Binuclear Mn^{2+} complexes of a biphenyltetracarboxylic acid with variable N-donor ligands: syntheses, structures, and magnetic properties

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Table S1 Selected bond lengths (Å) and angles (°) for compounds **1**−**4**.

Compound **1**			
Mn1−O5A	2.090 (3)	Mn2−O6E	2.105 (3)
Mn1−O3	2.108 (3)	Mn2−O4F	2.143 (3)
Mn1−O1	2.1194 (19)	Mn2−O4	2.143 (3)
Mn1−O1B	2.1194 (19)	Mn2−N2F	2.244 (3)
Mn1−N1	2.231 (3)	Mn2−N2	2.244 (3)
Mn2−O2B	2.105 (2)	O2−Mn2G	2.105 (2)
Mn2−O2C	2.105 (2)	O5−Mn1H	2.090 (3)
Mn2−O6D	2.105 (3)	O6−Mn2I	2.105 (3)
O5A−Mn1−O3	92.38 (15)	O6E−Mn2−O4F	52.11 (16)
O5A−Mn1−O1	130.04 (5)	O2B−Mn2−O4	88.59 (11)
O3−Mn1−O1	90.34 (7)	O2C−Mn2−O4	132.88 (12)
O5A−Mn1−O1B	130.04 (5)	O6iE−Mn2−O4	52.11 (16)
O3−Mn1−O1B	90.34 (7)	O6E−Mn2−O4	100.17 (16)
O1−Mn1−O1B	99.79 (10)	O4F−Mn2−O4	123.4 (2)
O5A−Mn1−N1	87.84 (12)	O2B−Mn2−N2F	175.59 (9)
O3−Mn1−N1	179.78 (11)	O2C−Mn2−N2F	87.99 (14)
O1−Mn1−N1	89.52 (7)	O6D−Mn2−N2F	48.78 (13)
O1B−Mn1−N1	89.52 (7)	O6F−Mn2−N2F	90.99 (13)
O2B−Mn2−O2C	92.54 (14)	O4F−Mn2−N2F	51.50 (13)
O2B−Mn2−O6D	126.81 (12)	O4−Mn2−N2F	87.84 (13)
O2C−Mn2−O6D	92.19 (11)	O2B−Mn2−N2	87.99 (14)
O2B−Mn2−O6E	92.19 (11)	O2C−Mn2−N2	175.59 (9)
O2C−Mn2−O6E	126.81 (12)	O6D−Mn2−N2	90.99 (13)
O6D−Mn2−O6E	125.1 (2)	O6E−Mn2−N2	48.78 (13)
O2B−Mn2−O4F	132.88 (12)	O4F−Mn2−N2	87.84 (13)
O2C−Mn2−O4F	88.59 (11)	O4−Mn2−N2	51.49 (13)
O6D−Mn2−O4F	100.17 (16)	N2F−Mn2−N2	91.8 (2)

Symmetry codes: A $x, y, z + 1$; B $-x, y, z$; C $x - 1/2, y, -z + 2$; D $-x, y, z + 1$; E $x - 1/2, y, -z + 1$; F $-x - 1/2, y, -z + 2$; G $x + 1/2, y, -z + 2$; H $x, y, z - 1$; I $x + 1/2, y, -z + 1$.

Compound **2**			
Mn1−O3A	2.1001(17)	Mn1−O4B	2.1245(16)
Mn1−N4C	2.2366(18)	Mn1−N1	2.2624(19)
Mn1−O1	2.3173(17)		

O3A−Mn1−O4B	106.29(5)	O3A−Mn1−N4C	87.58(6)
O4B−Mn1−N4C	85.59(6)	O3A−Mn1−O2	98.87(5)
O4B−Mn1−O2	154.75(5)	N4C−Mn1−O2	97.73(6)
O3A−Mn1−N1	98.79(6)	O4B−Mn1−N1	88.96(6)
N4C−Mn1−N1	172.58(6)	O2−Mn1−N1	85.10(6)
O3A−Mn1−O1	154.59(6)	O4B−Mn1−O1	97.99(6)
N4C−Mn1−O1	86.92(6)	O2−Mn1−O1	57.44(5)
N1−Mn1−O1	88.86(6)		

Symmetry codes: A $-x, -y+1, -z+1$; B $x-1, y, z$; C $x-1, y+1, z$; D $-x, -y+1, -z+2$

Compound **3**			
Mn1−O(1)	2.1025(17)	Mn1−O5A	2.1214(17)
Mn1−N4B	2.204(2)	Mn1−N1	2.215(2)
Mn1−O3B	2.2754(17)	Mn1−O4B	2.4378(17)
Mn2−O2	2.1301(17)	Mn2−O6A	2.1412(17)
Mn2−O7D	2.3022(17)	Mn2−O8D	2.3437(17)
Mn2−N5	2.225(2)	Mn2−N8C	2.227(2)
O1−Mn1−O5A	115.21(7)	O1−Mn1−N4B	94.63(8)
O5A−Mn1−N4B	91.43(8)	O1−Mn1−N1	90.25(7)
O5A−Mn1−N1	89.04(7)	N4B−Mn1−N1	174.36(8)
O1−Mn1−O3B	146.16(6)	O5A−Mn1−O3B	98.34(6)
N4B−Mn1−O3B	88.52(7)	N1−Mn1−O3B	85.85(7)
O1−Mn1−O4B	90.66(6)	O5A−Mn1−O4B	153.73(6)
N4B−Mn1−O4B	90.86(7)	N1−Mn1−O4B	86.25(7)
O3B−Mn1−O4B	55.57(6)	O2−Mn2−O6A	116.48(7)
O2−Mn2−N5	86.95(7)	O6−Mn2−N5	93.53(7)
O2−Mn2−N8C	86.92(7)	O6A−Mn2−N8C	95.84(8)
N5−Mn2−N8C	170.38(8)	O2−Mn2−O7D	154.03(6)
O6A−Mn2−O7D	88.96(6)	N5−Mn2−O7D	86.27(7)
N8C−Mn2−O7D	96.06(7)	O2−Mn2−O8D	98.33(7)
O6A−Mn2−O8D	145.19(6)	N5−Mn2−O8D	87.79(7)
N8C−Mn2−O8D	85.77(7)	O7D−Mn2−O8D	56.38(6)

Symmetry codes: A $x+1, y, z$; B $x+1/2, -y+3/2, -z$; C $x-1/2, -y+3/2, -z+1$;
D $x+1/2, -y+3/2, -z+1$

Compound **4**			
Mn1−O4A	2.120(2)	Mn1−O3B	2.122(2)
Mn1−N1	2.225(3)	Mn1−N4C	2.258(3)
Mn1−O1	2.260(2)	Mn1−O2	2.351(2)
O4A−Mn1−O3B	105.03(8)	O4A−Mn1−N1	89.19(10)
O3B−Mn1−N1	86.33(10)	O4A−Mn1−N4C	92.62(10)
O3B−Mn1−N4C	94.97(9)	N1−Mn1−N4C	177.42(10)
O4A−Mn1−O1	154.26(8)	O3B−Mn1−O1	100.69(8)
N1−Mn1−O1	91.47(9)	N4C−Mn1−O1	86.10(9)
O4A−Mn1−O2	97.33(8)	O3B−Mn1−O2	156.53(9)
N1−Mn1−O2	86.95(9)	N4C−Mn1−O2	90.99(9)
O1−Mn1−O2	57.04(7)		

Symmetry codes: A $x, y+1, z$; B $-x, -y, -z+1$; C $x-1, y-1, z+1$

Table S2 Hydrogen-bond geometry (Å, °) for compound **3**.

D−H···A	D−H	H···A	D···A	D−H···A
C44−H44...O9D	0.93	2.29	3.201(9)	167.0
C41−H41A...O10G	0.97	2.48	3.372(10)	152.6
C34−H34A...O4H	0.97	2.62	3.422(9)	140.3
C32−H32...O7D	0.93	2.61	3.122(10)	115.1
C27−H27B...O8I	0.97	2.57	3.458(9)	152.1
C17−H17...O10B	0.93	2.55	3.297(10)	137.4
O10−H10B...O4	0.82	2.12	2.883(8)	153.9
O10−H10A...O3E	0.82	2.00	2.785(7)	158.4
O9−H9B...O8D	0.82	1.94	2.754(7)	168.4
O9−H9A...O7	0.82	1.91	2.730(7)	176.2

Symmetry codes: D $x + 1/2, -y + 3/2, -z + 1$ E $x - 1/2, -y + 3/2, -z$ G $-x + 3/2, -y + 2, z + 1/2$ H $-x + 1, y + 1/2, -z + 1/2$ I $-x + 1/2, -y + 1, z - 1/2$

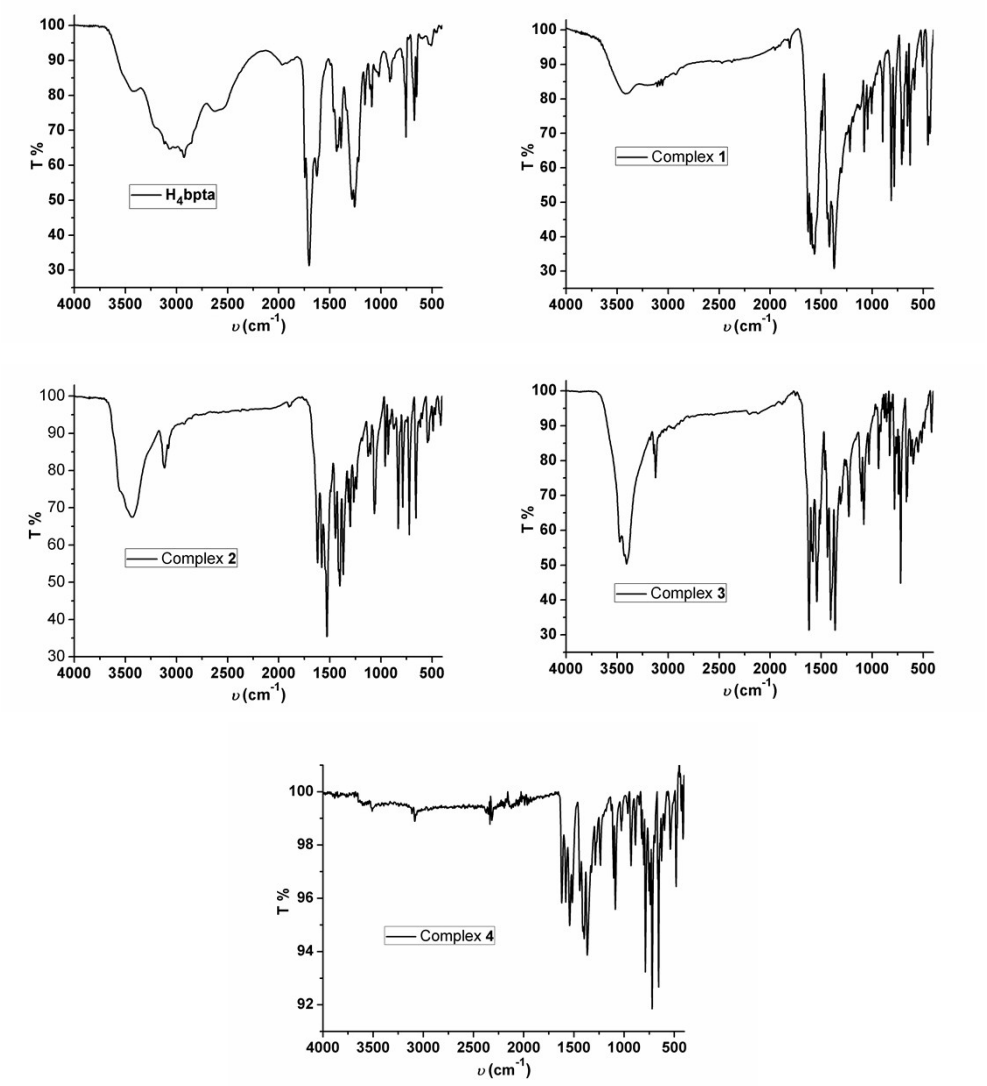

Fig. S1. The IR spectra of H_4bpta ligand and compounds **1**−**4**.

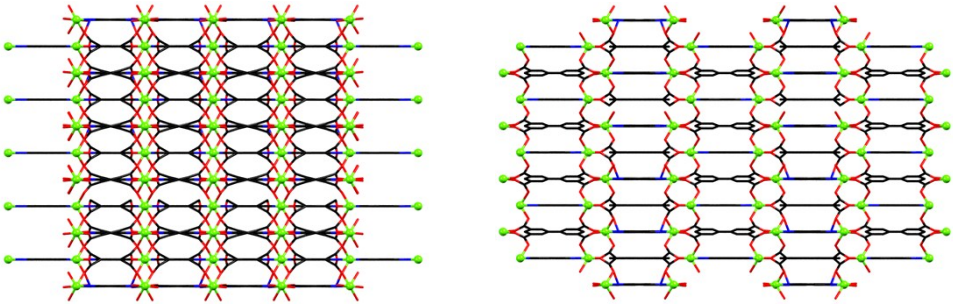

Fig. S2. The 3D network structure of compound **1** overlaying the $bpta^{4-}$ and 4,4′-bipy ligands viewed along the *b* and *c* axis.

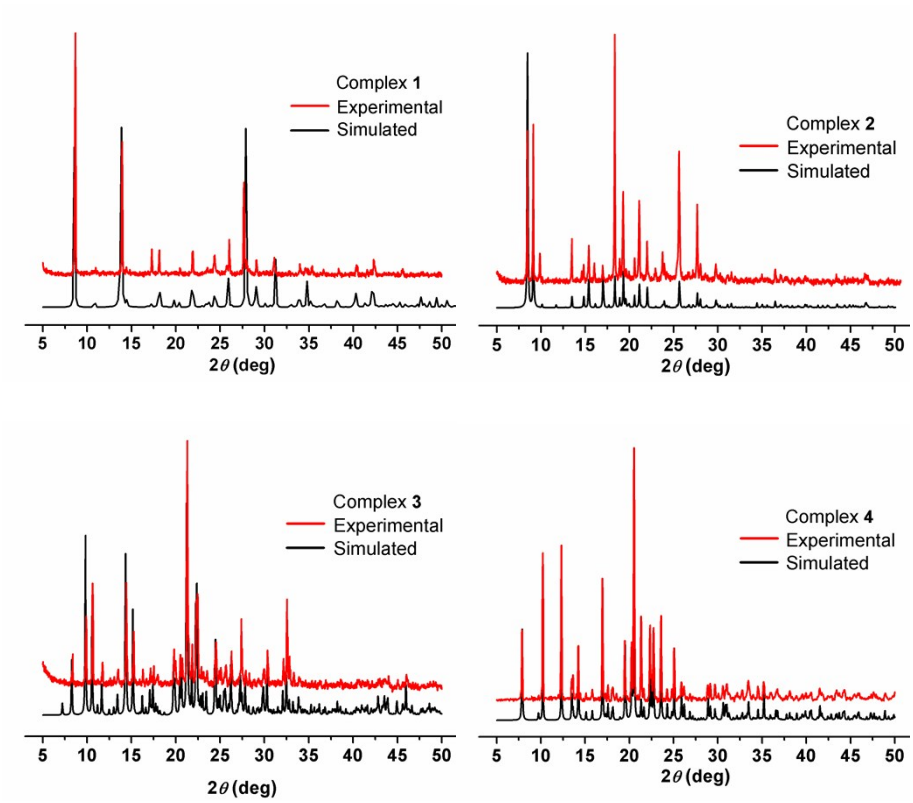

Fig. S3. Comparison of the simulated and experimental PXRD patterns of compounds **1**−**4**.

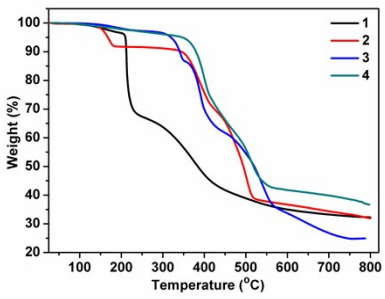

Fig. S4. TG curves of compounds **1**−**4**.

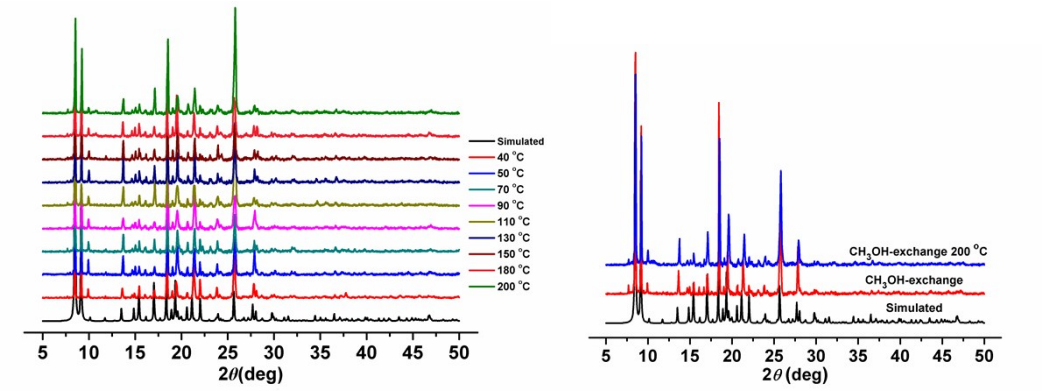

Fig. S5. (a) The PXRD patterns of compound **2** at 40−200 °C; (b) PXRD patterns of **2** immersed in MeOH for 3 days and PXRD patterns of **2**a after heated at 200 °C under vacuum for 3 h.

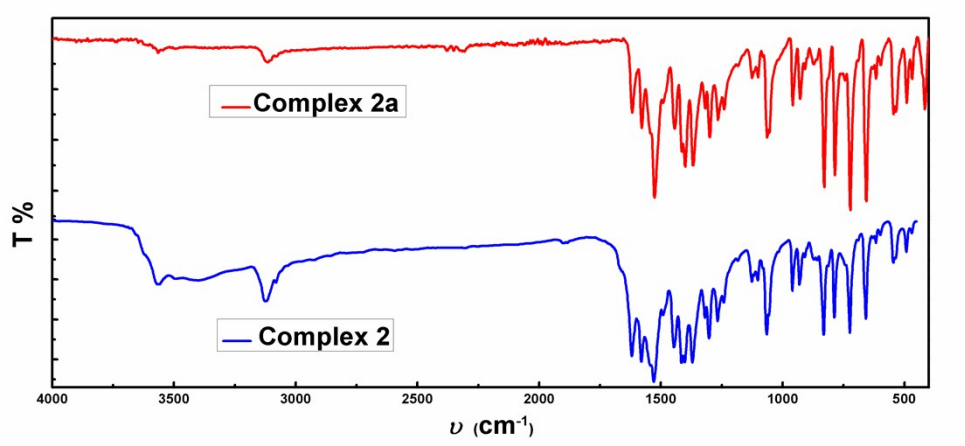

Fig. S6. The IR spectra of compounds **2** and **2a** without solvent molecules.