Temperature induced *in situ* reduction of 4,4'-azobispyridine *via* solvothermal reaction

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Figure S1. XRD patterns of complexes **1-6**

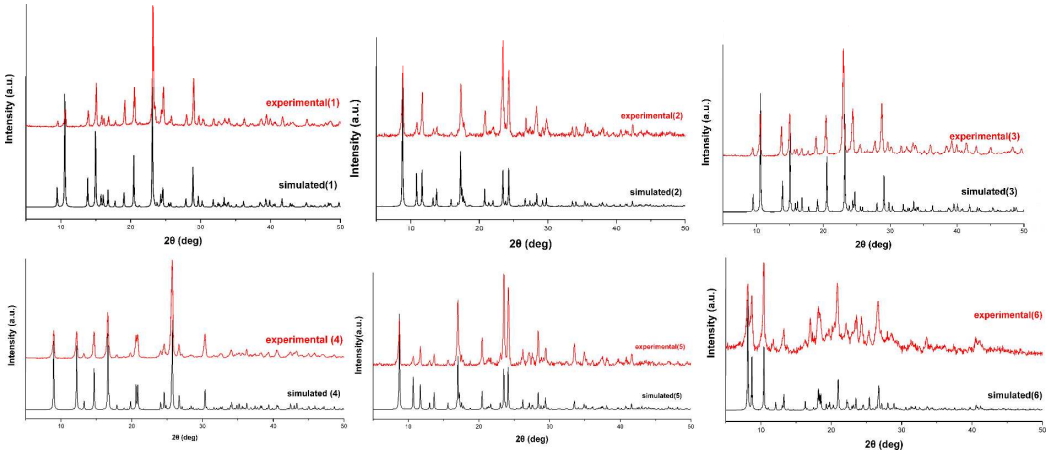


Figure S2. TGA diagrams of complexes **1-6**

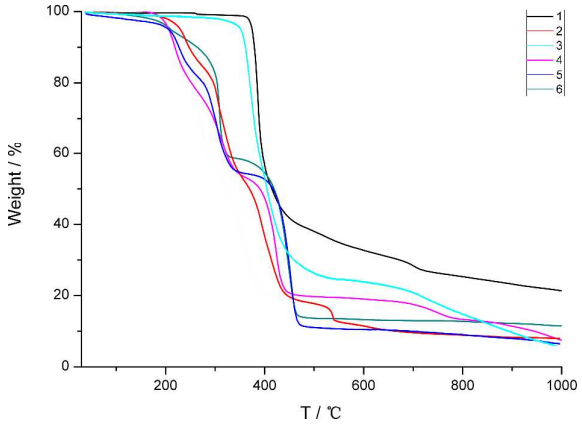


Figure S3. IR spectrum of complexes **1-6** at room temperature

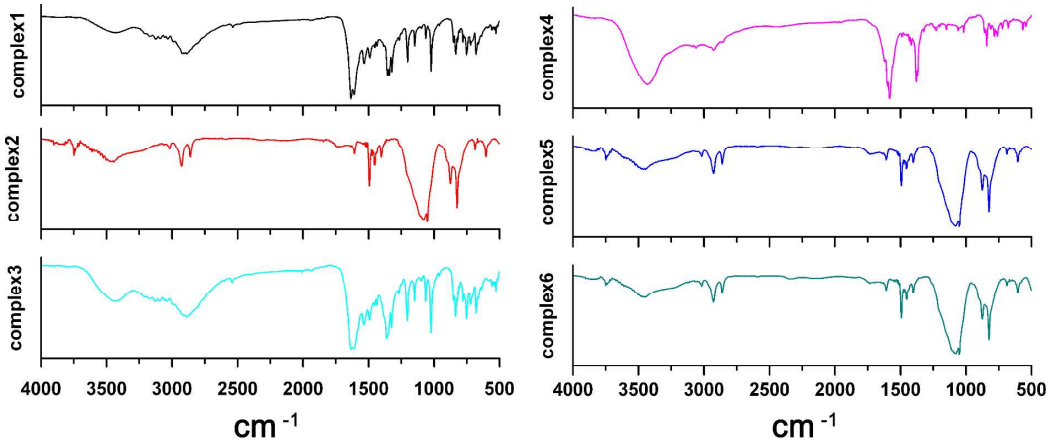


Figure S4. LC-MS (ESI) Spectrum for DMSO digested **1**, 1,2-bis(4-pyridyl)hydrazine (bphy). m/z = 187.4 ($M+H^+$)

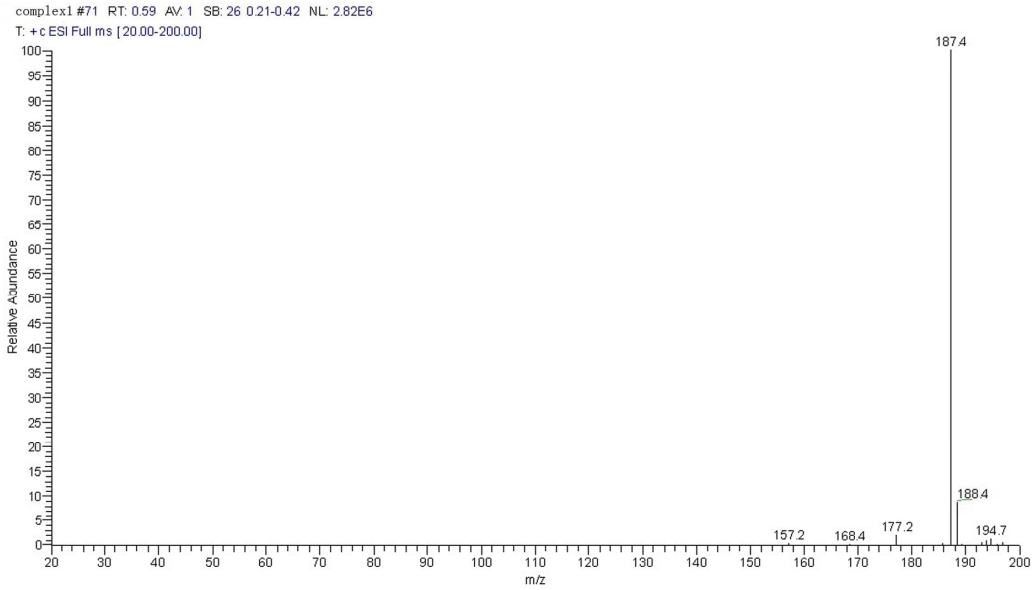


Figure S5. LC-MS (ESI) Spectrum for DMSO digested **2**, 4,4'-azobispyridine (azpy). m/z = 185.5 ($M+H^+$)

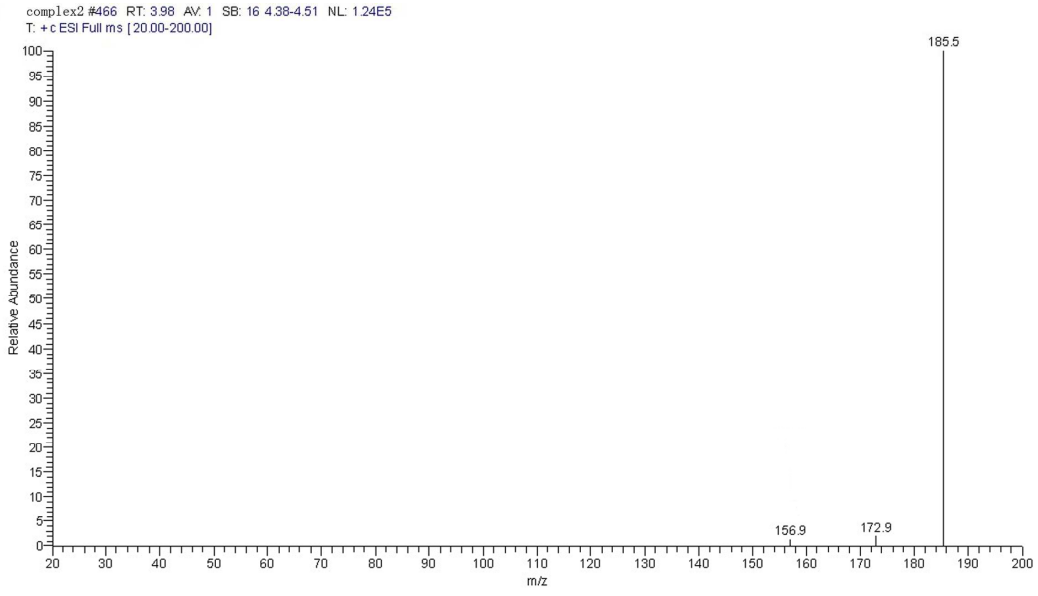


Figure S6. (a) The coordination environment of Zn(Ⅱ) atom in **3** with 30% thermal ellipsoids, all hydrogen atoms are omitted for clarity. (b) The one-dimensional chain in **3** along *a* axis. (c) The two-dimensional layer of **3** connected by H Bonds (red dot line) along *a* axis. (d) The three-dimensional framework of **3** built by C-H···π interaction (blue dot line) along *b* axis.

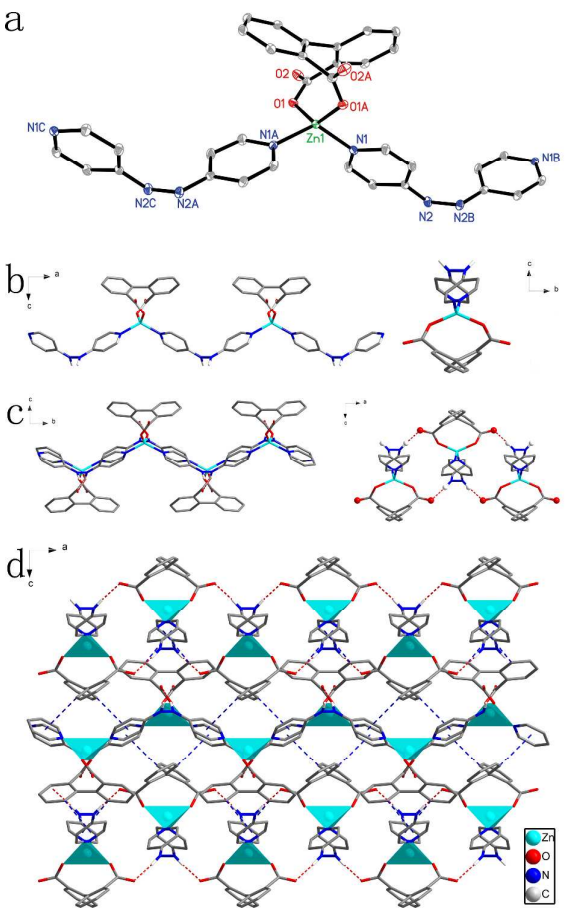


Figure S7. (a) The coordination environment of Mn(Ⅱ) atom in **5** with 30% thermal ellipsoids, all hydrogen atoms and solvent molecules are omitted for clarity. (b) The one-dimensional $[Mn_2(dpa)_2(H_2O)_2]$ chain in **5** along the *c* axis. (c) The two-dimensional layer of **5** pillared by azpy ligands. (d) The three-dimensional framework of **5** built by C-H···O interaction (two-colored dot line) along *b* axis.

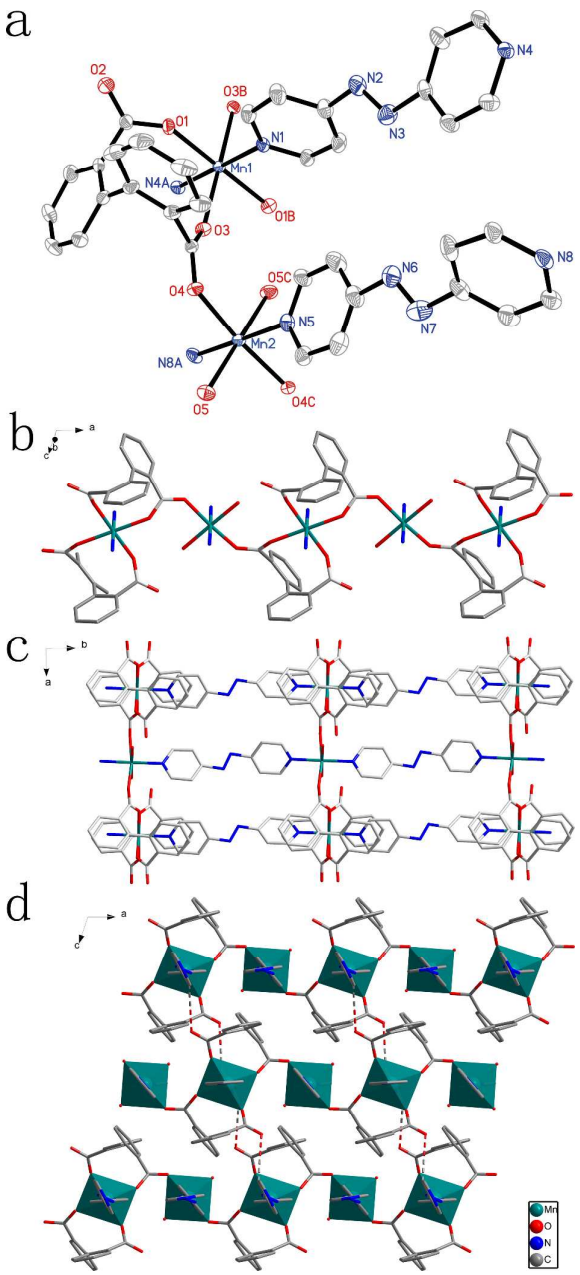


Table S1. Selected Bond Lengths (Å) and Bond Angles (°) for **1**

Bond	Dist.	Bond	Dist.
Co(1)-O(1)^{i}	1.955 (1)	Co(1)-N(1)	2.028 (1)
Co(1)-O(1)	1.955 (1)	Co(1)-N(1)^{i}	2.028 (1)
N2—N2^{ii}	1.391 (3)	N2—H2	0.86 (3)
Angle	(º)	Angle	(º)
O(1)^{i}-Co(1)-O(1)	133.54 (6)	O(1)^{i}-Co(1)-N(1)^{i}	97.40 (5)
O(1)^{i}-Co(1)-N(1)	103.41 (5)	O(1)-Co(1)-N(1)^{i}	103.41 (5)
O(1)-Co(1)-N(1)	97.40 (5)	N(1)-Co(1)-N(1)^{i}	125.58 (7)

Symmetry codes: (i) -*x*, 1-*y*, *z*; (ii) 1-*x*, 1-*y*, *z*.

Table S1-1. Hydrogen-bond Parameters (Å, °) for **1**

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠DHA
N(2)–H(2)···O(2^{i})	0.86(3)	1.94(3)	2.795 (2)	169(2)

Table S2. Selected Bond Lengths (Å) and Bond Angles (°) for **2**

Bond	Dist.	Bond	Dist.
Co1—O1	2.064 (1)	Co2—O4	2.101 (1)
Co1—O1^{i}	2.064(1)	Co2—O4^{iii}	2.101 (1)
Co1—N1	2.157 (3)	Co2—N8^{ii}	2.163 (3)
Co1—N4^{ii}	2.164 (3)	Co2—N5	2.173 (3)
Co1—O3	2.197 (1)	Co2—O5^{iii}	2.091 (1)
Co1—O3^{i}	2.197 (1)	N2—N3	1.217 (4)
Co2—O5	2.091 (1)	N6—N7	1.2313
Angle	(º)	Angle	(º)
O1—Co1—N1	89.44 (5)	O5—Co2—O5^{iii}	178.88 (10)
O1—Co1—O1^{i}	178.87 (11)	O5—Co2—O4	90.26 (5)
O1i—Co1—N1	89.44 (5)	O5^{iii}—Co2—O4	89.83 (5)
O1—Co1—N4^{ii}	90.56 (5)	O5—Co2—O4^{iii}	89.83 (5)
O1i—Co1—N4^{ii}	90.56 (5)	O5^{iii}—Co2—O4^{iii}	90.26 (5)
N1—Co1—N4^{ii}	180.0	O4—Co2—O4^{iii}	170.55 (10)
O1—Co1—O3	99.37 (5)	O5—Co2—N8^{ii}	89.44 (5)
O1i—Co1—O3	80.64 (5)	O5^{iii}—Co2—N8^{ii}	89.44 (5)
N1—Co1—O3	90.29 (4)	O4—Co2—N8^{ii}	94.72 (5)
N4^{ii}—Co1—O3	89.71 (4)	O4^{iii}—Co2—N8^{ii}	94.72 (5)
O1—Co1—O3^{i}	80.64 (5)	O5—Co2—N5	90.56 (5)
O1i—Co1—O3i	99.37 (5)	O5^{iii}—Co2—N5	90.56 (5)
N1—Co1—O3^{i}	90.29 (4)	O4—Co2—N5	85.28 (5)
N4^{ii}—Co1—O3^{i}	89.71 (4)	O4^{iii}—Co2—N5	85.28 (5)
O3—Co1—O3^{i}	179.43 (7)	N8^{ii}—Co2—N5	180.00 (1)

Symmetry codes: (i) -*x*, *y*, -*z*; (ii) *x*, 1+*y*, *z*; (iii) -*x*, *y*, 1-*z*.

Table S3. Selected Bond Lengths (Å) and Bond Angles (°) for **3**

Bond	Dist.	Bond	Dist.
Zn1—O1^{i}	1.963 (1)	Zn1—N1	2.016 (1)
Zn1—O1	1.963 (1)	N2—N2^{ii}	1.387 (3)
Zn1—N1^{i}	2.016 (1)	N2—H2	0.88
Angle	(º)	Angle	(º)
O1^{i}—Zn1—O1	132.25 (6)	O1^{i}—Zn1—N1	97.86 (5)
O1^{i}—Zn1—N1^{i}	103.42 (5)	O1—Zn1—N1	103.42 (5)

O1—Zn1—N1^{i}	97.86 (5)	N1^{i}—Zn1—N1	125.79 (7)

Symmetry codes: (i) 2-*x*, 1-*y*, *z*; (ii) 2-*x*, 2-*y*, *z*.

Table S3-1. Hydrogen-bond Parameters (Å, °) for **3**

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠DHA
N(2)–H(2)···O(2^{i})	0.88	1.95	2.787 (2)	157.8

Table S4. Selected Bond Lengths (Å) and Bond Angles (°) for **4**

Bond	Dist.	Bond	Dist.
Zn(1)-O(1)^{i}	1.989 (1)	Zn(1)-N(1)^{i}	2.183 (2)
Zn(1)-O(1)	1.989 (1)	Zn(1)-N(1)	2.183 (2)
Zn(1)-O(3)	2.020 (2)	N2—N2^{ii}	1.246 (4)
Angle	(º)	Angle	(º)
O(1)^{i}-Zn(1)-O(1)	128.04 (8)	O(3)-Zn(1)-N(1)^{i}	89.78 (4)
O(1)^{i}-Zn(1)-O(3)	115.98 (4)	O(1)^{i}-Zn(1)-N(1)	91.48 (5)
O(3)-Zn(1)-N(1)	115.98 (4)	O(1)-Zn(1)-N(1)	88.71 (5)
O(1)^{i}-Zn(1-N(1)^{i}	88.71 (5)	O(3)-Zn(1)-N(1)	89.78 (4)
O(1)-Zn(1)-N(1)^{i}	91.48 (5)	N(1)^{i}-Zn(1)-N(1)	179.55 (7)

Symmetry codes: (i) 2-*x*, *y*, 1/2-*z*; (ii) 3-*x*, *y*, 1/2-*z*.

Table S4-1. Hydrogen-bond Parameters (Å, °) for **4**

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠DHA
O(3)–H(3A)···O(2^{i})	0.88	1.81	2.684 (2)	173.6

Table S5. Selected Bond Lengths (Å) and Bond Angles (°) for **5**

Bond	Dist.	Bond	Dist.
Mn1—O1^{i}	2.145 (2)	Mn2—O4^{iii}	2.166 (2)
Mn1—O1	2.145 (2)	Mn2—O4	2.166 (2)
Mn1—O3	2.261 (2)	Mn2—O5	2.180 (2)
Mn1—O3^{i}	2.261 (2)	Mn2—O5^{iii}	2.180 (2)
Mn1—N1	2.268 (4)	Mn2—N8^{ii}	2.285 (5)
Mn1—N4^{ii}	2.283 (4)	Mn2—N5	2.302 (5)
N6—N7	1.232 (7)	N3—N2	1.228 (6)
Angle	(º)	Angle	(º)
O1^{i}—Mn1—O1	179.00 (15)	O4^{iii}—Mn2—O4	170.82 (15)
O1^{i}—Mn1—O3	80.69 (7)	O4^{iii}—Mn2—O5	89.68 (8)
O1—Mn1—O3	99.32 (7)	O4—Mn2—O5	90.51 (8)
O1^{i}—Mn1—O3^{i}	99.32 (7)	O4^{iii}—Mn2—O5^{iii}	90.51 (8)
O1—Mn1—O3^{i}	80.69 (7)	O4—Mn2—O5^{iii}	89.68 (8)
O3—Mn1—O3^{i}	178.73 (12)	O5—Mn2—O5^{iii}	177.56 (15)

O1^{i}—Mn1—N1	89.50 (8)	O4^{iii}—Mn2—N8^{ii}	94.59 (7)
O1—Mn1—N1	89.50 (8)	O4—Mn2—N8^{ii}	94.59 (7)
O3—Mn1—N1	90.63 (6)	O5—Mn2—N8^{ii}	88.78 (7)
O3^{i}—Mn1—N1	90.63 (6)	O5^{iii}—Mn2—N8^{ii}	88.78 (7)
O1^{i}—Mn1—N4^{ii}	90.50 (8)	O4^{iii}—Mn2—N5	85.41 (7)
O1—Mn1—N4^{ii}	90.50 (8)	O4—Mn2—N5	85.41 (7)
O3—Mn1—N4^{ii}	89.37 (6)	O5—Mn2—N5	91.22 (7)
O3^{i}—Mn1—N4^{ii}	89.37 (6)	O5^{iii}—Mn2—N5	91.22 (7)
N1—Mn1—N4^{ii}	180.00 (1)	N8^{ii}—Mn2—N5	180.00 (1)

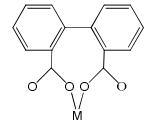
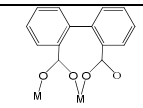
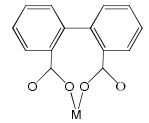
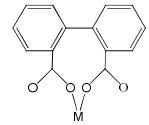
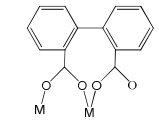
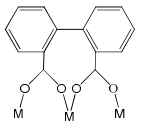
Symmetry codes: (i) 2-*x*, *y*, 1-*z*; (ii) *x*, -1+*y*, *z*; (iii) 2-*x*, *y*, -*z*.

Table S6. Selected Bond Lengths (Å) and Bond Angles (°) for **6**

Bond	Dist.	Bond	Dist.
Mn(1)-O(4)^{i}	2.152 (3)	Mn(2)-O(5)	2.166 (3)
Mn(1)-O(3)	2.166 (3)	Mn(2)-O(8)^{v}	2.169 (3)
Mn(1)-O(1)	2.180 (3)	Mn(2)-O(6)^{vi}	2.179 (3)
Mn(1)-O(2)^{ii}	2.203 (3)	Mn(2)-O(7)	2.193 (3)
Mn(1)-N(4)^{iii}	2.293 (3)	Mn(2)-N(7)	2.328 (3)
Mn(1)-N(1)	2.309 (3)	Mn(2)-N(5)	2.333 (3)
N8—N8^{vii}	1.204 (7)	N6—N6^{viii}	1.233 (7)
N3—N2	1.213 (5)		
Angle	(º)	Angle	(º)
O(4)^{i}-Mn(1)-O(3)	89.69 (10)	O(6)^{vi}-Mn(2)-O(7)	177.84 (10)
O(4)^{i}-Mn(1)-O(1)	170.33 (10)	O(5)-Mn(2)-N(7)	96.83 (11)
O(3)-Mn(1)-O(1)	97.39 (10)	O(8)^{v}-Mn(2)-N(7)	87.93 (11)
O(4)^{i}-Mn(1)-O(2)^{ii}	86.32 (10)	O(6)^{vi}-Mn(2)-N(7)	93.51 (11)
O(3)-Mn(1)-O(2)^{ii}	173.92 (10)	O(7)-Mn(2)-N(7)	84.91 (11)
O(1)-Mn(1)-O(2)^{ii}	87.12 (10)	O(5)-Mn(2)-N(5)	85.57 (11)
O(4)^{i}-Mn(1)-N(4)^{iii}	89.78 (11)	O(8)^{v}-Mn(2)-N(5)	89.65 (11)
O(3)-Mn(1)-N(4)^{iii}	82.58 (10)	O(6)^{vi}-Mn(2)-N(5)	86.24 (11)
O(1)-Mn(1)-N(4)^{iii}	97.62 (10)	O(7)-Mn(2)-N(5)	95.24 (10)
O(2)^{ii}-Mn(1)-N(4)^{iii}	92.81 (10)	N(7)-Mn(2)-N(5)	177.57 (12)
O(4)^{i}-Mn(1)-N(1)	90.13 (11)	O(5)-Mn(2)-O(8)^{v}	173.27 (10)
O(3)-Mn(1)-N(1)	96.04 (10)	O(5)-Mn(2)-O(6)^{vi}	85.39 (10)
O(1)-Mn(1)-N(1)	82.62 (10)	O(8)^{v}-Mn(2)-O(6)^{vi}	89.58 (10)
O(2)^{ii}-Mn(1)-N(1)	88.57 (11)	O(5)-Mn(2)-O(7)	96.28 (10)
N(4)^{iii}-Mn(1)-N(1)	178.62 (11)	O(8)^{v}-Mn(2)-O(7)	88.85 (10)

Symmetry codes: (i) -*x*, 2-*y*, -*z*; (ii) 1-*x*, 2-**y**, -*z*; (iii) *x*, 1+*y*, *z*; (iv) *x*, -1+*y*, *z*; (v) 1-*x*, 1-*y*, 1-*z*; (vi) -*x*, 1-*y*, 1-*z*.

Table S7. The list of the coordination modes and dihedral angles in complexes **1**, **2**, **3**, **4**, **5**, **6**

complex	Dihedral angle between phenyls	Dihedral angle between phenyl and carboxylate group	Coordination mode	
1	62.318	51.664	 chelating bis-monodentate mode	noncentrosymmetric
2	65.674	57.378 61.449	 bridging monodentate-bidentate mode	chiral
3	62.218	51.330	 chelating bis-monodentate mode	noncentrosymmetric
4	60.619	50.498	 chelating bis-monodentate mode	centrosymmetric
5	63.015	58.386 60.043	 bridging monodentate-bidentate mode	chiral
6	69.628	33.572 42.069	 bridging bis-bidentate mode	centrosymmetric