Supplementary Information

for

Synthesis, crystal structures and magnetic behaviour of four coordination compounds constructed with a phosphinic amide-TEMPO radical and [M(hfac)$_2$] (M=Cu^{II}, Co^{II} and Mn^{II})

Samira G. Reis,[a] Miguel A. del Águila-Sánchez,[b] Guilherme P. Guedes,[c] Glaucio B. Ferreira,[a] Miguel A. Novak,[d] Nivaldo L. Speziali,[e] Fernando López-Ortiz,*[b] and Maria G. F. Vaz*[a]

[a]Instituto de Química, Universidade Federal Fluminense, 24020-141 Niterói, RJ, Brazil.

[b]Área de Química Orgánica, Universidad de Almería, Crta. Sacramento s/n, 04230, Almería, Spain

[c] Instituto de Ciências Exatas, Departamento de Química, Universidade Federal Rural do Rio de Janeiro, 23890-000 Seropédica, RJ, Brazil

[d] Instituto de Física, Universidade Federal do Rio de Janeiro, 21941-972 Rio de Janeiro, RJ, Brazil

[e] Departamento de Física, Universidade Federal de Minas Gerais, 31270-901 Belo Horizonte, MG, Brazil

*Corresponding author: mariavaz@vm.uff.br

Table of Contents

Table S1: Summary of the crystal structure, data collection and refinement for compounds **1**-**4**.....S2
Table S2: Selected bond angles for **1** and **2**.....S3
Table S3: Selected bond angles for **3** and **4**.....S3
Figure S1. ORTEP view of the asymmetric unit of compound **1**.....S4
Figure S2. ORTEP view of the asymmetric of compound **2**.....S4
Figure S3. ORTEP view of the asymmetric unit of compound **3**.....S5
Figure S4. ORTEP view of the asymmetric unit of compound **4**.....S5
Figure S5. $1/\chi_M$ data as a function of the temperature for compound **1**.....S6
Figure S6. Dependence of the magnetization of compound **1** as a function of the magnetic field.....S6
Figure S7. $1/\chi_M$ data as a function of the temperature for compound **2**.....S7
Figure S8. Dependence of the magnetization of compound **2** as a function of the magnetic field.....S7
Figure S9. $1/\chi_M$ data as a function of the temperature for compound **3**.....S8
Figure S10. Dependence of the magnetization of compound **3** as a function of the magnetic field.....S8
Figure S11. Dependence of the magnetization of compound **4** as a function of the magnetic field.....S9
Figure S12. $1/\chi_M$ data as a function of the temperature for compound **4**.....S9
Table S4. Absolute energies and Δ_{Energy} for compound **1**.....S10
Table S5. Absolute energies and Δ_{Energy} for compound **2**.....S10
Table S6. Absolute energies and Δ_{Energy} for compound **3**.....S10
Table S7. Absolute energies and Δ_{Energy} for compound **4**.....S10

Table S1. Summary of the crystal structure, data collection and refinement for compounds **1**-**4**.

Compound reference	**1**	**2**	**3**	**4**
Chemical formula	$C_{52}H_{58}CuF_{12}N_4O_8P_2 \cdot 2(C_{31}H_{30}CuF_{12}N_2O_6P) \cdot 2(C_7H_{16})$	$C_{72}H_{62}Co_3F_{36}N_4O_{16}P_2 \cdot 2(C_7H_{16})$	$C_{31}H_{30}F_{12}MnN_2O_6P$	$C_{31}H_{30}F_{12}CoN_2O_6P$
Formula Mass	3119.09	2362.39	840.48	844.47
Crystal system	Monoclinic	Triclinic	Tetragonal	Tetragonal
Space group	P 2_1/n	P-1	I 4_1cd	I 4_1cd
Radiation type	MoKα	MoKα	MoKα	MoKα
Temperature/K	120(2)	293(2)	120(2)	293(2)
a/Å	12.0520(3)	13.0336(9)	28.2516(7)	28.414(4)
b/Å	30.2136(7)	13.2483(9)	28.2516(7)	28.414(4)
c/Å	20.5874(6)	16.6020(11)	17.7052(9)	18.162(4)
$\alpha/^o$	90	79.807(5)	90	90
$\beta/^o$	99.114(3)	86.092(5)	90	90
$\gamma/^o$	90	73.575(6)	90	90
Unit cell volume/Å^3	7401.9(3)	2705.8(3)	14131.5(9)	14663(5)
No. of formula units per unit cell, *Z*	2	1	16	16
Density (calculated), Mg.m^{-3}	1.40	1.45	1.580	1.530
Absorption coefficient, mm^{-1}	0.58	0.60	0.53	0.62
No. of reflections measured	83125	16437	15052	56145
No. of independent reflections	13082	9561	6222	6429
θ range/^{o}	1.8–25.0°	2.0–25.0	2.0-25.0	2.0-25.0
Index range	h = −14→14 k = −35→35 l = −24→24	h = −12→15 k = −15→15 l = −19→19	h = −32→27 k = −33→21 l = −14→21	h = −33→33 k = −33→33 l = −21→21
R_{int}	0.064	0.080	0.073	0.066
Final R_1 values (I>2σ(I))	0.059	0.073	0.051	0.053
Final $wR(F^2)$ values (I>2σ(I))	0.156	0.221	0.162	0.147
Final R_1 values (all data)	0.821	0.154	0.051	0.083
Final $wR(F^2)$ values (all data)	0.1429	0.170	0.120	0.121
Goodness of fit on F^2	1.03	1.01	1.06	1.12
CCDC Deposition	997015	997016	997017	997018

Table S2. Selected bond angles for **1** and **2**

Labels	Bond angles (°)	Labels	Bond angles (°)
O4B^{i}—Cu1B—O4B	179.9980 (10)	O3—Co1—O3^{i}	180
O4B^{i}—Cu1B—O3B	88.38 (11)	O3—Co1—O4^{i}	88.64 (18)
O4B—Cu1B—O3B	91.61 (11)	O3i—Co1—O4^{i}	91.36 (18)
O4B^{i}—Cu1B—O3B^{i}	91.62 (11)	O3—Co1—O4	91.36 (18)
O4B—Cu1B—O3B^{i}	88.38 (11)	O3i—Co1—O4	88.65 (18)
O3B—Cu1B—O3B^{i}	179.998 (19)	O4i—Co1—O4	180
O4B^{i}—Cu1B—O2B	95.47 (10)	O3—Co1—O1	88.56 (17)
O4B—Cu1B—O2B	84.53 (10)	O3i—Co1—O1	91.44 (17)
O3B—Cu1B—O2B	85.84 (10)	O4i—Co1—O1	81.75 (17)
O3B^{i}—Cu1B—O2B	94.16 (10)	O4—Co1—O1	98.25 (17)
O4B^{i}—Cu1B—O2B^{i}	84.53 (10)	O3—Co1—O1^{i}	91.44 (17)
O4B—Cu1B—O2B^{i}	95.47 (10)	O3i—Co1—O1^{i}	88.56 (17)
O3B—Cu1B—O2B^{i}	94.17 (10)	O4i—Co1—O1^{i}	98.25 (17)
O3B^{i}—Cu1B—O2B^{i}	85.84 (10)	O4—Co1—O1^{i}	81.76 (17)
O2B—Cu1B—O2B^{i}	180	O1—Co1—O1^{i}	180
O3A—Cu1A—O6A	172.83 (12)	O7—Co2—O5	172.42 (16)
O3A—Cu1A—O5A	87.04 (11)	O7—Co2—O6	90.68 (15)
O6A—Cu1A—O5A	91.76 (10)	O5—Co2—O6	87.31 (15)
O3A—Cu1A—O4A	91.24 (10)	O7—Co2—O8	87.51 (18)
O6A—Cu1A—O4A	86.97 (10)	O5—Co2—O8	85.05 (17)
O5A—Cu1A—O4A	155.82 (12)	O6—Co2—O8	85.41 (16)
O3A—Cu1A—O2A	97.60 (11)	O7—Co2—O2^{ii}	95.29 (14)
O6A—Cu1A—O2A	89.56 (11)	O5—Co2—O2^{ii}	87.70 (14)
O5A—Cu1A—O2A	97.05 (11)	O6—Co2—O2^{ii}	170.44 (15)
O4A—Cu1A—O2A	107.08 (11)	O8—Co2—O2^{ii}	102.27 (15)
		O7—Co2—O2	92.89 (15)
		O5—Co2—O2	94.46 (15)
		O6—Co2—O2	91.01 (14)
		O8—Co2—O2	176.40 (14)

Table S3. Selected bond angles for **3** and **4**.

Labels	Bond angles (°)	Labels	Bond angles (°)
O1—Mn1—O5	95.1(2)	O2—Co1—O6	96.16 (16)
O1—Mn1—O3	87.0(2)	O2—Co1—O4	173.62 (16)
O1—Mn1—O6	99.3(2)	O6—Co1—O4	89.17 (16)
O1—Mn1—O4	166.7(2)	O2—Co1—O3	88.65 (16)
O1—Mn1—O2	89.5(2)	O6—Co1—O3	174.08 (15)
O5—Mn1—O3	89.5(2)	O4—Co1—O3	85.83 (16)
O5—Mn1—O6	81.7(2)	O2—Co1—O1^{i}	87.96 (16)
O5—Mn1—O4	80.2(2)	O6—Co1—O1^{i}	86.70 (17)
O5—Mn1—O2	170.4(2)	O4—Co1—O1^{i}	95.87 (17)
O3—Mn1—O6	169.6(2)	O3—Co1—O1^{i}	96.94 (17)
O3—Mn1—O4	80.6(2)	O2—Co1—O5	93.74 (16)
O3—Mn1—O2	99.2(2)	O6—Co1—O5	85.58 (16)
O6—Mn1—O4	92.3(2)	O4—Co1—O5	83.15 (16)
O6—Mn1—O2	89.2(2)	O3—Co1—O5	90.68 (17)
O4—Mn1—O2	97.2(2)	O1i—Co1—O5	172.23 (16)

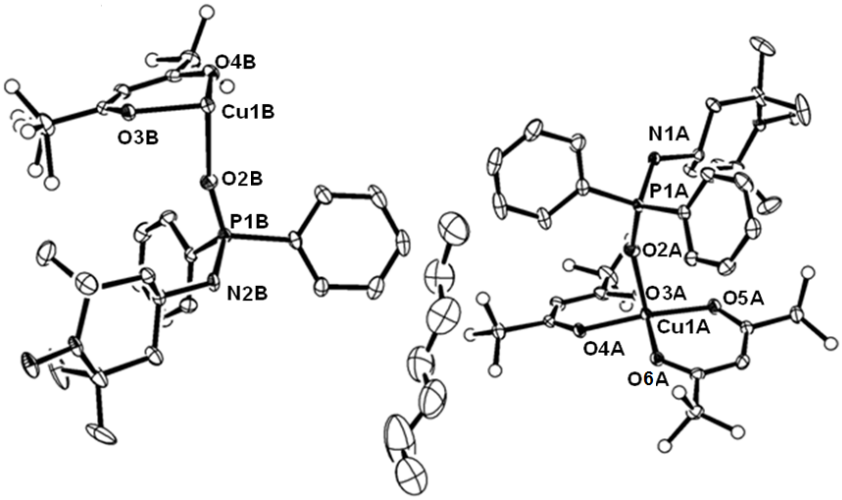

Figure S1. ORTEP view of the asymmetric unit of compound **1**. Fluorine atoms are shown as open circles and hydrogen atoms were omitted for clarity. Ellipsoids are at 50 % of probability.

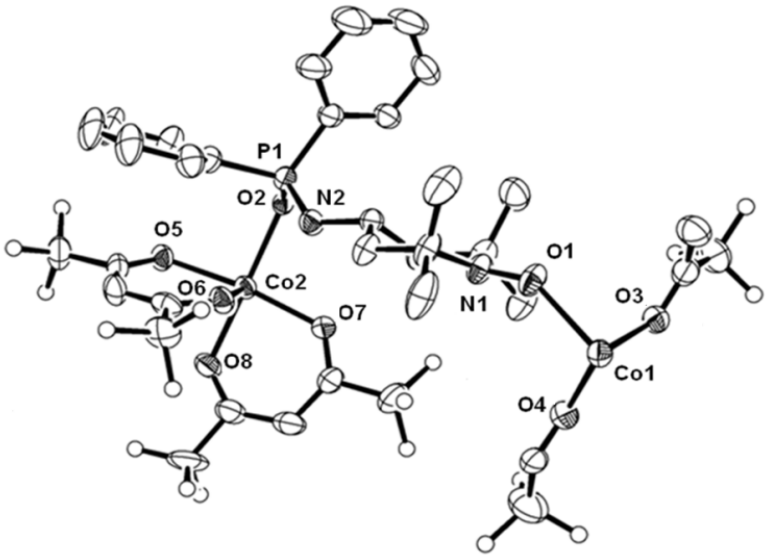

Figure S2. ORTEP view of the asymmetric of compound **2**. Fluorine atoms are shown as open circles and hydrogen atoms were omitted for clarity. Ellipsoids are at 50 % of probability.

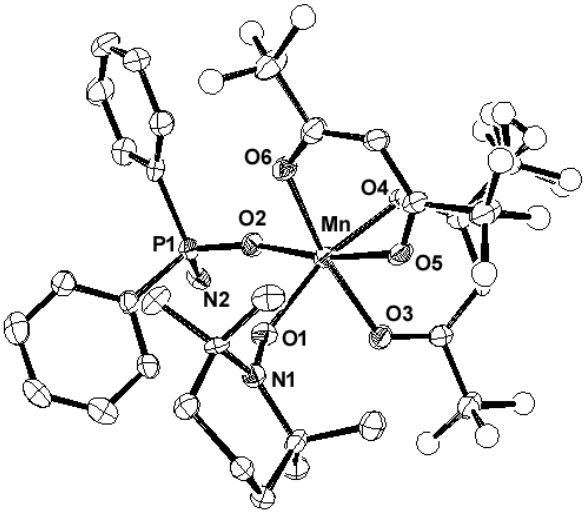

Figure S3. ORTEP view of the asymmetric unit of compound **3**. Fluorine atoms are shown as open circles and hydrogen atoms were omitted. Ellipsoids are at 50 % of probability.

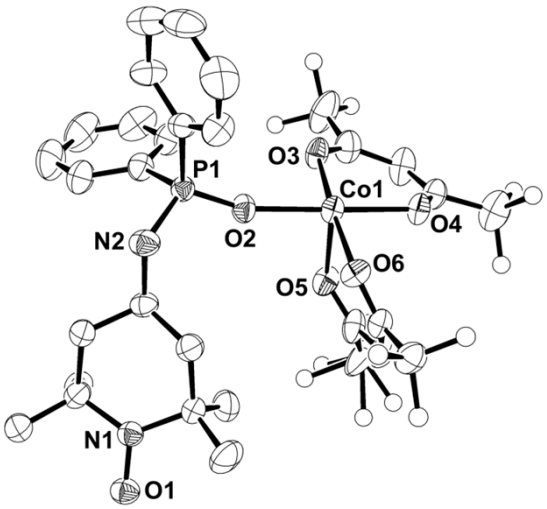

Figure S4. ORTEP view of the asymmetric unit of compound **4**. Fluorine atoms are shown as open circles and hydrogen atoms were omitted for clarity. Ellipsoids are at 40 % of probability.

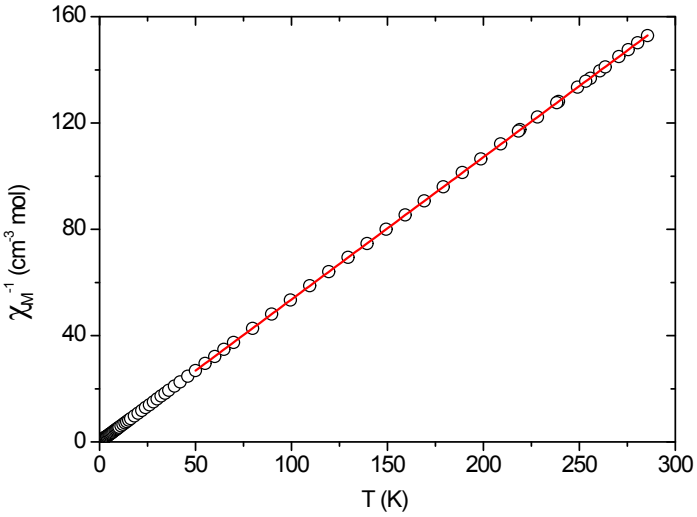

Figure S5. $1/\chi_M$ data as a function of the temperature for compound (**1**) fitted to the Curie-Weiss law (solid line).

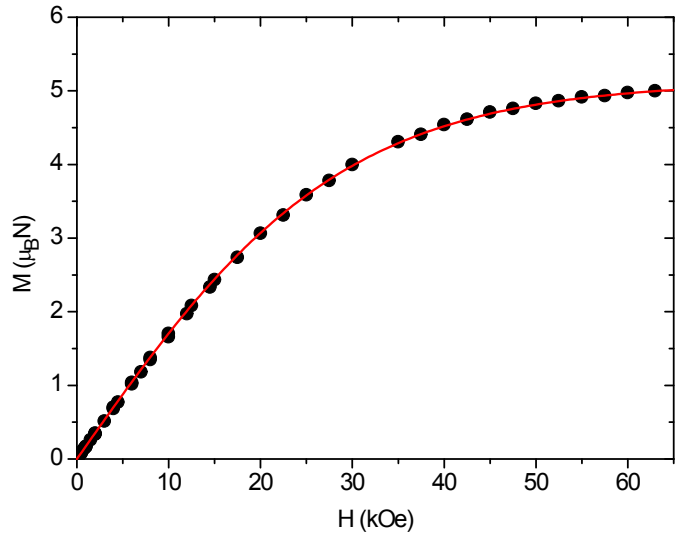

Figure S6. Dependence of the magnetization of compound **1** as a function of the magnetic field at 1.8 K. Solid line represents the simulation with a sum of five Brillouin functions S=1/2 (g = 2.05).

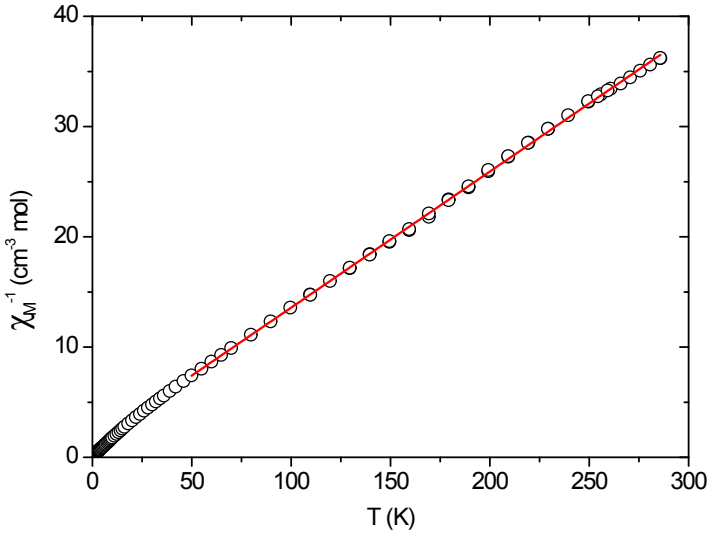

Figure S7. $1/\chi_M$ data as a function of the temperature for compound (**2**) fitted to the Curie-Weiss law (solid line).

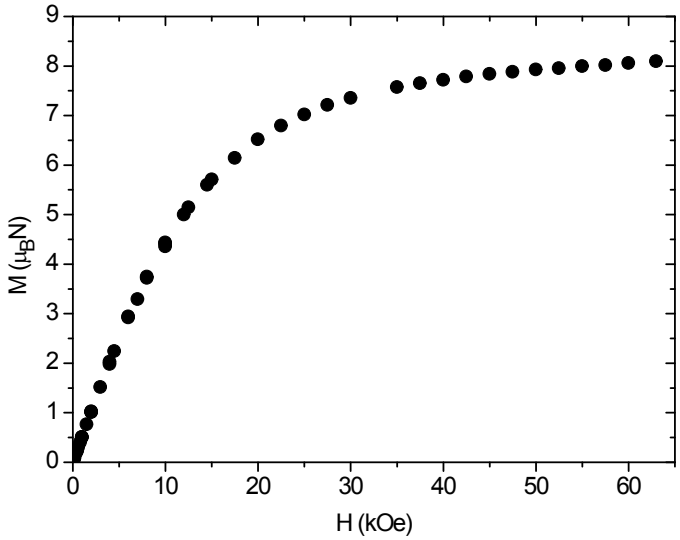

Figure S8. Dependence of the magnetization of compound **2** as a function of the magnetic field at 1.8 K.

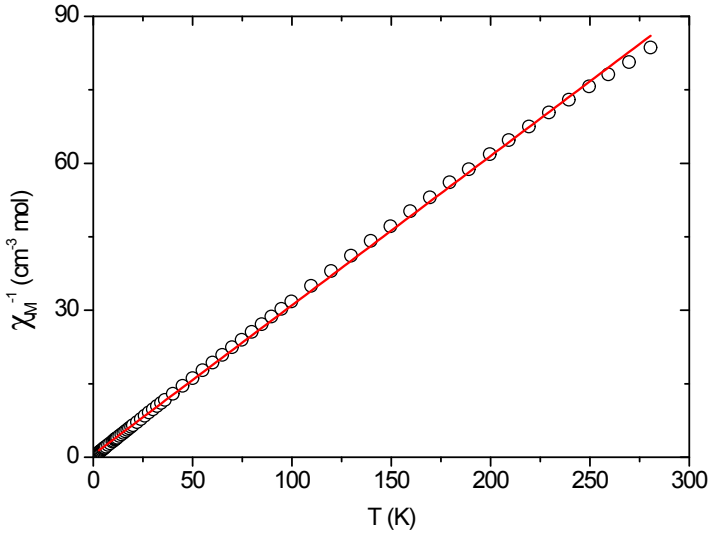

Figure S9. $1/\chi_M$ data as a function of the temperature for compound (**3**) fitted to the Curie-Weiss law (solid line).

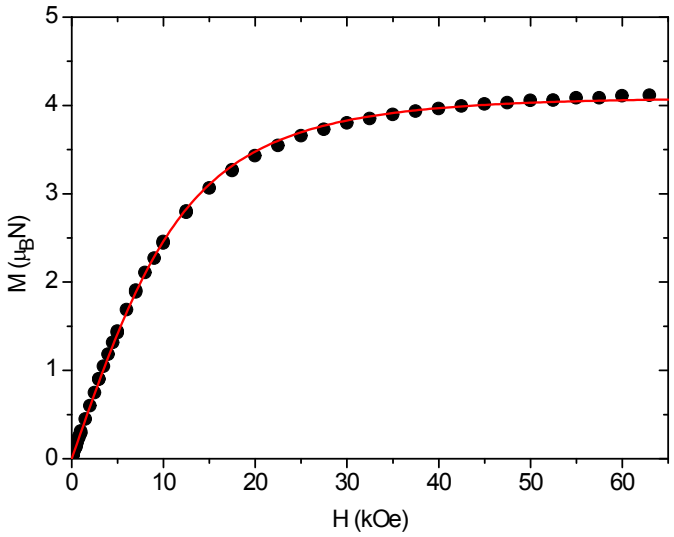

Figure S10. Dependence of the magnetization of compound **3** as a function of the magnetic field at 1.8 K. Solid line represents the simulation with the Brillouin function (g = 2.04 and S = 2).

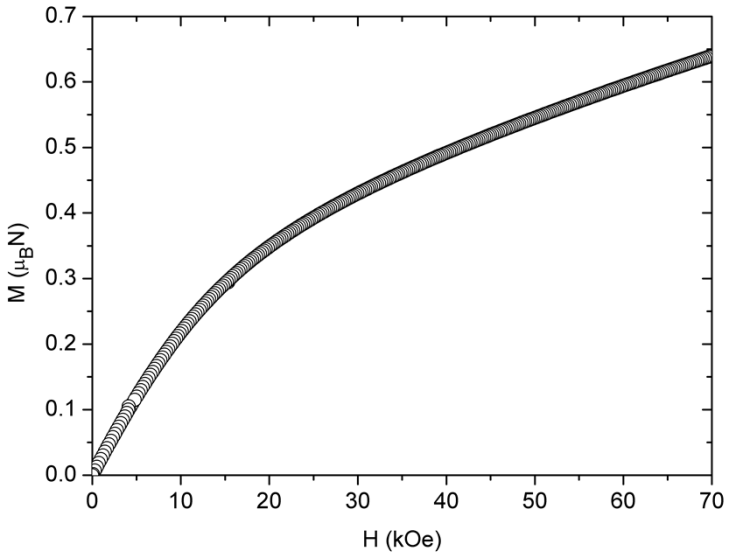

Figure S11. Dependence of the magnetization of compound **4** as a function of the magnetic field at 2.0 K.

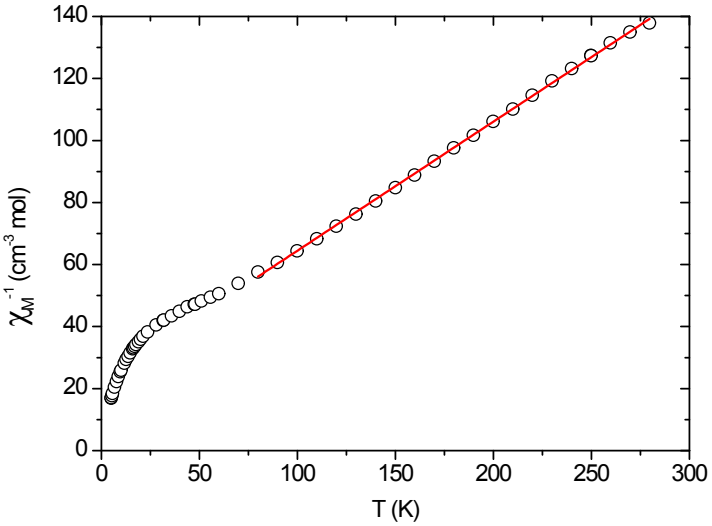

Figure S12. $1/\chi_M$ data as a function of the temperature for compound (4) fitted to the Curie-Weiss law (solid line).

Table S4. Absolute energies and Δ_{Energy} for complex **1**.

Multiplicity	Energy (Hartree)	Δ_{Energy} (E_{BS}- E_{HS}) (kJ/mol)
Unit A		
3 (HS)	-3160.07719839	
1 (BS)	-3160.07719841	-5.25E^{-05}
Unit B		
4 (HS)	-4242.77054487	
2 (BS)	-4242.77054489	-5.25E^{-05}
Supermolecula		
6 (HS)	-7402.86076047	
2 (BS)	-7402.86076156	-0.00286

Table S5. Absolute energies and Δ_{Energy} for complex **2**.

Multiplicity	Energy (Hartree)	Δ_{Energy} (E_{BS}- E_{HS}) (kJ/mol)
Unit i		
6 (HS)	-4191.77858490	
2 (BS)	-4191.78726240	-22.7828
Unit ii		
9 (HS)	-6218.02652000	
1 (BS)	-6218.02648670	0.0874
Supermolecula		
13 (HS)	-9327.04180719	
7 (BS)	-9327.04282718	-2.6779
1 (BS)	-9327.04254778	-1.9444

Table S6. Absolute energies and Δ_{Energy} for complex **3**.

Multiplicity	Energy (Hartree)	Δ_{Energy} (E_{BS}- E_{HS}) (kJ/mol)
Unit i		
8 (HS)	-4150,79331000	
6 (BS)	-4150,79930000	-15,7267
Supermolecula		
14 (HS)	-7218,80304690	
8 (BS)	-7218,81515730	-31,7958

Table S7. Absolute energies and Δ_{Energy} for complex **4**.

Multiplicity	Energy (Hartree)	Δ_{Energy} (E_{BS}- E_{HS}) (kJ/mol)
Unit i		
6 (HS)	-4191,73945850	
2 (BS)	-4191,74052100	-2,7895
Supermolecula		
10 (HS)	-7300,70207670	
4 (BS)	-7300,70608820	-10,5321