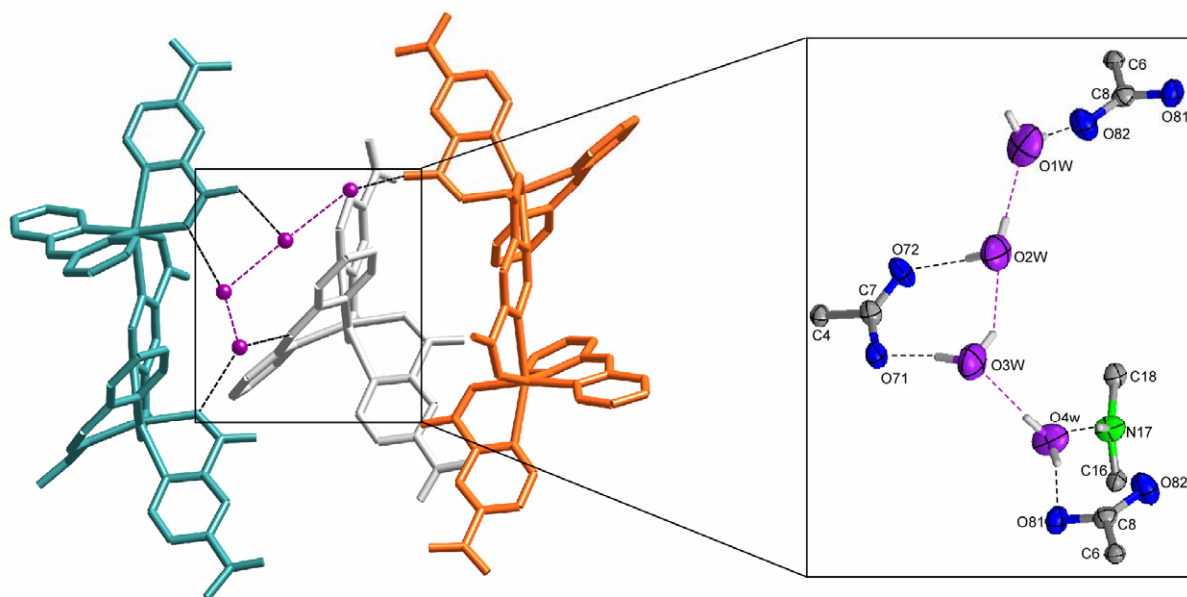


**Figure S5.** Hydrogen bonding interaction scheme among four polymeric chains and one crystallization water molecule in compounds (a) **4–7** and (b) in compound **8**. Dotted lines represent hydrogen-bonding interactions.

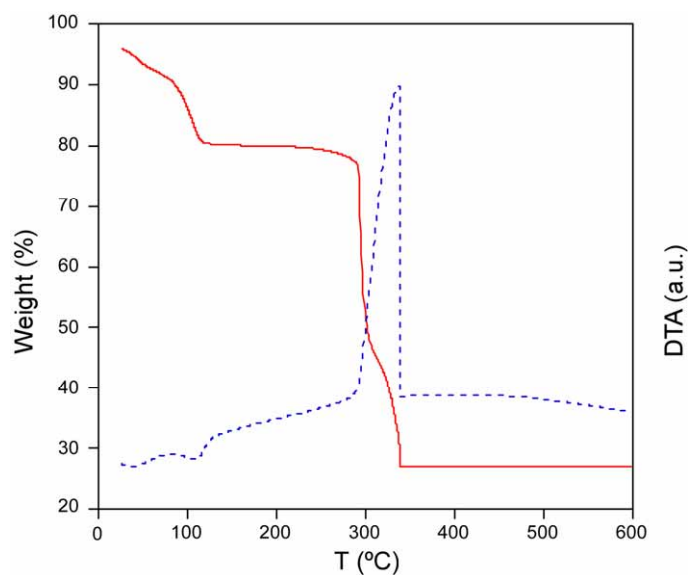
The polymeric chains of compounds **4**, **5** and **7** run along the  $[001]$  crystallographic direction (Figure S4) and each chain interacts with four surrounding ones by means of three direct hydrogen bonds (see Supporting Information) established between the coordinated water molecules and noncoordinated O atoms of the carboxylate groups. Each solvation water molecule (Figure S5a) is hydrogen bonded to the coordinated carboxylate-O atoms of two symmetry related *pmdc* ligands belonging to the same chain and binds another chain by means of the hydrogen interaction established with one of the coordinated water molecules. In the case of compound **8**, the coordinated water molecules is solely hydrogen-bonded to the noncoordinated O atoms of the carboxylate group (Figure S5b) due to the partial release of crystallization water molecule, but although this compound crystallizes in a different space group there is not other remarkable difference in the crystal packing.



**Figure S6.** View of the crystal packing of compound **9** along the [001] crystallographic direction. Hydrogen atoms have been omitted for clarity.



**Figure S7.** Perspective view of three polymeric chains hosting the water cluster. The enhanced area shows the immediate environment of the water cluster. Dotted lines represent hydrogen-bonding interactions.



**Figure S8.** Thermogravimetric curves (TG/DTA) of compound **8**.

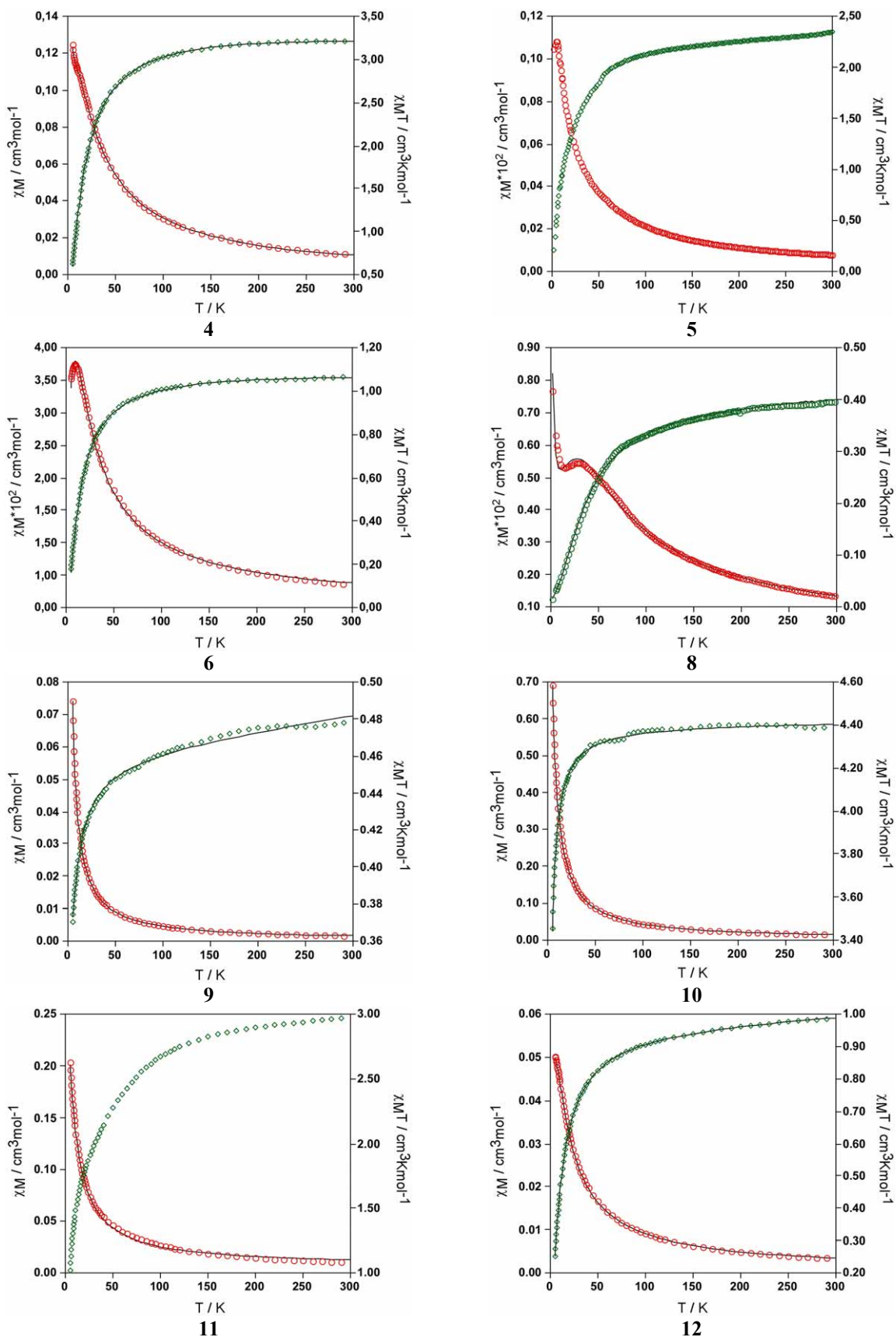


Figure S9.  $\chi_M T$  vs  $T$  plots for compounds 4–6 and 8–12; (–) best theoretical fit.

1. Calculated coupling constants as function of V–N<sub>pym</sub> distance for [(VO)<sub>2</sub>(μ-pym)(H<sub>2</sub>O)<sub>6</sub>]<sup>4+</sup> dimer model. Calculations have been performed in an idealised C<sub>2v</sub> symmetry using the following structural parameters:

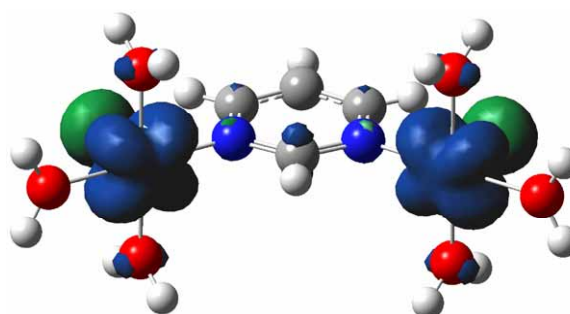
- Bond lengths (Å): V–N<sub>pym</sub> 1.90–2.40, V=O 1.58, V–O<sub>w</sub> 2.00, C1–N2 1.36, N2–C3 1.35, C3–C4 1.41, C–H 1.00, O<sub>w</sub>–H 1.00.
- Coordination geometry around the metal atom: square pyramid.
- O=V–N–C torsion angle: 0.0°.

Structural parameters concerning the pyrimidine bridge and water have been kept unchanged in all analyzed models.

$$\langle S^2 \rangle_{\text{HS}} = 2.0583 - 2.0675; \langle S^2 \rangle_{\text{BS}} = 1.0537 - 1.0674.$$

**Table S6.** Calculated  $J$  values (cm<sup>-1</sup>) as function of V–N<sub>pym</sub> distance (Å).

V–N <sub>pym</sub>	$J_{\text{calc}}$
1.90	+39.1
2.00	+12.7
2.10	+2.1
2.20	-2.1
2.30	-4.1
2.40	-6.3



**Figure S10.** Calculated spin-density distribution of the triplet ( $S = 1$ ) state at V–N<sub>pym</sub> 2.00 Å.

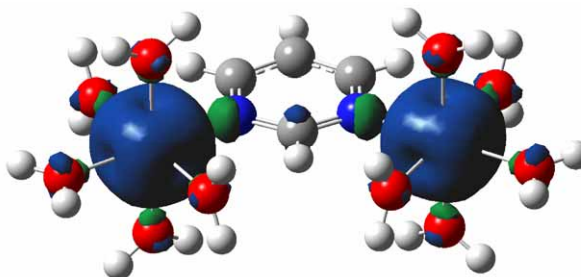
2. Calculated coupling constants as function of Cr–N<sub>pym</sub> distance for [Cr<sub>2</sub>(μ-pym)(H<sub>2</sub>O)<sub>10</sub>]<sup>6+</sup> dimer model. Calculations have been performed in an idealised C<sub>2v</sub> symmetry using the following structural parameters:

- Bond lengths (Å): Cr–N<sub>pym</sub> 1.90–2.40, Cr–O<sub>w</sub> 2.00.
- Coordination geometry around the metal atom: octahedral.
- O<sub>w</sub>–Cr–N–C torsion angles: 90.0 and 0.0°.

$$\langle S^2 \rangle_{\text{HS}} = 12.0318 - 12.0413; \langle S^2 \rangle_{\text{BS}} = 3.0283 - 3.0413.$$

**Table S7.** Calculated  $n^2 \cdot J$  values as function of Cr–N<sub>pym</sub> distance.

Cr–N <sub>pym</sub> (Å)	$n^2 \cdot J_{\text{calc}}$ (cm <sup>-1</sup> )
1.90	+37.0
2.00	+16.8
2.10	+6.9
2.20	+1.7
2.30	-1.2
2.40	-2.9



**Figure S11.** Calculated spin-density distribution of the heptuplet ( $S = 3$ ) state at Cr–N<sub>pym</sub> 2.00 Å.

3. Calculated coupling constants as function of the metal displacement from the mean plane of the pyrimidine ring for  $[\text{Cu}_2(\mu\text{-pym})(\text{H}_2\text{O})_6]^{4+}$  and  $[\text{M}_2(\mu\text{-pym})(\text{H}_2\text{O})_{10}]^{4+}$  [ $\text{M}(\text{II}) = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$ ] dimer models. Calculations have been performed in an idealised  $C_2$  symmetry using the following structural parameters:

- Bond lengths (Å): Cu–N<sub>pym</sub> 2.00, Cu–O<sub>w</sub> 2.00; Ni–N<sub>pym</sub> 2.00, Ni–O<sub>w</sub> 2.00; Co–N<sub>pym</sub> 2.20, Co–O<sub>w</sub> 2.20; Fe–N<sub>pym</sub> 2.20, Fe–O<sub>w</sub> 2.20; Mn–N<sub>pym</sub> 2.20, Mn–O<sub>w</sub> 2.20.
- Coordination geometry around the metal atom: square planar for Cu and octahedral for Mn, Fe, Co, and Ni.
- Ow–M–N–C torsion angles: 90.0 and 0.0°.

Cu(II) models:  $\langle S^2 \rangle_{\text{HS}} = 2.0038 - 2.0040$ ;  $\langle S^2 \rangle_{\text{BS}} = 1.0011 - 1.0021$ .

Ni(II) models:  $\langle S^2 \rangle_{\text{HS}} = 6.0050 - 6.0051$ ;  $\langle S^2 \rangle_{\text{BS}} = 2.0038 - 2.0039$ .

Mn(II) models:  $\langle S^2 \rangle_{\text{HS}} = 30.0040 - 30.0043$ ;  $\langle S^2 \rangle_{\text{BS}} = 5.0035 - 5.0038$ .

Fe(II) models:  $\langle S^2 \rangle_{\text{HS}} = 20.0176 - 20.0179$ ;  $\langle S^2 \rangle_{\text{BS}} = 4.0159 - 4.0161$ .

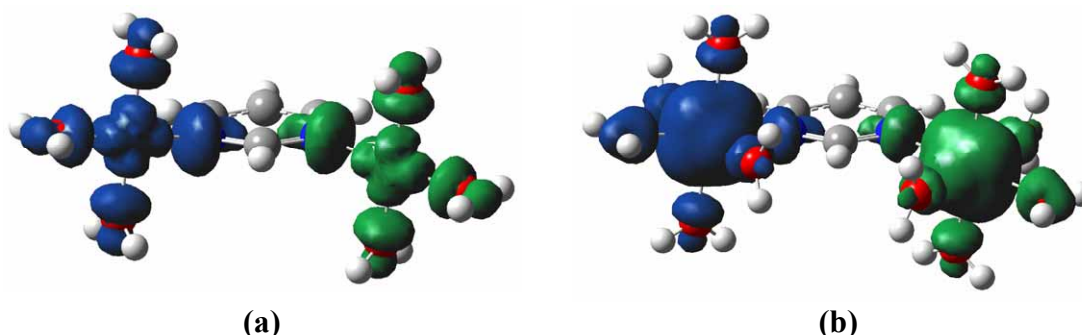
Co(II) models:  $\langle S^2 \rangle_{\text{HS}} = 12.0037 - 12.0038$ ;  $\langle S^2 \rangle_{\text{BS}} = 3.0033 - 3.0034$ .

**Table S8.** Calculated  $J$  and  $n^2 \cdot J$  values ( $\text{cm}^{-1}$ ) as function of metal for Cu and Ni dimer models.

$d_{\text{M}}$ (Å)	Cu		Ni	
	$J_{\text{calc}}$	$n^2 \cdot J_{\text{calc}}$	$J_{\text{calc}}$	$n^2 \cdot J_{\text{calc}}$
0	-31.5	-31.5	-17.3	-69.2
0.174	-29.4	-29.4	-7.8	-31.2
0.347	-26.5	-26.5	+1.2	+4.8
0.517	-23.7	-23.7		
0.684	-20.7	-20.7		

**Table S9.** Calculated  $J$  and  $n^2 \cdot J$  values ( $\text{cm}^{-1}$ ) as function of metal displacement for Mn, Fe and Co dimer models.

$d_{\text{M}}$ (Å)	Mn		Fe		Co	
	$J_{\text{calc}}$	$n^2 \cdot J_{\text{calc}}$	$J_{\text{calc}}$	$n^2 \cdot J_{\text{calc}}$	$J_{\text{calc}}$	$n^2 \cdot J_{\text{calc}}$
0	-3.0	-75.0	-4.6	-73.6	-9.8	-88.2
0.191	-1.6	-40.0	-1.2	-19.2	-4.3	-38.7
0.382	+0.4	+10.0	1.7	+27.2	+1.3	+11.7



**Figure S12.** Calculated spin-density distribution of the singlet state ( $S = 0$ ) state of (a)  $[\text{Cu}_2(\mu\text{-pym})(\text{H}_2\text{O})_6]^{4+}$  and (b)  $[\text{Co}_2(\mu\text{-pym})(\text{H}_2\text{O})_{10}]^{4+}$  with a surface threshold level of 0.0015. The corresponding metal displacements from the mean plane of the pyrimidine ring are 0.347 and 0.382 Å for Cu(II) and Co(II) models, respectively.

4. Calculated coupling constants as function of the metal displacement from the mean plane of the pyrimidine ring at different M–N<sub>pym</sub> distances for [Ni<sub>2</sub>(μ-pym)(H<sub>2</sub>O)<sub>10</sub>]<sup>4+</sup> and [Cr<sub>2</sub>(μ-pym)(H<sub>2</sub>O)<sub>10</sub>]<sup>6+</sup> dimer models.

Ni(II) model:  $\langle S^2 \rangle_{\text{HS}} = 6.0029 - 6.0051$ ;  $\langle S^2 \rangle_{\text{BS}} = 2.0026 - 2.0045$ .

Cr(III) model:  $\langle S^2 \rangle_{\text{HS}} = 12.0317 - 12.0383$ ;  $\langle S^2 \rangle_{\text{BS}} = 3.0284 - 3.0382$ .

**Table S10.** Calculated  $J$  values (cm<sup>-1</sup>) as function of metal displacement ( $d_{\text{M}}$ ) for Ni dimer model at different Ni–N<sub>pym</sub> distances.

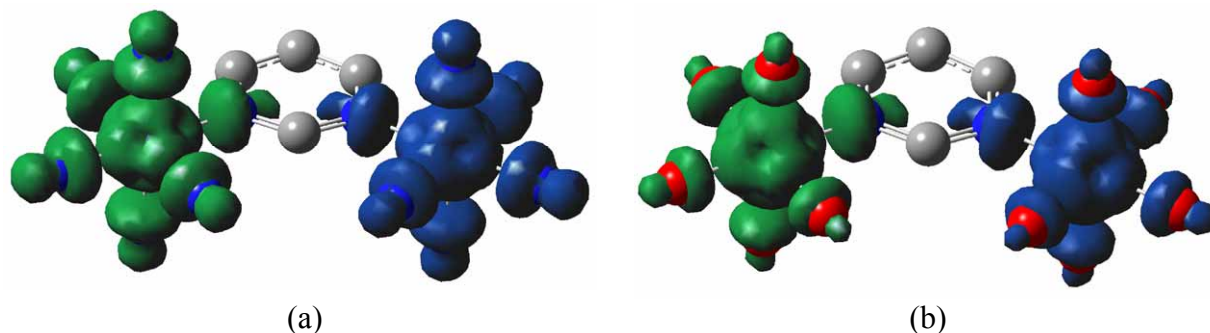
2.00 Å		2.20 Å		2.40 Å	
$d_{\text{M}}$ (Å)	$J_{\text{calc}}$ (cm <sup>-1</sup> )	$d_{\text{M}}$ (Å)	$J_{\text{calc}}$ (cm <sup>-1</sup> )	$d_{\text{M}}$ (Å)	$J_{\text{calc}}$ (cm <sup>-1</sup> )
0	-17.27	0	-14.09	0	-11.30
0.174	-7.82	0.191	-6.92	0.209	-6.44
0.347	+1.20	0.382	+1.32	0.416	+2.17

**Table S11.** Calculated  $J$  values (cm<sup>-1</sup>) as function of metal displacement ( $d_{\text{M}}$ ) for Cr dimer model at different Cr–N<sub>pym</sub> distances.

1.90 Å		2.10 Å		2.30 Å	
$d_{\text{M}}$ (Å)	$J_{\text{calc}}$ (cm <sup>-1</sup> )	$d_{\text{M}}$ (Å)	$J_{\text{calc}}$ (cm <sup>-1</sup> )	$d_{\text{M}}$ (Å)	$J_{\text{calc}}$ (cm <sup>-1</sup> )
0	+4.11	0	+0.76	0	-0.13
0.166	+4.07	0.183	+0.76	0.200	-0.12
0.329	+3.91	0.365	+0.77	0.399	-0.08

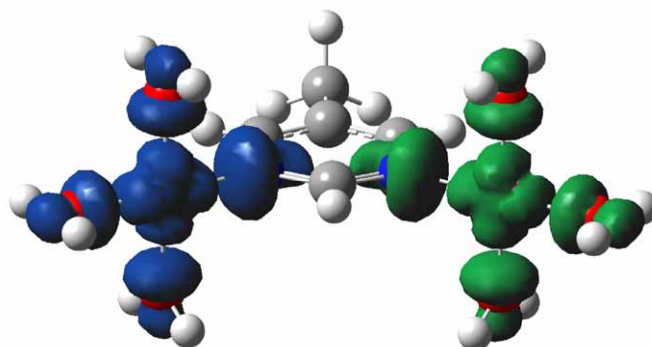
5. Calculated coupling constants for  $[\text{Ni}_2(\mu\text{-pym})(\text{NH}_3)_{10}]^{4+}$ ,  $[\text{Ni}_2(\mu\text{-pym})(\text{H}_2\text{O})_{10}]^{4+}$ ,  $[\text{Cu}_2(\mu\text{-5mpym})(\text{H}_2\text{O})_6]^{4+}$ , and  $[\text{Cu}_2(\mu\text{-5pymcH})(\text{H}_2\text{O})_6]^{4+}$  dimer models (*5mpym*: 5-methylpyrimidine; *5pymcH*: 5-pyrimidinecarboxylic acid) in the idealised  $C_2$ ,  $C_s$ , and  $C_1$  symmetries, respectively.

- $[\text{Ni}_2(\mu\text{-pym})(\text{NH}_3)_{10}]^{4+}$   $J = -10.2 \text{ cm}^{-1}$
- $[\text{Ni}_2(\mu\text{-pym})(\text{H}_2\text{O})_{10}]^{4+}$   $J = -17.3 \text{ cm}^{-1}$



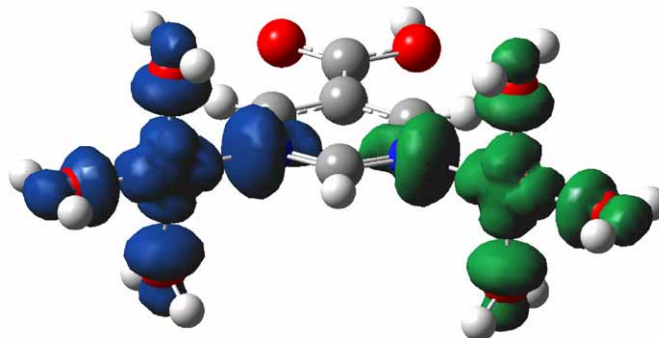
**Figure S13.** Calculated spin-density distribution of the ground state ( $S = 0$ ) of (a)  $[\text{Ni}_2(\mu\text{-pym})(\text{NH}_3)_{10}]^{4+}$  and (b)  $[\text{Ni}_2(\mu\text{-pym})(\text{H}_2\text{O})_{10}]^{4+}$  with a surface threshold level of 0.0015. Hydrogen atoms were omitted for clarity.

- $[\text{Cu}_2(\mu\text{-5mpym})(\text{H}_2\text{O})_6]^{4+}$   $J = -33.5 \text{ cm}^{-1}$



**Figure S14.** Calculated spin-density distribution of the ground state ( $S = 0$ ) of  $[\text{Cu}_2(\mu\text{-5mpym})(\text{H}_2\text{O})_6]^{4+}$  with a surface threshold level of 0.0015.

- $[\text{Cu}_2(\mu\text{-5pymcH})(\text{H}_2\text{O})_6]^{4+}$   $J = -28.5 \text{ cm}^{-1}$



**Figure S15.** Calculated spin-density distribution of the ground state ( $S = 0$ ) of  $[\text{Cu}_2(\mu\text{-5pymcH})(\text{H}_2\text{O})_6]^{4+}$  with a surface threshold level of 0.0015.