Electronic Supplementary Information for

Influence of the Auxiliary Ligands on Crystal Structure and Magnetic Behavior of New $[Mn^{II}_2Mn^{III}_2]$ Clusters Supported by *p*-Adamantylcalix[4]arene

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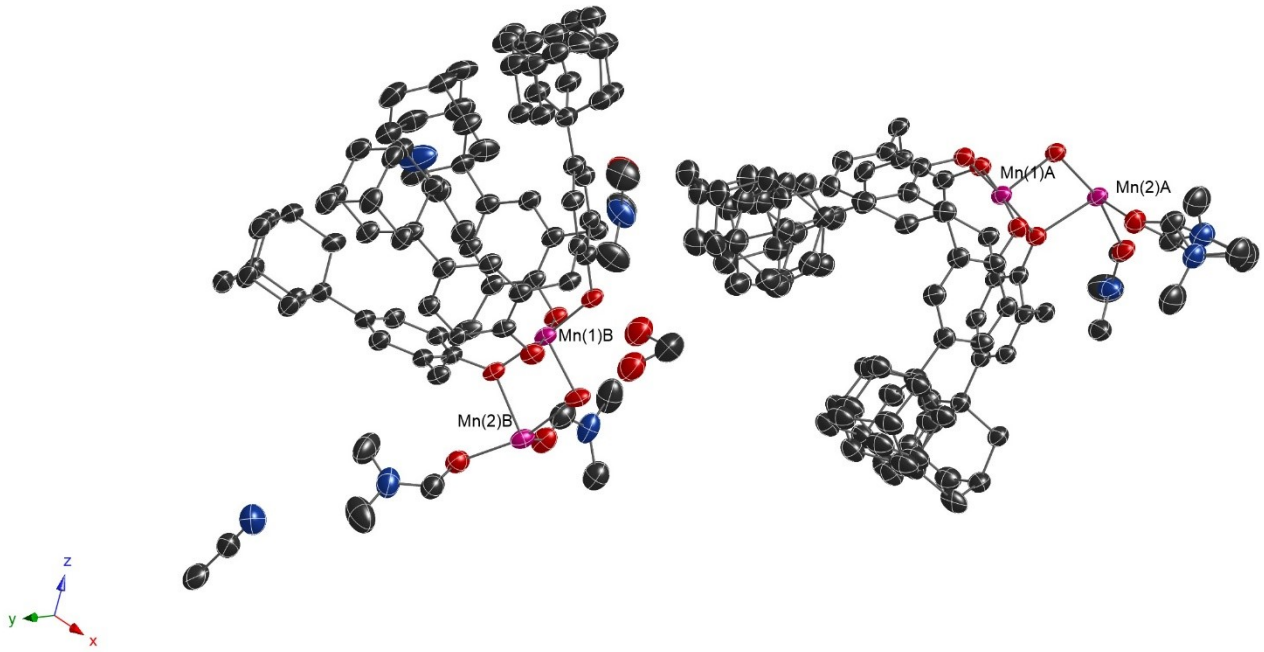

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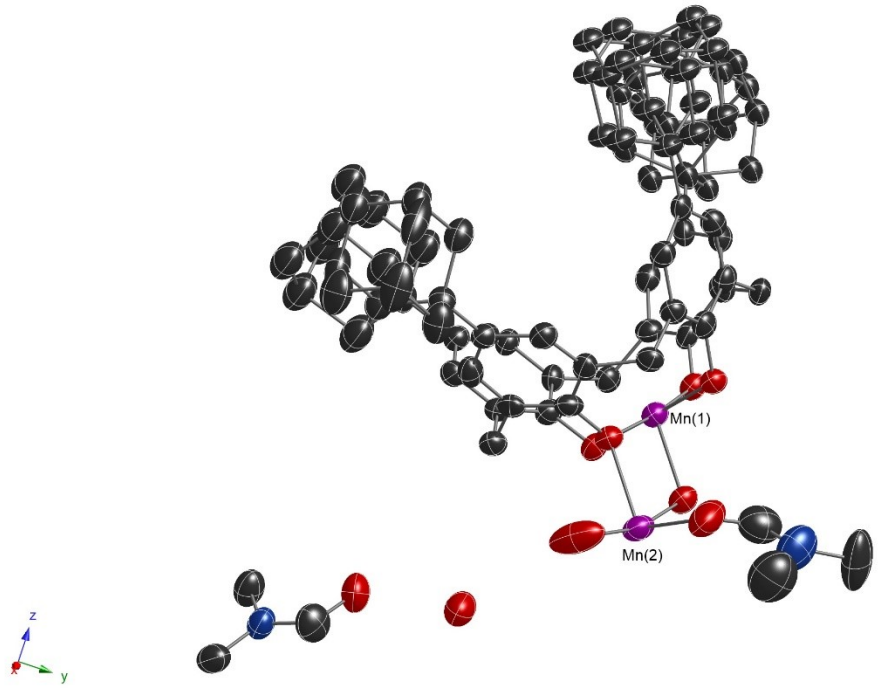

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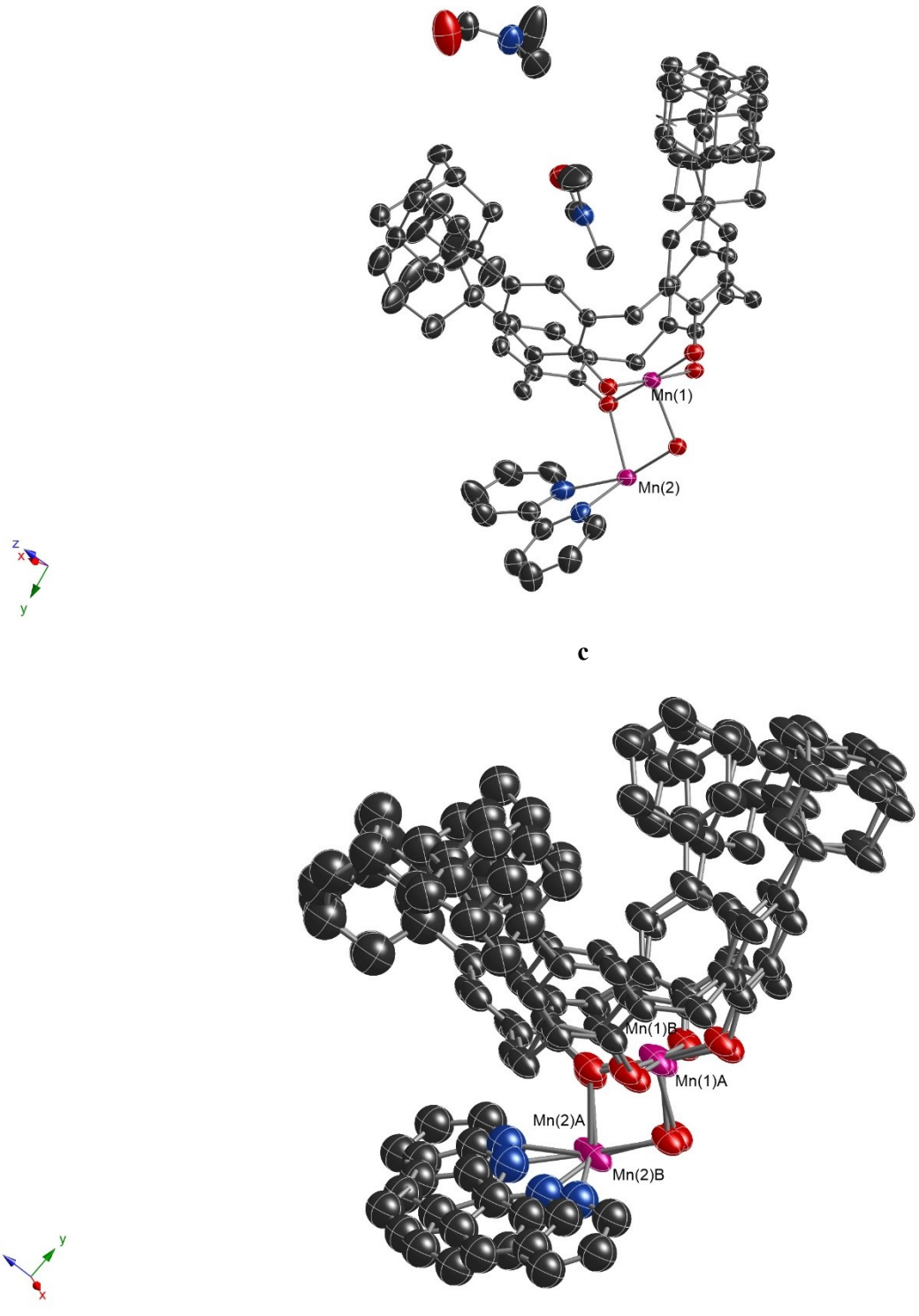


Figure S1. The thermal ellipsoids representation with 50% probability of asymmetric unit for (a) **3_2-$Mn_4(dmf)_4$**, (b) **3_2-$Mn_4(dmf)_2(H_2O)_2$**, (c) **3_2-$Mn_4(bipy)_2$**, (d) **3_2-$Mn_4(phen)_2$**, H-atoms are omitted for clarity.

Details of refinement procedure for crystal structures of studied Mn-complexes

For **3_2-$Mn_4(dmf)_4$**, C(30), C(31), C(32), C(33), C(34), C(35), C(36), C(37), C(38) atoms are found to be disordered over two positions with occupancies 0.80:0.20; C(40), C(41), C(42), C(43), C(44), C(45), C(46), C(47), C(48) atoms – with occupancies 0.76:0.24; C(60), C(61), C(62), C(63), C(64), C(65), C(66), C(67), C(68) – with occupancies 0.85:0.15 (all belonging to adamantyl groups); C(76), N(77), C(78), C(79) atoms – with occupancies 0.73:0.27 (all belonging to coordinated DMF molecule); O(91) atom – with occupancies 0.81:0.19 (belonging to MeOH molecule).

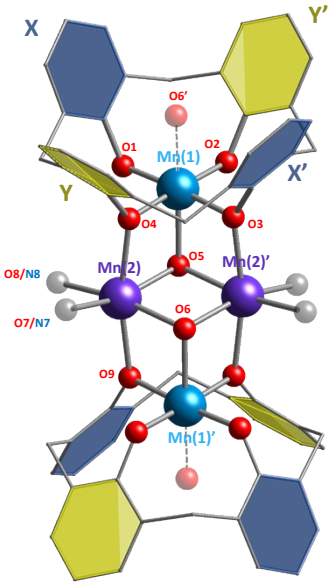
For **3_2-$Mn_4(dmf)_2(H_2O)_2$**, C(30), C(31), C(32), C(33), C(34), C(35), C(36), C(37), C(38), C(60), C(61), C(62), C(63), C(64), C(65), C(66), C(67), C(68) are found to be disordered over two positions with occupancies 0.50:0.50 (all belonging to adamantyl groups). For **3_2-$Mn_4(bipy)_2$**, the disordering model with 0.68:0:38 occupancies for C-atoms belonging to one adamantyl group (C(50):C(51), C(52):C(53), C(54):C(55), C(56):C(57), C(58):C(59), C(60):C(67), C(61):C(62), C(63):C(64), C(65):C(66)) per asymmetric unit was applied in order to refine the structure. For **3_2-$Mn_4(phen)_2$**, the disordering model with 0.57:0:43 occupancies for all C-, H-, N-, O- and Mn-atoms per asymmetric unit was applied in order to refine the structure.

Checkcifs reports responses

For **3_2-$Mn_4(dmf)_2(H_2O)_2$** (CCDC 2299404), the Alerts of B level appeared upon checkcif procedure:
230_ALERT_2_B Hirshfeld Test Diff for C49 -C51 . 8.8 s.u.
Response: *This Alert A is caused by a poor quality of the crystal. Unfortunately, all attempts to obtain the crystal of better quality were failed.*
420_ALERT_2_B D—H Bond Without Acceptor O6 --H6A . Please Check
420_ALERT_2_B D—H Bond Without Acceptor O6 --H6B . Please Check
Response: *Crystal structure of the compound contains squeezed electron density, corresponding to disordered solvent molecules, which could be an acceptor for this bond.*

For **3_2-$Mn_4(bipy)_2$** (CCDC 2299407), the Alerts of B level appeared upon checkcif procedure:
029_ALERT_3_B _diffrn_measured_fraction_theta_full value Low . 0.959 Why?
Response: *For the performed synchrotron experiment, only φ -scanning was carried out, which didn't not allow to collect more data for crystals in the lowest syngonies and with low reflectivity.*
420_ALERT_2_B D—H Bond Without Acceptor O5 --H5 . Please Check
Response: *Crystal structure of the compound contains squeezed solvent molecules which could be an acceptor for this bond.*

For **3_2-$Mn_4(phen)_2$** (CCDC 2299405), the Alerts of A and B level appeared upon checkcif procedure:
SHFSU01_ALERT_2_A The absolute value of parameter shift to su ratio > 0.20
Absolute value of the parameter shift to su ratio given 1.744
Additional refinement cycles may be required.
080_ALERT_2_A Maximum Shift/Error ..... 1.45 Why ?
Response: *These Alerts A are caused by a poor diffraction ability of the crystal and related with a high disordering of calix[4]arene moieties as well as the metallic cluster units. Additionally, the crystal contains large pores (the solvent accessible volume is 23.8%, calculated by PLATON[1]), filled by highly disordered solvent molecules, which also significantly contributed in diminishing its reflection ability.*
084_ALERT_3_B High wR2 Value (i.e. > 0.25) ..... 0.42 Report
Response: *The crystal was of poor quality. The molecule contains a large number of disordered fragments, which further reduces the reflection ability of the crystal.*
420_ALERT_2_B D—H Bond Without Acceptor O5A --H5A . Please Check
Response: *The crystal structure contains squeezed electron density that correspond to disordered solvate molecules with potential hydrogen bond acceptors for a mentioned hydrogen atom.*



Scheme S1. An overall scheme of obtained {Mn_4}-clusters with adopted atoms numeration, denoted in the tables below (dihedral angle ∠XX' < dihedral angle ∠YY'. Mn(1), Mn(2) and O-atoms are represented as light blue and violet spheres, respectively. Grey spheres represent the coordinated O- /N- atoms of solvate molecules or N,N'-chelating auxiliary ligands)

Table S1. Coordination bond distances of Mn(1)-atoms for complexes **3_2-$Mn_4(dmf)_4$**, **3_2-$Mn_4(dmf)_2(H_2O)_2$**, **3_2-$Mn_4(bipy)_2$** and **3_2-$Mn_4(phen)_2$**, and comparison with those earlier reported for compounds **1_2-$Mn_4(dmf)_6$**[2], **1_2-$Mn_4(dmf)_4(H_2O)_2$**[2], **2_2-$Mn_4(bipy)_2(MeOH)_2$**[3]. The independent cluster molecules and disordered molecules, presenting in the unit cell, are denoted as MolA, MolB and MolA*, MolB*, respectively. The independed cluster molecules and disordered molecules, presenting in the unit cell, are denoted as MolA, MolB and MolA*, MolB*, respectively.

	OX	**3_2-$Mn_4(dmf)_4$**		**1_2-$Mn_4(dmf)_6$**	**3_2-$Mn_4(dmf)_2(H_2O)_2$**	**1_2-$Mn_4(dmf)_4(H_2O)_2$**	**3_2-$Mn_4(bipy)_2$**	**2_2-$Mn_4(bipy)_2$**			**3_2-$Mn_4(phen)_2$**	
		Mol(A)	Mol(B)					Mol(A)	Mol(B)		Mol(A)*	Mol(B)*
$d_{Mn(1)-OX}$, Å	**O1**	1.891(3)	1.899(3)	1.925(1)	1.914(5)	1.944(8)	1.899(2)	1.917(7)	1.921(7)	1.919(6)	1.91(1)	1.89(2)
	O2	1.892(2)	1.911(2)	1.924(1)	1.884(6)	1.933(8)	1.900(2)	1.922(6)	1.875(6)	1.902(7)	1.89(1)	1.89(2)
	O3	1.963(3)	1.961(3)	1.967(1)	1.950(6)	1.999(8)	1.952(2)	1.968(6)	1.962(7)	1.982(6)	1.94(2)	1.95(3)
	O4	1.958(2)	1.952(2)	1.957(1)	1.961(6)	1.949(8)	1.953(2)	1.958(6))	1.970(6)	1.947(6)	1.97(2)	1.93(2)
	O5	2.073(3)!	2.075(3)	2.145(2)	2.063(6)	2.153(7)	2.092(2)	2.145(6)	2.173(6)	2.156(6)	2.10(1)	2.14(1)
	O6'	-	-	2.298(2)	-	2.311(9)	-	2.456(7)	2.388(7)	2.433(7)	-	-

Table S2. Coordination bond angles of Mn(1)-atoms for complexes **3_2-$Mn_4(dmf)_4$**, **3_2-$Mn_4(dmf)_2(H_2O)_2$**, **3_2-$Mn_4(bipy)_2$** and **3_2-$Mn_4(phen)_2$**, and comparison with those earlier reported for compounds **1_2-$Mn_4(dmf)_6$**[2], **1_2-$Mn_4(dmf)_4(H_2O)_2$**[2], **2_2-$Mn_4(bipy)_2(MeOH)_2$**[3]. The independent cluster molecules and disordered molecules, presenting in the unit cell, are denoted as MolA, MolB and MolA*, MolB*, respectively.

	OX/ OY	**3_2-$Mn_4(dmf)_4$**		**1_2-$Mn_4(dmf)_6$**	**3_2-$Mn_4(dmf)_2(H_2O)_2$**	**1_2-$Mn_4(dmf)_4(H_2O)_2$**	**3_2-$Mn_4(bipy)_2$**	**2_2-$Mn_4(bipy)_2$**			**3_2-$Mn_4(phen)_2$**	
		Mol(A)	Mol(B)					Mol(A)	Mol(B)		Mol(A)*	Mol(B)*
∠ OX – Mn(1) - OY, °	**O1/O2**	91.5(1)	90.1(1)	90.04(7)	90.8(2)	90.6(3)	91.37(9)	91.9(3)	91.9(3)	91.0(3)	89.2(5)	90.5(7)
	O1/O3	175.5(1)	175.5(1)	175.95(7)	178.6(2)	174.2(3)	176.83(9)	175.9(3)	177.3(3)	176.9(3)	177.7(7)	177(1)
	O1/O4	90.0(1)	90.8(1)	90.46(7)	91.2(2)	89.1(3)	90.62(9)	89.0(3)	89.5(3)	89.8(3)	89.9(6)	93.5(8)
	O1/O5	99.2(1)	101.6(1)	95.38(6)	97.8(2)	93.4(2)	98.93(9)	93.9(3)	97.6(2)	95.6(2)	93.0(5)	106.1(6)
	O2/O3	90.5(1)	90.3(1)	91.01(6)	89.3(2)	90.3(3)	90.22(9)	89.6(3)	89.8(3)	91.0(3)	92.9(7)	90.7(9)
	O2/O4	174.4(1)	177.2(1)	177.61(7)	174.3(2)	174.5(3)	176.03(9)	176.0(3)	178.2(3)	176.8(3)	174.5(6)	175.1(8)
	O2/O5	101.9(1)	99.6(1)	96.34(6)	102.1(2)	90.6(2)	99.91(9)	94.6(3)	99.0(2)	95.8(2)	101.7(5)	98.4(6)
	O3/O4	87.7(1)	88.7(1)	88.33(6)	88.6(2)	89.5(3)	87.63(8)	89.3(2)	88.7(3)	88.0(2)	87.8(7)	85(1)
	O3/O5	84.4(1)	82.8(1)	80.61(6)	83.5(2)	80.9(2)	83.49(8)	82.1(2)	80.1(2)	81.8(2)	87.5(7)	76.6(9)
	O4/O5	83.2(1)	82.8(1)	81.29(6)	83.0(2)	83.9(2)	83.16(8)	81.4(2)	79.7(2)	81.0(2)	83.8(5)	83.2(7)
	O1/O6'	-	-	92.87(6)	-	94.6(3)	-	92.2(3)	92.4(3)	90.1(2)	-	-
	O2/O6'	-	-	94.46(6)	-	97.1(3)	-	92.6(3)	92.1(3)	95.7(2)	-	-
	O3/O6'	-	-	90.95(6)	-	91.0(2)	-	91.6(2)	89.6(3)	92.1(2)	-	-
	O4/O6'	-	-	87.85(6)	-	88.5(3)	-	91.3(3)	88.9(3)	87.4(2)	-	-
	O5/O6'	-		166.39(6)	-	168.9(2)	-	170.3(2)	164.7(2)	167.0(2)	-	-

Table S3. Coordination bond distances of Mn(2)-atoms for complexes **3_2-$Mn_4(dmf)_4$**, **3_2-$Mn_4(dmf)_2(H_2O)_2$**, **3_2-$Mn_4(bipy)_2$** and **3_2-$Mn_4(phen)_2$**, and comparison with those earlier reported for compounds **1_2-**

$Mn_4(dmf)_6$[2], **1_2-$Mn_4(dmf)_4(H_2O)_2$**[2], **2_2-$Mn_4(bipy)_2(MeOH)_2$**[3]. The independent cluster molecules and disordered molecules, presenting in the unit cell, are denoted as MolA, MolB and MolA*, MolB*, respectively.

		3_2-$Mn_4(dmf)_4$		**1_2-$Mn_4(dmf)_6$**		**3_2-$Mn_4(dmf)_2(H_2O)_2$**	**1_2-$Mn_4(dmf)_4(H_2O)_2$**	**3_2-$Mn_4(bipy)_2$**	**2_2-$Mn_4(bipy)_2$**			**3_2-$Mn_4(phen)_2$**	
	OX/NX	Mol(A)	Mol(B)	Mol(A)*	Mol(B)*				Mol(A)	Mol(B)		Mol(A)*	Mol(B)*
$d_{Mn(2)-O}$, Å	**O4**	2.220(3)	2.204(3)	2.218(2)	2.218(2)	2.198(5)	2.270(7)	2.211(2)	2.171(6)	2.194(6)	2.267(5)	2.27(1)	2.12(2)
	O5	2.177(3)	2.201(2)	2.169(1)	2.169(1)	2.167(7)	2.202(8)	2.103(2)	2.124(6)	2.149(6)	2.133(7)	2.17(1)	2.16(1)
	O6	2.159(3)	2.193(3)	2.162(1)	2.162(1)	2.179(6)	2.196(8)	2.148(2)	2.139(6)	2.133(7)	2.149(6)	2.14(1)	2.16(1)
	O7/N7	2.143(3)	2.198(3)	2.223(9)	2.04(2)	2.138(9)	2.181(8)	2.175(3)	2.220(7)	2.245(8)	2.259(8)	2.232(8)	2.21(1)
	O8/N8	2.154(3)	2.134(3)	2.27(1)	2.125(4)	2.17(1)	2.198(9)	2.272(3)	2.243(9)	2.259(8)	2.245(8)	2.237(7)	2.235(9)
	O9	2.204(3)	2.136(3)	2.216(2)	2.216(2)	2.221(6)	2.190(6)	2.201(2)	2.249(6)	2.267(5)	2.194(6)	2.20(2)	2.21(3)

Table S4. Coordination bond angles of Mn(2)-atoms for obtained complexes **3_2-$Mn_4(dmf)_4$**, **3_2-$Mn_4(dmf)_2(H_2O)_2$**, **3_2-$Mn_4(bipy)_2$** and **3_2-$Mn_4(phen)_2$**, and comparison with those earlier reported for compounds **1_2-$Mn_4(dmf)_6$**[2], **1_2-$Mn_4(dmf)_4(H_2O)_2$**[2], **2_2-$Mn_4(bipy)_2(MeOH)_2$**[3]. The independent cluster molecules and disordered molecules, presenting in the unit cell, are denoted as MolA, MolB and MolA*, MolB*, respectively.

	OX/OY or **OX/NY** or **NX/NY**	**3_2-$Mn_4(dmf)_4$**		**1_2-$Mn_4(dmf)_6$**		**3_2-$Mn_4(dmf)_2(H_2O)_2$**	**1_2-$Mn_4(dmf)_4(H_2O)_2$**	**3_2-$Mn_4(bipy)_2$**	**2_2-$Mn_4(bipy)_2$**			**3_2-$Mn_4(phen)_2$**	
		Mol(A)	Mol(B)	Mol(A)*	Mol(B)*				Mol(A)	Mol(B)		Mol(A)*	Mol(B)*
∠ **OX** – Mn(2) - **OY**, ° or ∠ **OX** – Mn(2) - **NY**, ° or ∠ **NX** – Mn(2) - **NY**, °	**O4/O5**	75.03(9)	74.47(9)	75.14(6)	75.14(6)	75.3(2)	75.8(2)	76.99(8)	77.2(2)	75.5(2)	74.6(2)	75.4(4)	78.5(6)
	O4/O6	91.85(9)	92.72(9)	95.83(6)	95.83(6)	95.5(2)	88.3(2)	91.89(8)	93.2(2)	90.4(2)	92.3(2)	93.6(5)	88.3(6)
	O4/O7 or **O4/N7**	89.5(1)	85.6(1)	87.2(2)	89.7(4)	89.8(3)	86.9(2)	86.84(9)	89.3(3)	90.5(3)	82.3(2)	88.8(4)	91.5(6)
	O4/O8 or **O4/N8**	102.1(1)	103.3(1)	103.6(3)	95.1(1)	102.8(3)	92.8(2)	107.90(9)	109.5(3)	113.1(2)	104.3(2)	103.5(4)	111.9(6)
	O4/O9	166.62(9)	165.30(9)	167.54(6)	167.54(6)	165.7(2)	163.9(2)	167.51(8)	168.1(2)	161.6(2)	161.6(2)	168.4(6)	159.4(9)
	O5/O6	83.92(9)	83.0(1)	84.16(6)	84.16(6)	82.2(2)	82.6(2)	84.13(8)	82.8(2)	85.5(2)	85.5(2)	86.4(4)	85.9(5)
	O5/O7 or **O5/N7**	164.5(1)	160.0(1)	161.8(2)	164.0(4)	163.6(3)	162.3(3)	162.0(1)	163.8(3)	160.3(3)	156.6(2)	163.9(4)	165.1(5)
	O5/O8 or **O5/N8**	94.7(1)	95.2(1)	88.4(3)	96.5(1)	100.7(3)	82.2(2)	103.21(9)	102.6(3)	99.7(2)	108.8(3)	104.5(3)	96.5(4)
	O5/O9	96.35(9)	95.80(9)	95.32(6)	95.32(6)	92.8(2)	99.1(2)	96.82(8)	96.2(2)	92.3(2)	90.4(2)	94.2(6)	98.9(8)
	O6/O7 or **O6/N7**	95.7(1)	96.2(1)	93.4(2)	103.0(4)	92.7(3)	100.9(3)	104.4(1)	107.2(3)	108.8(3)	99.7(2)	97.3(3)	104.9(4)
	O6/O8 or **O6/N8**	165.2(1)	162.8(1)	156.6(3)	168.8(1)	161.7(3)	164.0(2)	159.9(1)	157.3(3)	156.6(2)	160.3(3)	161.5(4)	159.7(5)
	O6/O9	76.88(9)	74.90(9)	74.93(6)	74.93(6)	74.9(2)	75.8(2)	76.57(8)	76.0(2)	74.6(2)	75.5(2)	80.2(6)	71.1(8)
	O7/O8 or **N7/N8**	89.5(1)	91.3(1)	100.2(4)	79.3(4)	89.1(4)	95.1(3)	74.1(1)	73.2(3)	72.7(3)	72.7(3)	76.3(3)	76.9(3)
	O7/O9	98.6(1)	103.3(1)	101.5(2)	100.4(4)	100.9(3)	98.6(3)	100.5(1)	98.7(3)	104.3(2)	113.1(2)	101.8(6)	94.3(7)
	O8/O9 or **N8/O9**	88.67(9)	88.3(1)	83.8(3)	93.9(1)	86.9(3)	101.7(2)	83.96(9)	81.5(3)	82.3(2)	90.5(3)	84.1(5)	88.6(7)

Table S5. Dihedral angles (∠XX' and ∠YY', °) between the opposite aryl units of **3** and its Δ (°) for complexes **3_2-$Mn_4(dmf)_4$**, **3_2-$Mn_4(dmf)_2(H_2O)_2$**, **3_2-$Mn_4(bipy)_2$** and **3_2-$Mn_4(phen)_2$**, and comparison with those earlier reported for compounds **1_2-$Mn_4(dmf)_6$**[2], **1_2-$Mn_4(dmf)_4(H_2O)_2$**[2], **2_2-$Mn_4(bipy)_2(MeOH)_2$**[3].

	3_2-$Mn_4(dmf)_4$		**1_2-$Mn_4(dmf)_6$**	**3_2-$Mn_4(dmf)_2(H_2O)_2$**	**1_2-$Mn_4(dmf)_4(H_2O)_2$**	**3_2-$Mn_4(bipy)_2$**	**2_2-$Mn_4(bipy)_2$**		**3_2-$Mn_4(phen)_2$**	
	Mol(A)	Mol(B)					Mol(A)	Mol(B)	Mol(A)*	Mol(B)*
∠XX', °	59.5(3)	62.3(1)	54.01(9)	49.5(3)	55.2(3)	62.6(1)	62.5(3)	66.2(3) 66.64(3)	70.6(5)	53.0(6)
∠YY', °	61.5(2)	47.8(2)	75.3(1)	76.3(3)	75.6(2)	65.7(1)	70.3(4)	60.7(3) 73.6(3)	71.4(5)	73.3(7)
Δ(∠YY'-∠XX'), °	2.0(3)	14.5(2)	21.29(9)	26.8(3)	20.4(3)	3.1(1)	7.8(5)	0.44(4) 12.9(4)	0.8(7)	20.3(9)

Table S6. The CShM deviation values, calculated by SHAPE program[4], for Mn(III) atoms in **3_2-$Mn_4(dmf)_4$**, **3_2-$Mn_4(dmf)_2(H_2O)_2$**, **3_2-$Mn_4(bipy)_2$** and **3_2-$Mn_4(phen)_2$**, and comparison with those earlier reported for compounds **1_2-$Mn_4(dmf)_6$**[2], **1_2-$Mn_4(dmf)_4(H_2O)_2$**[2], **2_2-$Mn_4(bipy)_2(MeOH)_2$**[3].

Complex name	**Mn**	**PP-5**	**vOC-5**	**TBPY-5**	**SPY-5**	**JTBPY-5**	**HP-6**	**PPY-6**	**OC-6**	**TPR-6**	**JPPY-6**
3_2-$Mn_4(dmf)_4$	Mn(A)	27.656	0.627	6.671	1.423	8.564	-	-	-	-	-
	Mn(B)	26.950	0.687	6.808	1.622	8.648	-	-	-	-	-
1_2-$Mn_4(dmf)_6$	Mn(A)	-	-	-	-	-	32.153	26.994	0.887	14.753	30.544
3_2-$Mn_4(dmf)_2(H_2O)_2$	Mn(A)	27.345	0.632	6.446	1.612	8.238	-	-	-	-	-
1_2-$Mn_4(dmf)_4(H_2O)_2$	Mn(A)	-	-	-	-	-	32.757	27.904	0.812	14.782	30.958
3_2-$Mn_4(bipy)_2$	Mn(A)	27.857	0.582	6.884	1.497	8.756	-	-	-	-	-

2_2-$Mn_4(bipy)_2(MeOH)_2$	Mn(A)	-	-	-	-	-	31.571	27.601	1.146	15.793	30.802
	Mn(B)	-	-	-	-	-	32.139 and 31.024	27.568 and 26.482	1.190 and 1.227	15.026 and 14.603	30.728 and 30.007
3_2-$Mn_4(phen)_2$	Mn(A)*	29.371	0.500	6.079	1.360	8.122	-	-	-	-	-
	Mn(B)*	26.648	1.181	7.405	2.000	9.356	-	-	-	-	-

Label	Symmetry	Shape
PP-5	D_{5h}	Pentagon
vOC-5	C_{4v}	Vacant octahedron (Johnson square pyramid, J1)
TBPY-5	D_{3h}	Trigonal bipyramid
SPY-5	C_{4v}	Square pyramid
JTBPY-5	D_{3h}	Johnson trigonal bipyramid (J12)
HP-6	D_{6h}	Hexagon
PPY-6	C_{5v}	Pentagonal pyramid
OC-6	O_h	Octahedron
TPR-6	D_{3h}	Trigonal prism
JPPY-6	C_{5v}	Johnson pentagonal pyramid (J2)

Table S7. The CShM deviation values, calculated by SHAPE program[4], for Mn(II) atoms in **3_2-$Mn_4(dmf)_4$, 3_2-$Mn_4(dmf)_2(H_2O)_2$, 3_2-$Mn_4(bipy)_2$** and **3_2-$Mn_4(phen)_2$**, and comparison with those earlier reported for compounds **1_2-$Mn_4(dmf)_6$**[2], **1_2-$Mn_4(dmf)_4(H_2O)_2$**[2], **2_2-$Mn_4(bipy)_2(MeOH)_2$**[3].

Complex name	Mn	HP-6	PPY-6	OC-6	TPR-6	JPPY-6
3_2-$Mn_4(dmf)_4$	Mn(A)	31.283	24.538	1.534	12.353	27.927
	Mn(B)	32.256	23.273	2.047	12.110	26.614
1_2-$Mn_4(dmf)_6$	Mn(A)*	30.240	24.104	1.572	12.472	28.189
	Mn(B)*	32.148	22.605	2.220	10.676	25.697
3_2-$Mn_4(dmf)_2(H_2O)_2$	Mn(A)	31.283	23.291	1.923	11.591	26.443
1_2-$Mn_4(dmf)_4(H_2O)_2$	Mn(A)	30.652	23.408	1.646	11.258	27.393
3_2-$Mn_4(bipy)_2$	Mn(A)	29.952	19.692	3.100	11.093	22.707
2_2-$Mn_4(bipy)_2(MeOH)_2$	Mn(A)	29.764	19.721	3.291	10.615	22.741
	Mn(B)	27.130 and 29.493	22.664 and 17.971	2.792 and 4.053	12.383 and 9.875	25.970 and 20.902
3_2-$Mn_4(phen)_2$	Mn(A)*	30.860	20.330	2.406	11.480	23.446
	Mn(B)*	30.396	20.177	3.117	8.859	23.746

Table S8. For obtained complexes, the oxidation state of Mn1 and Mn2 atoms calculated, using BVS method [5].

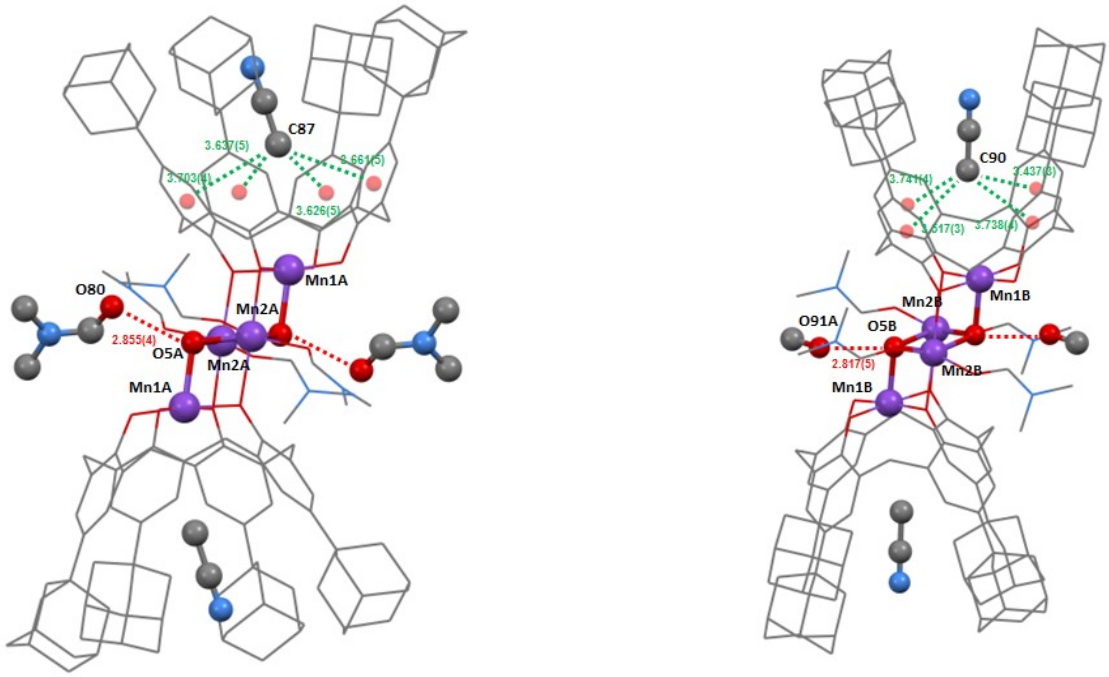
Complex name	BVS Mn1	BVS Mn2
3_2-$Mn_4(dmf)_4$	2.996	1.953
3_2-$Mn_4(dmf)_2(H_2O)_2$	2.994	1.940
3_2-$Mn_4(bipy)_2$	2.967	1.921
3_2-$Mn_4(phen)_2$	3.473	2.209

Table S9. The Mn…Mn bond distances and angles within the {Mn_4} cluster units for obtained complexes **3_2-$Mn_4(dmf)_4$**, **3_2-$Mn_4(dmf)_2(H_2O)_2$**, **3_2-$Mn_4(bipy)_2$** and **3_2-$Mn_4(phen)_2$**, and comparison with those earlier reported for compounds **1_2-$Mn_4(dmf)_6$**[2], **1_2-$Mn_4(dmf)_4(H_2O)_2$**[2], **2_2-$Mn_4(bipy)_2(MeOH)_2$**[3].

	3_2-$Mn_4(dmf)_4$		**1_2-$Mn_4(dmf)_6$**	**3_2-$Mn_4(dmf)_2(H_2O)_2$**	**1_2-$Mn_4(dmf)_4(H_2O)_2$**	**3_2-$Mn_4(bipy)_2$**	**2_2-$Mn_4(bipy)_2$**		**3_2-$Mn_4(phen)_2$**	
	Mol(A)	Mol(B)					Mol(A)	Mol(B)	Mol(A)*	Mol(B)*
$d_{Mn(1)-Mn(2)}$, Å	3.243(1)	3.254(1)	3.2906(5)	3.233(2)	3.264(6)	3.1925(9)	3.224(2)	3.288(2) 3.360(2)	3.271(6)	3.119(8)
$d_{Mn(1)-Mn(2)'}$, Å	3.202(1)	3.255(1)	3.3021(5)	3.235(2)	3.307(7)	3.215(1)	3.280(2)	3.296(2) 3.265(2)	3.108(8)	3.37(1)
$d_{Mn(1)-Mn(1)'}$, Å	5.581(2)	5.616(2)	5.7556(6)	5.577(2)	5.68(1)	5.577(1)	5.664(2)	5.789(2)	5.553(8)	5.68(1)
$d_{Mn(2)-Mn(2)'}$, Å	3.224(1)	3.292(1)	3.2151(6)	3.276(2)	3.304(7)	3.1554(9)	3.197(2)	3.177(2)	3.144(8)	3.16(1)
∠ Mn(2) - Mn(1) - Mn(2)', °	60.03(2)	60.75(2)	58.38(1)	60.85(4)	60.37(4)	59.00(2)	58.88(4)	57.09(4) 57.93(4)	59.0(2)	58.1(2)
∠ Mn(1) – Mn(2) - Mn(1)', °	119.97(2)	119.25(2)	121.62(1)	119.15(5)	119.63(6)	121.00(2)	121.12(6)	123.12(6) 121.83(2)	121.0(2)	121.9(3)

Table S10. The {Mn_4}…{Mn_4} cluster units distances and dihedral angle (∠, °) between the molecules of **3_2-$Mn_4(dmf)_4$**, **3_2-$Mn_4(dmf)_2(H_2O)_2$**, **3_2-$Mn_4(bipy)_2$** and **3_2-$Mn_4(phen)_2$**, denoted as dihedral angle between the planes, built on four C-atoms of CH_2-bridging moieties of **3**, belonging to adjacent coordination species within crystal packing, presented in comparison with those earlier reported for compounds **1_2-$Mn_4(dmf)_6$**[2], **1_2-$Mn_4(dmf)_4(H_2O)_2$**[2], **2_2-$Mn_4(bipy)_2(MeOH)_2$**[3].

	3_2-$Mn_4(dmf)_4$	**1_2-$Mn_4(dmf)_6$**	**3_2-$Mn_4(dmf)_2(H_2O)_2$**	**1_2-$Mn_4(dmf)_4(H_2O)_2$**	**3_2-$Mn_4(bipy)_2$**	**2_2-$Mn_4(bipy)_2(MeOH)_2$**	**3_2-$Mn_4(phen)_2$**
$d_{\{Mn4\}centr-\{Mn4\}centr}$, Å	14.296(6) 16.780(3) 17.502(5)	12.5350(8) 13.3430(7) 19.3706(9)	14.071(3) 16.059(2) 21.891(4)	12.47(3) 12.76(3) 18.94(4)	16.357(3) 17.375(3) 18.043(4)	10.9280(4) 11.1261(2) 12.0689(5)	13.162(3) 18.609(3) 19.513(3)
∠, °	89.35(6)	36.32(4)	84.7(1)	0	78.62(5)	24.9(1)	66.4(3)



a **b**

Figure S2. For **3_2-$Mn_4(dmf)_4$**, a formation of solvates, due to CH/π- and H-bonding interactions, with CH_3CN and DMF molecules for **3_2-$Mn_4(dmf)_4$-A** (a) and with CH_3CN and MeOH molecules for **3_2-$Mn_4(dmf)_4$-B** (b).

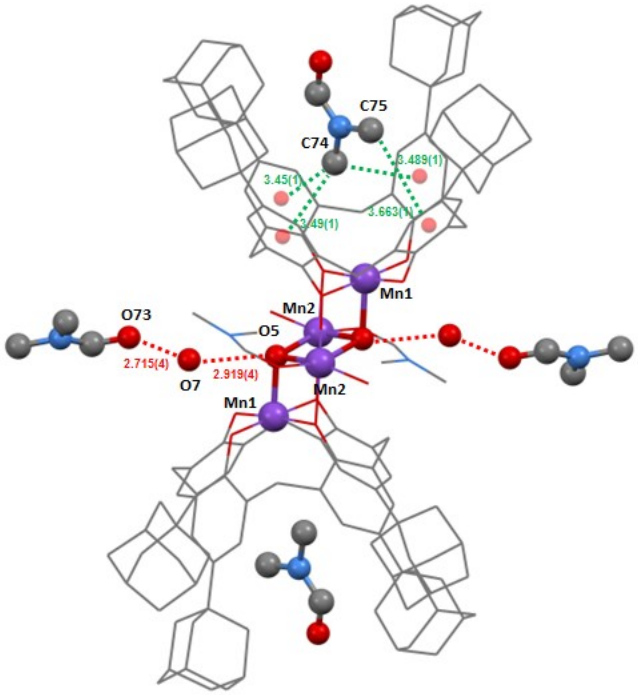
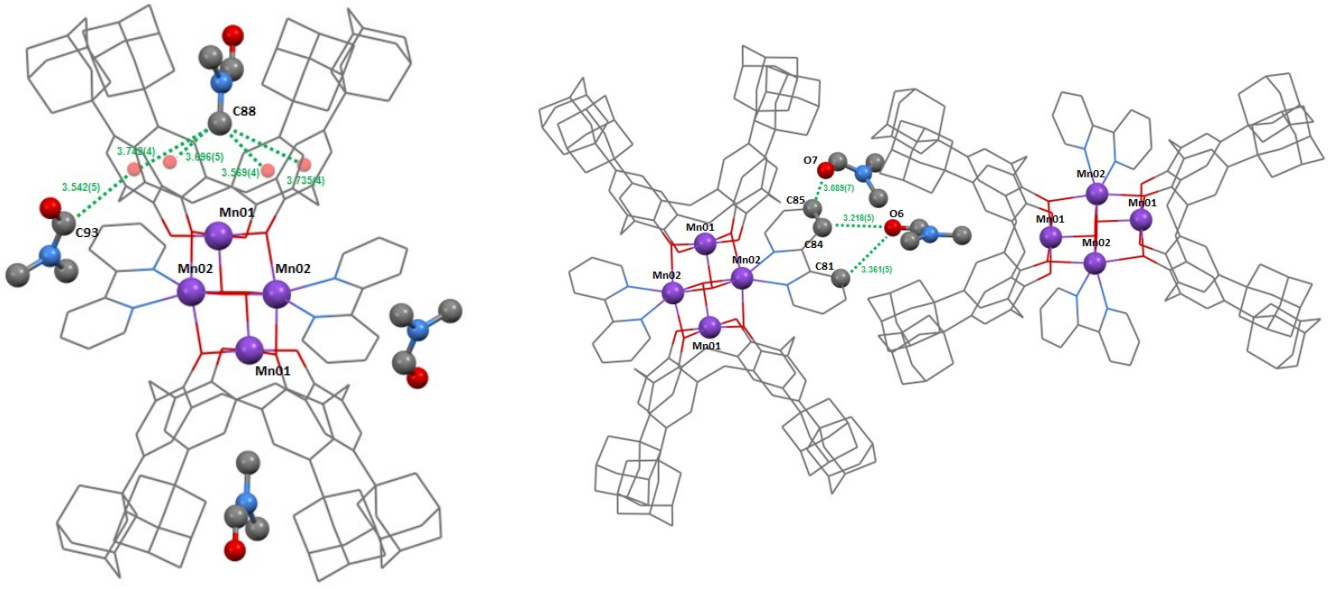


Figure S3. For **3_2-$Mn_4(dmf)_2(H_2O)_2$**, the formation of solvates, supported by CH/π- and H-bonding interactions, with DMF and H_2O molecules.



a **b**

Figure S4. For **3_2-$Mn_4(bipy)_2$**, (a) the formation of solvate with DMF molecules, supported by CH/π-interactions, involving C(88)-atom of accommodated DMF molecule located inside the calix[4]arene cavity or C(93) -atom belonging to carbonyl group, belonging to DMF molecule, disposed outside the calix[4]arene cavity with a aryl units of the calix[4]arene platform, and (b) the short contacts between the O(7)-carbonyl atom of DMF molecule with C(81)-, C(84)- and C(85)-atoms belonging to **bipy** molecule.

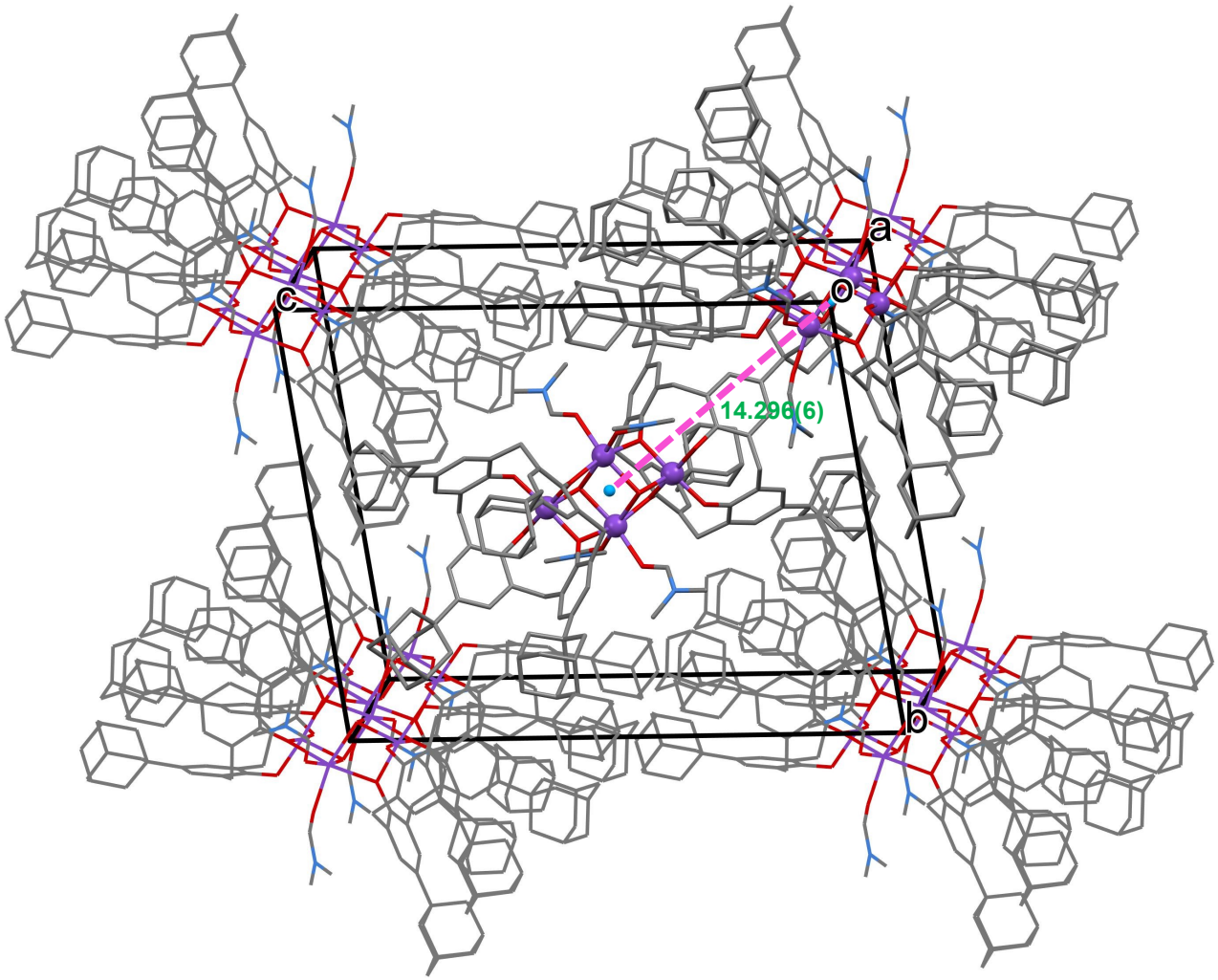


Figure S5. For **3_2-Mn_4(dmf)$_4$**, a portion of crystal packing, showing the shortest {Mn_4}…{Mn_4} distance between **3_2-Mn_4(dmf)$_4$-A** and **3_2-Mn_4(dmf)$_4$-B** molecules.

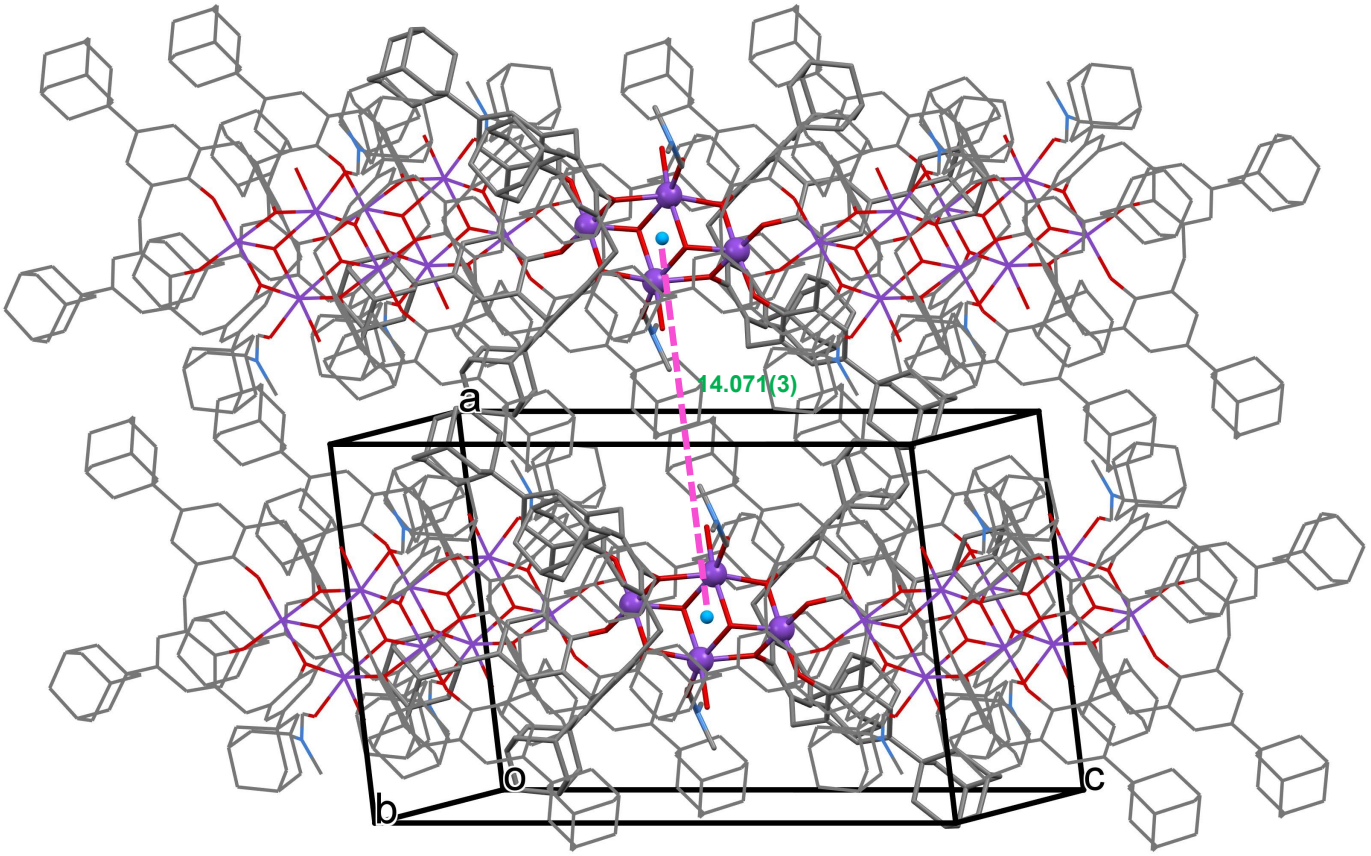


Figure S6. For **3_2-$Mn_4(dmf)_2(H_2O)_2$**, a portion of crystal packing, showing the shortest $\{Mn_4\}\ldots\{Mn_4\}$ distance.

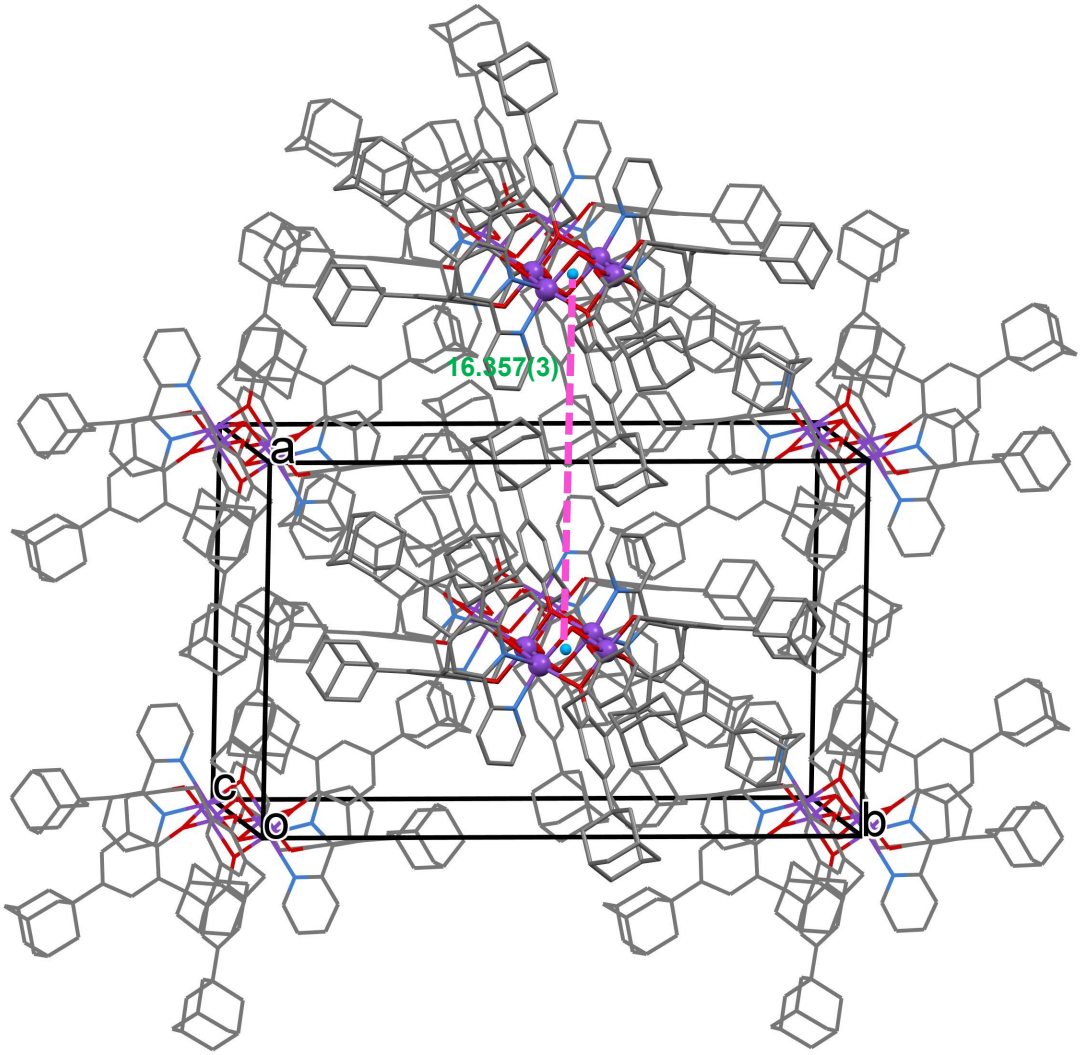


Figure S7. For **3_2-Mn_4(bipy)$_2$**, a portion of crystal packing, showing the shortest $\{Mn_4\}\ldots\{Mn_4\}$ distance.

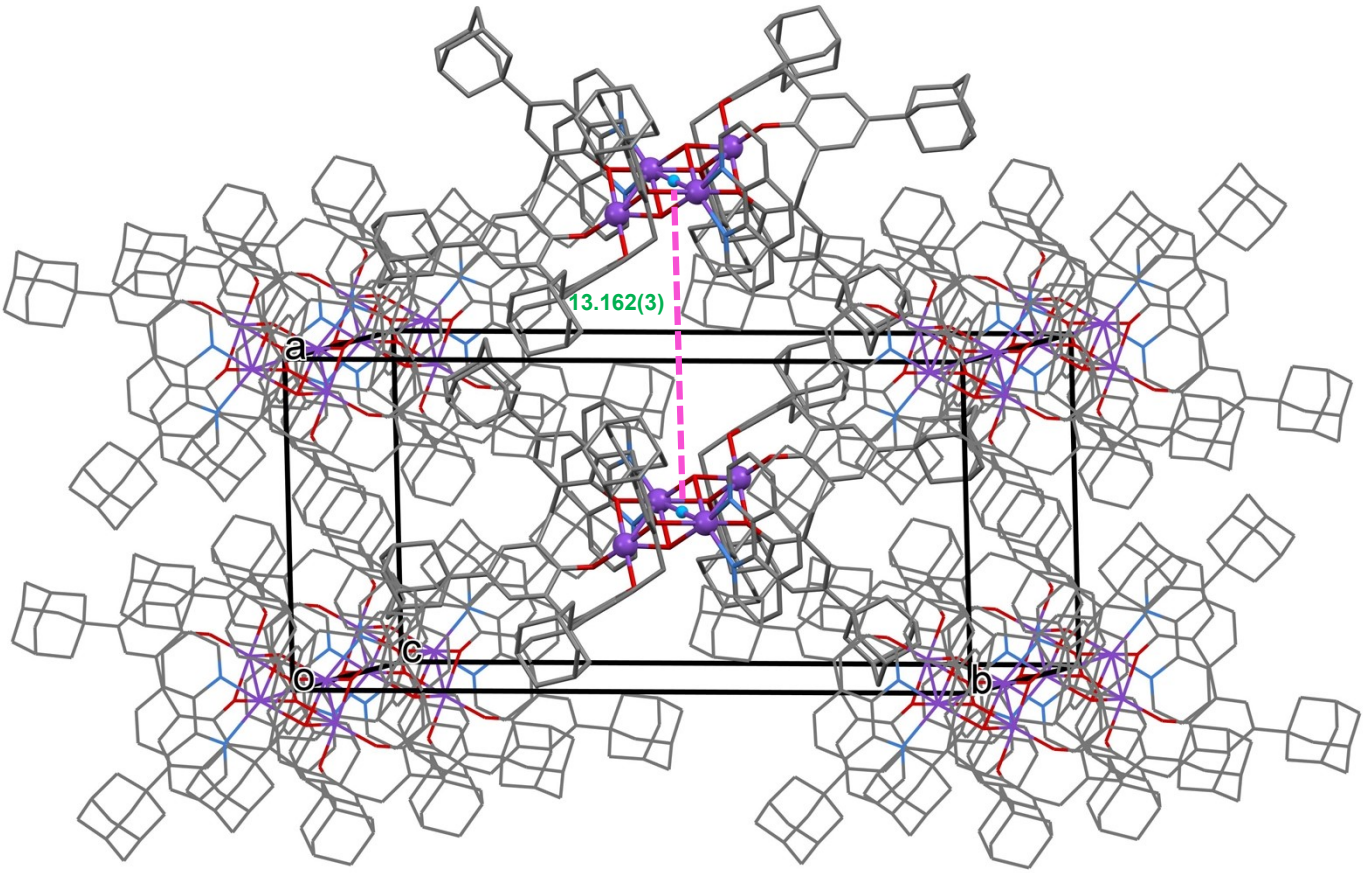


Figure S8. For **3_2-Mn_4(phen)$_2$**, a portion of crystal packing, showing the shortest {Mn_4}…{Mn_4} distance.

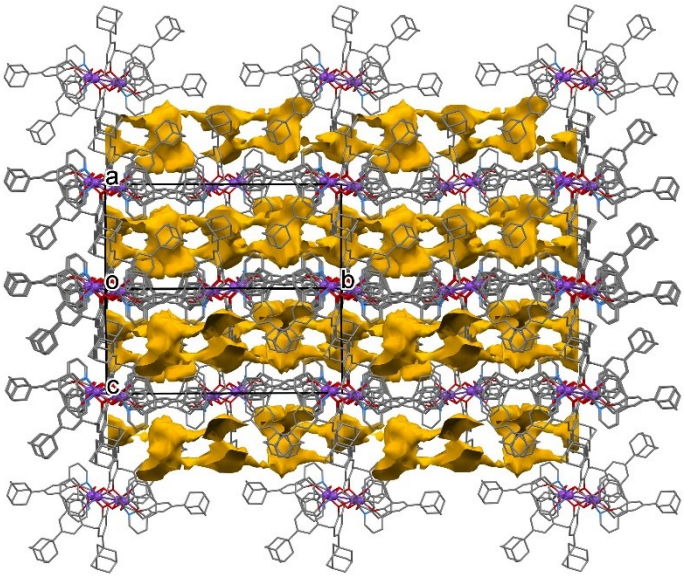


Figure S9. For **3_2-Mn_4(phen)$_2$**, a portion of crystal packing, showing the pores, located in the interstices between the cluster species.

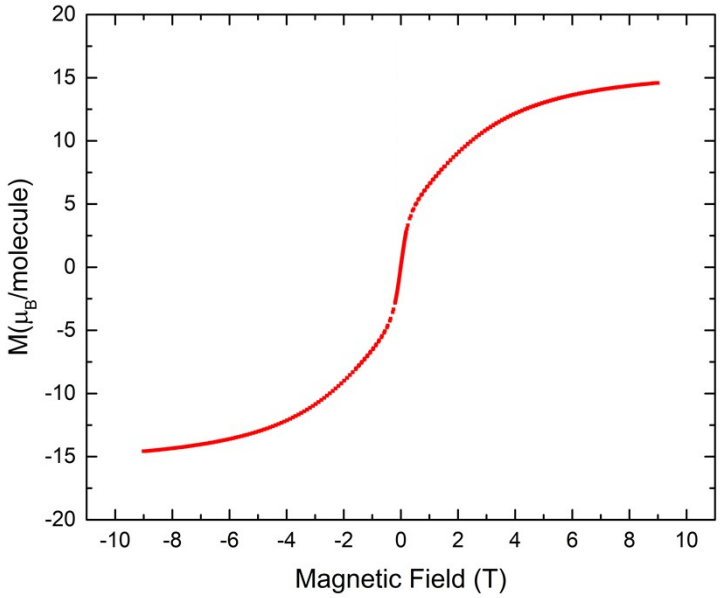


Figure S10. For **3_2-$Mn_4(phen)_2$**, a field-dependent magnetization, measured at T=2K.

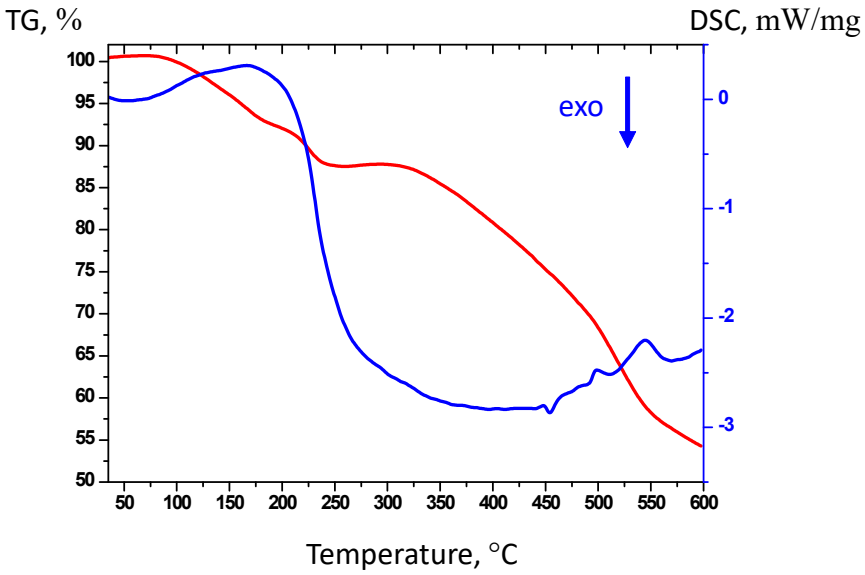


Figure S11. TG (red) DSC (blue) traces for **3_2-$Mn_4(dmf)_2(H_2O)_2$**. The samples release solvent molecules starting from 100 °C till 252 °C in two steps. The first step observed in the temperature range from 100 C till 182 is consistent with 8.40 % of mass loss which can be associated with the release of two DMF, two noncoordinated and two coordinated H_2O molecules (calculated mass loss 8.62%). The second step, revealed at 182-252 °C temperature range, corresponds to mass loss of 5.42%, can be consistent with the release of two remained DMF molecules (calculated mass loss 5.8%). The quantity of released solvent molecules was found to be in in good accordance with single crystal X-ray diffraction analysis. The complex decomposes, starting from 312 °C.

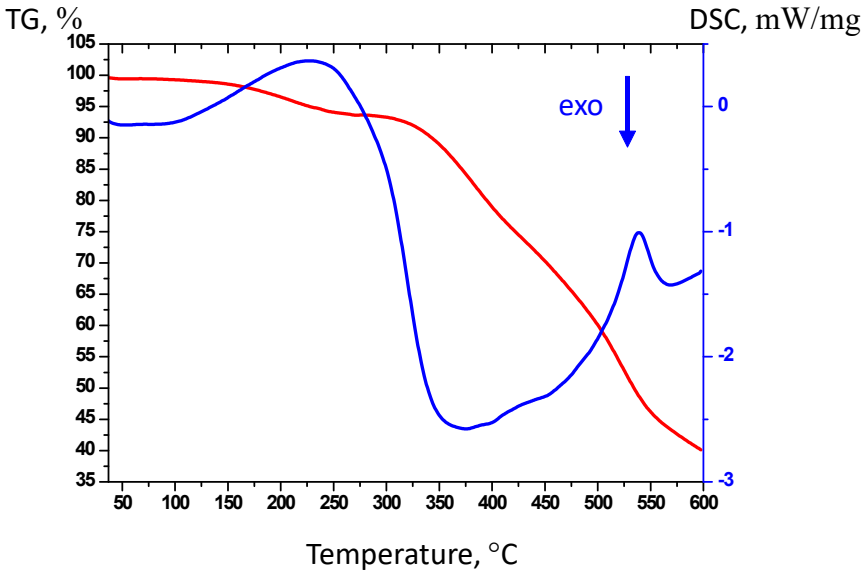


Figure S12. TG (red) DSC (blue) traces for **3_2-Mn_4(bipy)$_2$**. The sample releases solvent molecules, starting from 126 °C till 263 °C. The corresponding mass loss of 6.25% can be associated with the release of 2 DMF molecules, presenting in the crystal lattice (calculated mass loss 5.56%), which corresponds reduced quantity of solvent molecules, refined by single crystal X-ray diffraction analysis. The complex decomposes, starting from 310 °C.

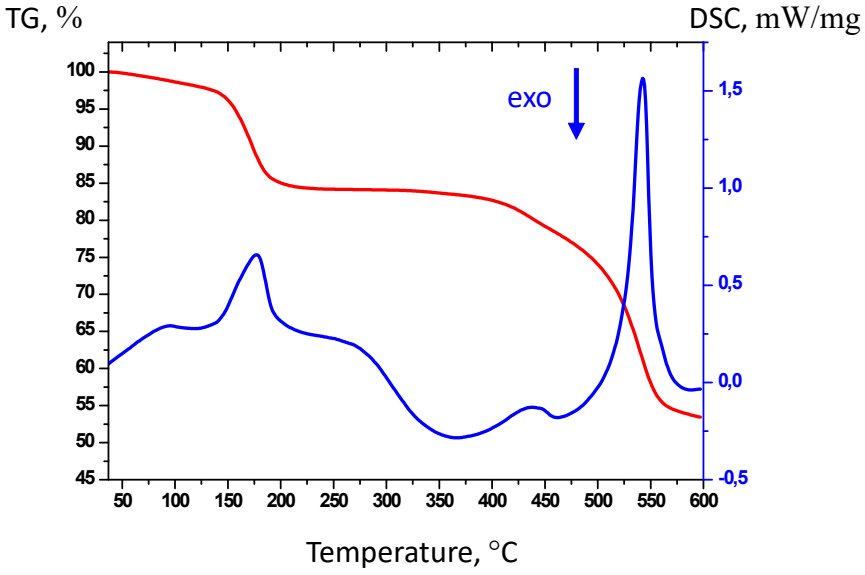


Figure S13. TG (red) DSC (blue) traces for **3_2-Mn_4(phen)$_2$**. The overall mass loss, observed from 30°C till 210 °C, was found to be equal 15.87%, which can be associated with the release of 1 MeCN, 2 MeOH and 5 DMF molecules, presenting in pores (calculated mass loss 15.7%). The complex decomposes, starting from 350 °C.

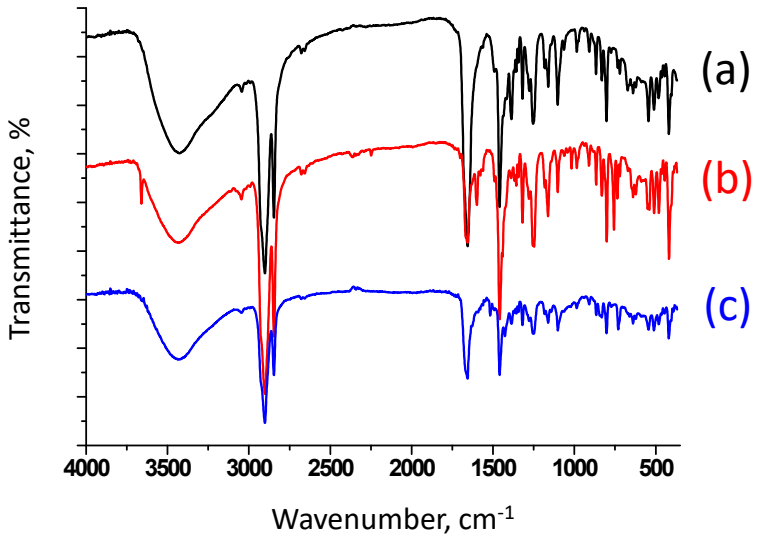


Figure S14. IR-spectra of $\mathbf{3_2\text{-}Mn_4(dmf)_2(H_2O)_2}$ (a), $\mathbf{3_2\text{-}Mn_4(bipy)_2}$ (b), $\mathbf{3_2\text{-}Mn_4(phen)_2}$ (c), recorded at 25 °C in KBr pellets.

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