

***Electronic Supplementary Information***

**A versatile V-shaped tetracarboxylate building block for  
constructing mixed-ligand Co(II) and Mn(II) complexes  
incorporating with various N-donor co-ligands**

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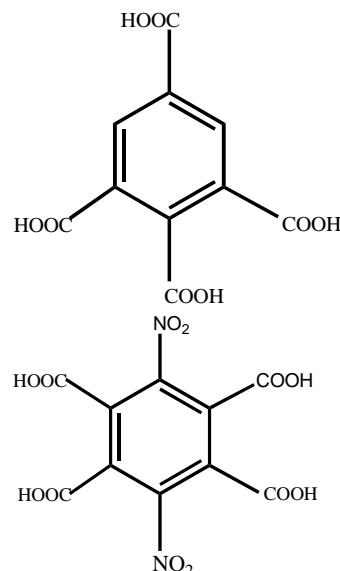
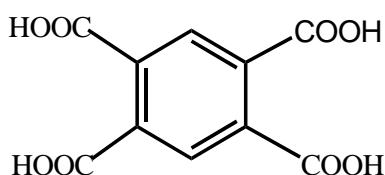
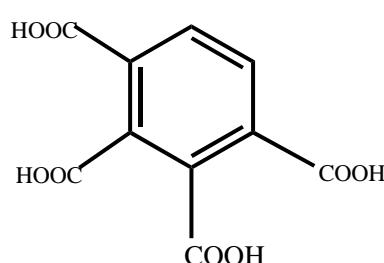
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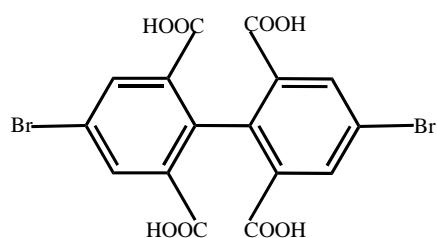
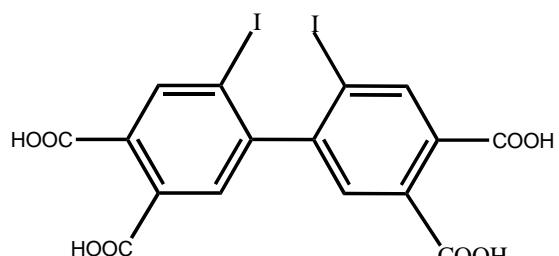
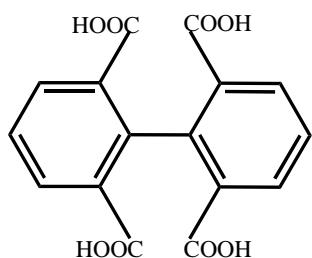
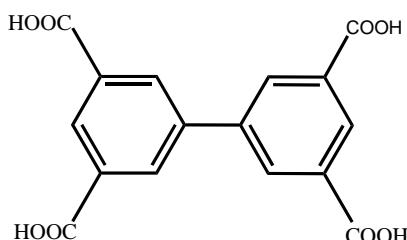
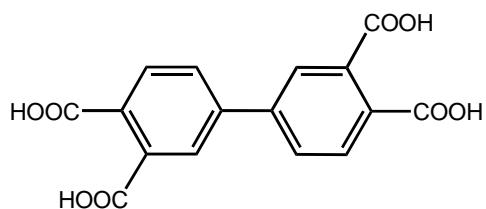
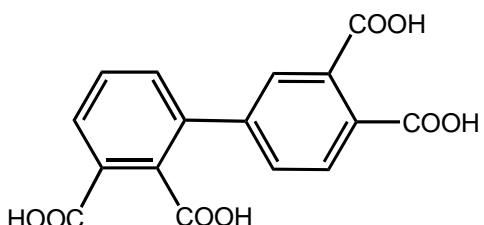
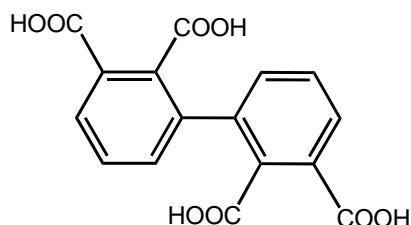
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**Chart S1. Representation for the reported aromatic polycarboxylic acids**

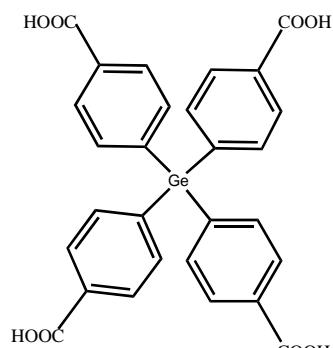
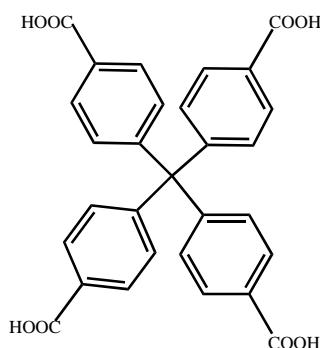
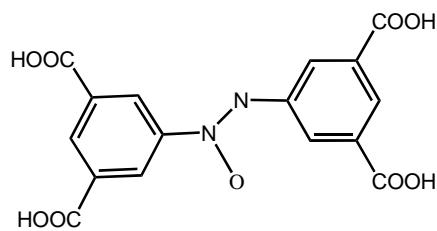
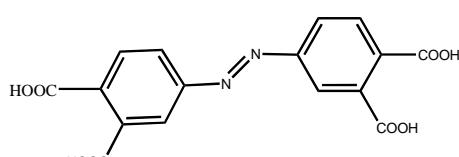
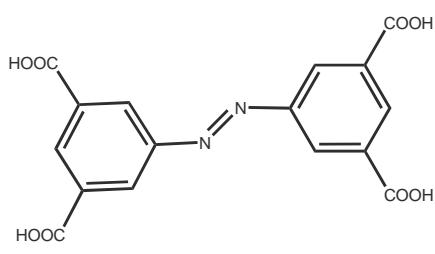
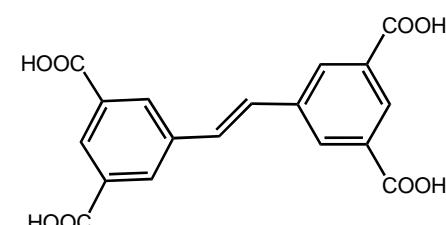
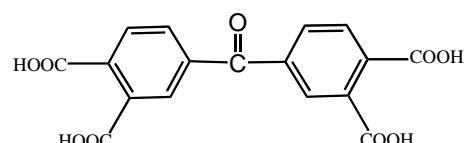
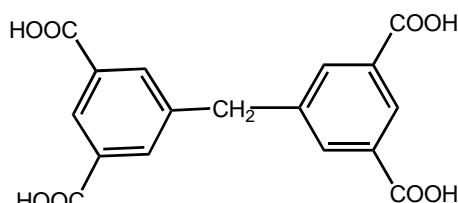
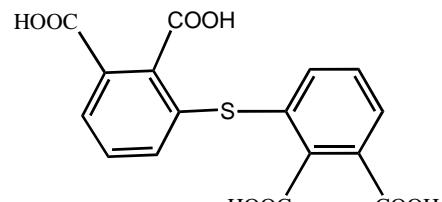
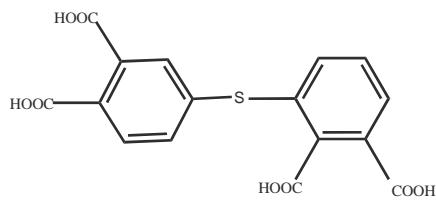
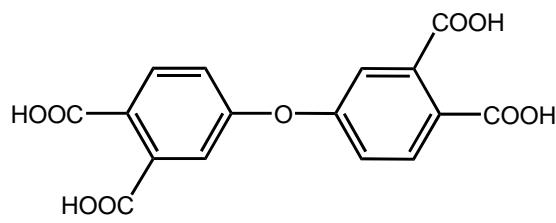
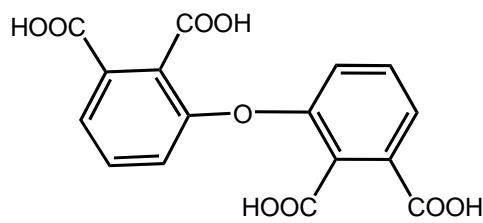
**a) Monophenyl-tetracarboxyl compounds**

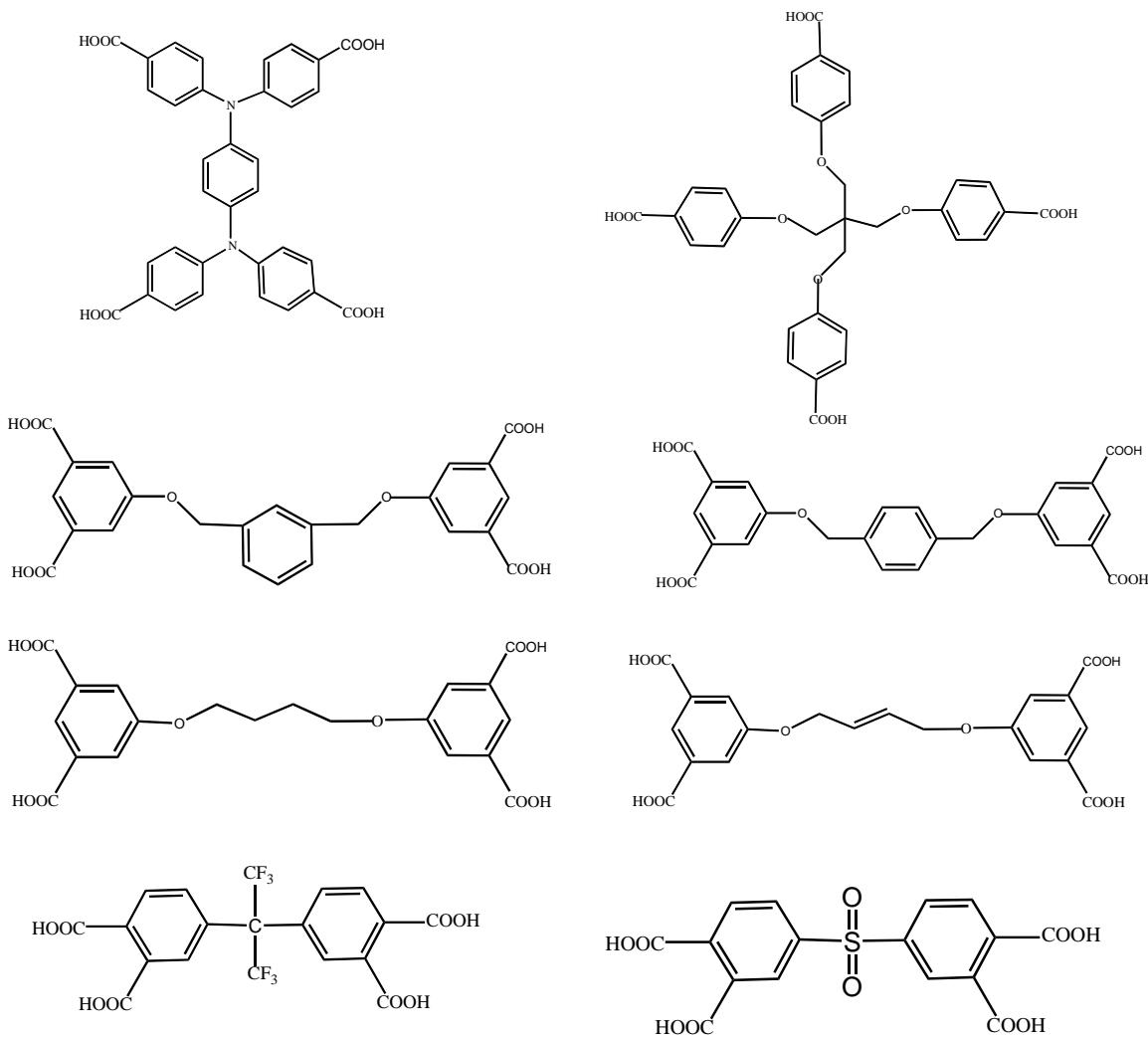


**b) Biphenyl-tetracarboxyl compounds**

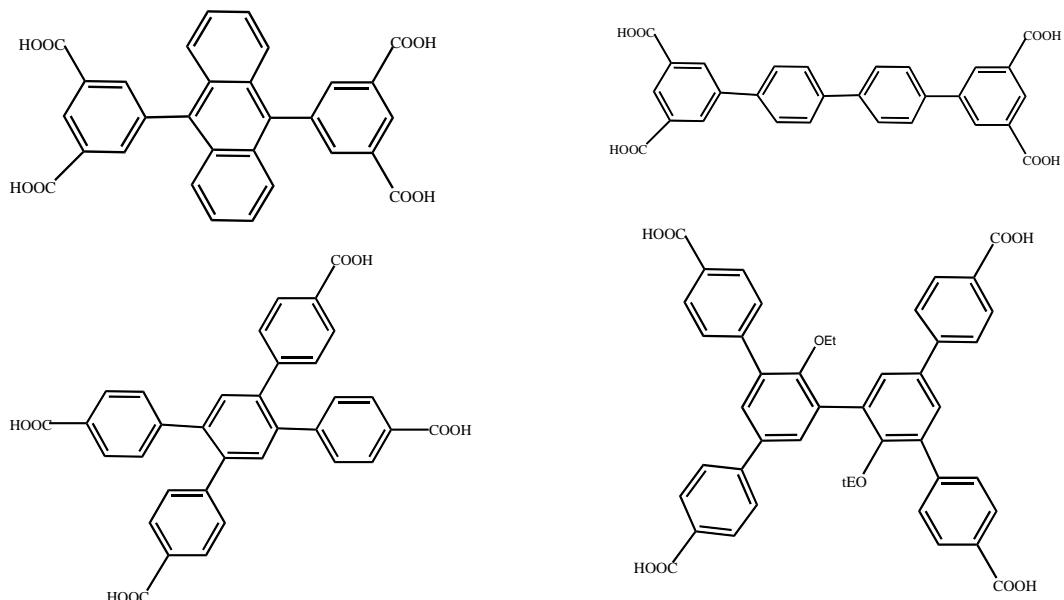


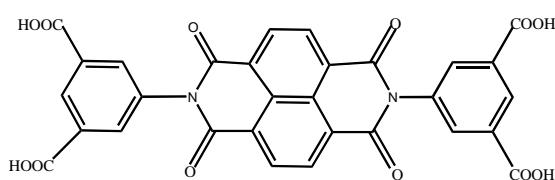
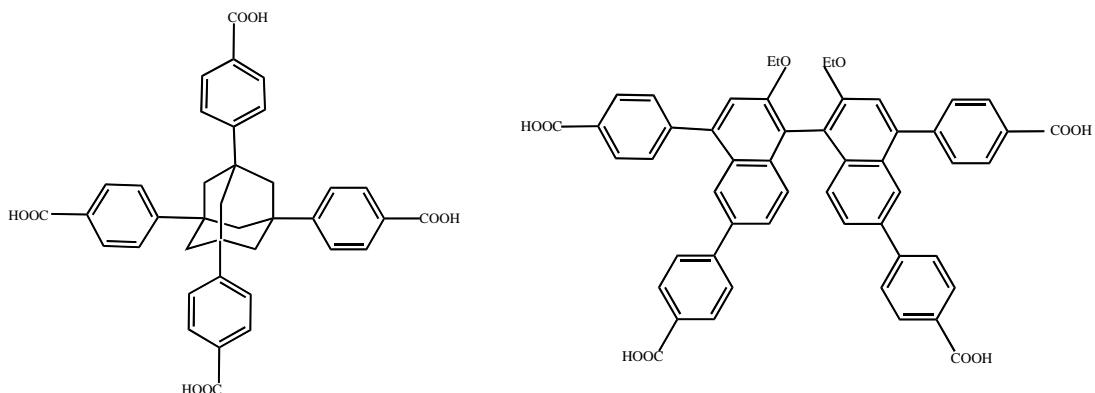
c) Tetracarboxyl compounds containing interval group



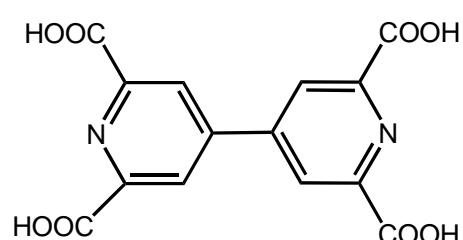
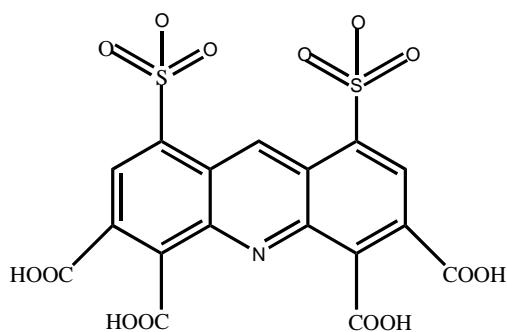
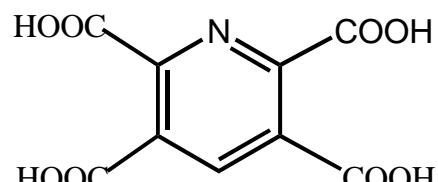
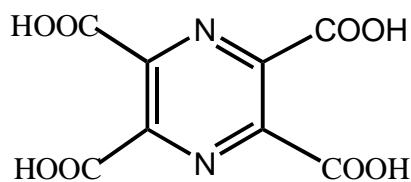


**d) Mutiphenyl-tetracarboxyl compounds**





**e) N-heterocyclic-based tetracarboxyl compounds**



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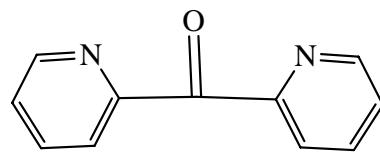
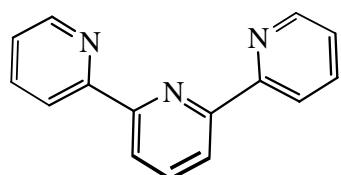
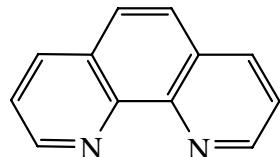
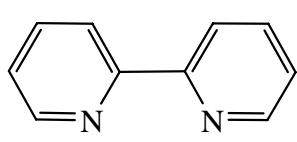
S2 For examples(for Biphenyl-tetracarboxylate), see: (a) X. R. Hao, Z. M. Su, Y. H. Zhao, K. Z. Shao, Y. Wang, *Acta Crystallogr.,Sect.C(Cr.Str.Comm.)*, 2005,**61**,m469;(b)X.L. Wang, C. Qin, E.B. Wang, L. X., *Eur.J.Inorg.Chem.*, 2005,3418;(c)G.P. Yang, Y.Y. Wang, Ho. Wang, C.J. Wang, G.L. Wen, Q.Z. Shi, S.M. Peng , *J.Mol.Struct.*, 2008,**888**,366;(d)S.R. Zhu, H. Zhang, M. Shao, Y.M. Zhao, M.X. Li ,*Transition Met.Chem.*, 2008,**33**,669;(e)D. Zhou, M. Shao, X. He, Y.M. Zhao, S.R. Zhu , *Acta Crystallogr.,Sect.E(Structure Rep.Online)*, 2009,**65**,m562;(f)G.X. Liu, K. Zhu, H. Chen, R.Y. Huang, X.M. Ren , *Z.Anorg.Allg.Chem.*, 2009,**635**,156;(g)S.J. Deng, N. Zhang, W.M. Xiao, C. Chen , *Inorg. Chem. Commun.*, 2009,**12**,157; (h)G.P. Yang, Y.Y. Wang, L.F. Ma, J.Q.Liu, Y.P.Wu, W.P. Wu, Q.Z. Shi , *Eur.J.Inorg.Chem.*, 2007, 3892;(i)C. Qin, X.L. Wang, E.B. Wang , *Acta Crystallogr.,Sect.E(Structure Rep.Online)*, 2007,**63**,m3073;(j)D.F. Weng, X.J. Zheng, L.C. Li, W.W. Yang, L.P. Jin , *Discuss. Far. Soc.*, 2007,4822;(k)J.J. Wang, M.L.Yang, H.M. Hu, G.L. Xue, D.S. Li, Q.Z. Shi ,*Z.Anorg.Allg.Chem.*, 2007,**633**,341; (l)Y. Wang, Y.Q. Li, Y.Z. Shen *Acta Crystallogr.,Sect.E(Structure Rep.Online)* 2008,**64**,m1203; (m)P.Holy, J.Zavada, J.Zezula, I.Cisarova, J.Podlaha *Collect.Czech.Chem.Commun.* 2001,**66**, 820.

S3 For examples (for contained interval group-tetracarboxylate),see: (1)P.X. Yin, Z.J. Li, X.Y. Cao, Y.Y. Qin, Y.G. Yao , *Acta Crystallogr.,Sect.E(Structure Rep.Online)*, 2007,**63**,m2258;(2)Q. Chu, G.X. Liu, Y.Q.Huang, X.F. Wang, W.Y. Sun , *Dis. Far.Soc.*, 2007,4302;(3)W. Zhang, L. Yao, R.J. Tao , *Acta Crystallogr.,Sect.E(Structure Rep.Online)*, 2008,**64**,m169;(4)Q. Chu, G.X.Liu, Y.Q.Huang, X.F. Wang, W.Y. Sun, *Disc Far. Soc.*, 2007,4302; (5)Y.Y. Yang, L.Szeto, W.T. Wong, *Appl. Organometallic Chem.*, 2003,**17**,958; (6)J. Zhang, Z.J.Li, J.K.Cheng, Y. Kang, Y.Y. Qin, Y.G. Yao , *New J.Chem.(Nouv.J.Chim.)*, 2005,**29**,421;(7)J. Hong, *J.Mol.Struct.*, 2005,**752**,166;(8)X. Zhou, Z. W. Wang, Z. R. Pan, Y. Z. Li, H. G. Zheng , *J.Coord.Chem.*, 2008,**61**,1078; (9)Z.F. Li, S.W. Wang, Q. Zhang, X.J. Yu ,*Acta Crystallogr.,Sect.E(Structure Rep.Online)*, 2007,**63**, m2312;(10)Y.X. Gao, L. B. Wang, Y. L. Niu , *Acta Crystallogr.,Sect.E (Structure Rep.Online)*, 2007,**63**,m1844;(11)L.J. Hao, T.L.Yu , *Acta Crystallogr.,Sect.E (Structure Rep.Online)*, 2007,**63**, m2184; (12)X.H. Yuan, W.Z. Zhang, Y.H. Chu , *Acta Crystallogr.,Sect.E(Structure Rep.Online)*, 2008,**64**,m810;(13)Q.B. Bo, Z.X. Sun, G.L. Song, F. Li, G.X.Sun , *Peptide Science*, 2007,**17**,615;(14)X.M. Li, Y. H.Dong, Q.W.Wang, Y.C. Cui, B. Liu , *Chinese J.Struct. Chem.(Jiegou Huaxue)*, 2007,**26**,1495; (15)Z. Lin, Y.J. Zhong, M.X. Wang, J.F. Huang, Y.M. Dai ,*Acta Crystallogr.,Sect.E(Structure Rep.Online)*, 2007,**63**,m656; (16)L. Lu, J. Wang, J.W. Bai, Y. Hou, B. Yang, Ba.Z. Zhao, *Cryst.Res.and Technol.*, 2008,**43**,1327;(17)J.W. Bai, J. Wang, Y. Hou, Ba.Z. Zhao, Qi. Fu, *Acta Crystallogr., Sect.E(Structure Rep.Online)*, 2008,**64**,m3; (18)J.B.Lambert, Zhongqiang Liu, *Chunqing Liu Organometallics* 2008,

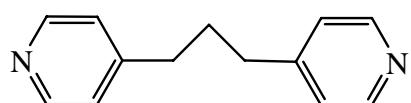
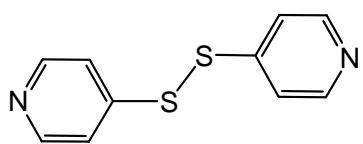
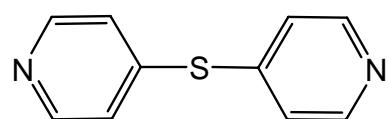
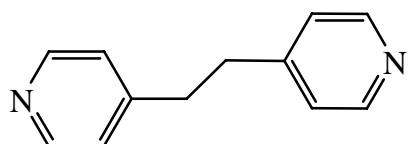
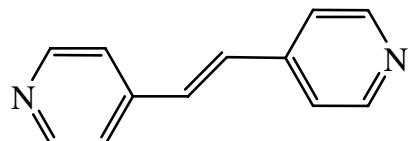
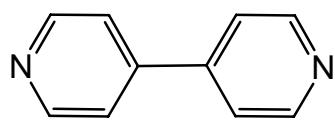
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**Chart S2. Representation for the reported N-donor co-ligands**

**a) Chelating N-donor ligands**



**b) Bridging N-donor ligands**



**Table S1 Selected bond lengths [Å] and angles [°] for complexes 1<sup>a</sup>, 2<sup>b</sup>, 3,4<sup>c</sup> and 5<sup>d</sup>**

<b>1</b>			
Co1-O11	2.040(5)	O11-Co1-O1	93.8(2)
Co1-N2	2.067(5)	N2-Co1-O1	89.16(19)
Co1-O1	2.111(5)	O11-Co1-N1	101.2(2)
Co1-N1	2.140(6)	N2-Co1-N1	76.5(2)
Co1-O9#1	2.159(4)	O1-Co1-N1	93.5(2)
Co1-N3	2.171(6)	O11-Co1-O9#1	87.05(19)
O9-Co1#2	2.158(4)	N2-Co1-O9#1	89.92(18)
O11-Co1-N2	176.4(2)	O1-Co1-O9#1	178.69(18)
N1-Co1-O9#1	85.34(19)	N1-Co1-N3	152.2(2)
O11-Co1-N3	106.4(2)	O9#1-Co1-N3	93.38(19)
N2-Co1-N3	75.8(2)	O1-Co1-N3	87.3(2)
<b>2</b>			
Co1-O3#1	2.068(3)	Co2-O9	2.024(3)
Co1-O1	2.075(3)	Co2-O7	2.053(3)
Co1-N2	2.098(4)	Co2-O13	2.076(3)
Co1-O11	2.130(3)	Co2-N4	2.135(3)
Co1-O12	2.131(3)	Co2-O14	2.140(3)
Co1-N1	2.142(4)	Co2-N3	2.170(4)
O3#1-Co1-O1	87.97(12)	O9-Co2-O7	88.38(12)
O3#1-Co1-N2	93.90(13)	O9-Co2-O13	170.71(14)
O1-Co1-N2	172.73(14)	O7-Co2-O13	88.18(13)
O3#1-Co1-O11	178.06(13)	O9-Co2-N4	91.09(13)
O1-Co1-O11	91.14(12)	O7-Co2-N4	179.23(13)
N2-Co1-O11	87.19(13)	O13-Co2-N4	92.43(14)
O3#1-Co1-O12	90.44(12)	O9-Co2-O14	87.63(13)
O1-Co1-O12	91.60(13)	O7-Co2-O14	89.48(12)
O11-Co1-O12	87.86(13)	O13-Co2-O14	83.72(13)
O3#1-Co1-N1	85.88(13)	N4-Co2-O14	91.05(13)
O1-Co1-N1	95.15(15)	O9-Co2-N3	102.02(13)
N2-Co1-N1	77.99(16)	O7-Co2-N3	102.42(13)
O11-Co1-N1	95.92(14)	O13-Co2-N3	87.15(14)
O12-Co1-N1	172.18(15)	N4-Co2-N3	77.15(14)
<b>3</b>			
Mn1-O1	2.071(2)	Mn2-O15	2.032(2)
Mn1-O7	2.074(2)	Mn2-O12	2.038(2)
Mn1-N2	2.120(3)	Mn2-O5	2.110(2)
Mn1-N1	2.129(3)	Mn2-N4	2.126(3)
Mn1-O2	2.137(2)	Mn2-N3	2.129(2)
Mn1 -O3	2.224(2)	Mn2-O4	2.170(2)
O1-Mn1-O7	98.19(8)	O15-Mn2-O12	87.70(10)
O1-Mn1-N2	93.32(9)	O15-Mn2-O5	85.98(9)
O7-Mn1-N2	163.62(9)	O12-Mn2-O5	168.60(9)
O1-Mn1-N1	88.39(9)	O15-Mn2-N4	179.52(10)
O7-Mn1-N1	90.25(9)	O12-Mn2-N4	92.23(10)
N2-Mn1-N1	78.42(10)	O5-Mn2-N4	94.17(9)
O1-Mn1-O2	172.02(9)	O15-Mn2-N3	101.30(10)
O7-Mn1-O2	83.30(8)	O12-Mn2-N3	100.21(10)
N2-Mn1-O2	86.91(9)	O5-Mn2-N3	90.34(9)
N1-Mn1-O2	99.46(10)	N4-Mn2-N3	78.25(10)
O1-Mn1-O3	84.96(8)	O15-Mn2-O4	90.62(10)
O7-Mn1-O3	92.15(8)	O12-Mn2-O4	83.72(9)
N2-Mn1-O3	100.47(9)	O5-Mn2-O4	86.86(9)

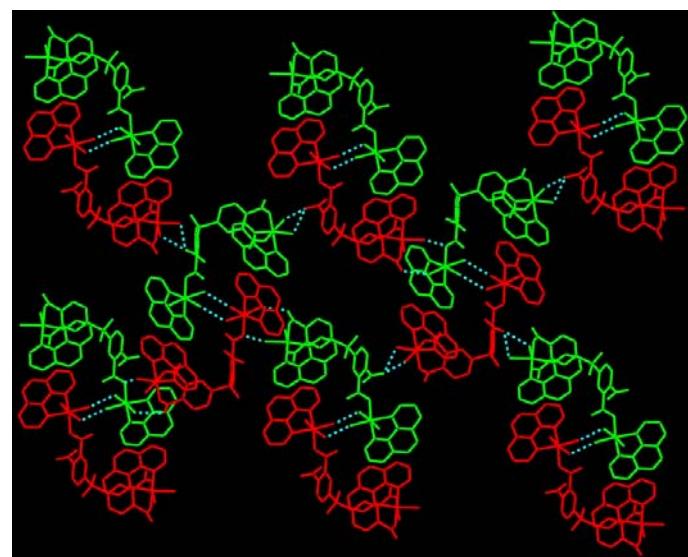
N1-Mn1-O3	173.19(9)	N4-Mn2-O4	89.84(9)
O2-Mn1-O3	87.15(9)	N3-Mn2-O4	167.55(9)
<b>4</b>			
Mn1-O6	2.162(2)	Mn2-O5	2.132(2)
Mn1-O8#1	2.185(2)	Mn2-O12#2	2.153(2)
Mn1-O3	2.205(2)	Mn2-O1	2.157(2)
Mn1-O2	2.225(2)	Mn2-O13#2	2.211(2)
Mn1-N1	2.292(3)	Mn2-N3	2.289(3)
Mn1-N2	2.306(3)	Mn2-N4	2.293(2)
O8-Mn1#3	2.185(2)	O13-Mn2#4	2.211(2)
O6-Mn1-O8#1	91.00(8)	O5-Mn2-O12#2	98.90(8)
O6-Mn1-O3	84.27(9)	O5-Mn2-O1	86.05(8)
O8-Mn1-O3	143.52(9)	O12-Mn2-O1	169.96(8)
O6-Mn1-O2	139.29(8)	O5-Mn2-O13	95.17(8)
O8-Mn1-O2	80.87(8)	O12#2-Mn2-O13#2	81.21(8)
O3-Mn1-O2	79.55(9)	O1-Mn2-O13#2	89.68(8)
O6-Mn1-N1	84.03(9)	O5-Mn2-N3	96.09(9)
O8-Mn1-N1	81.01(9)	O12-Mn2-N3	88.43(9)
O3-Mn1-N1	133.95(9)	O1-Mn2-N3	99.79(9)
O2-Mn1-N1	132.85(9)	O13-Mn2-N3	165.74(8)
O6-Mn1-N2	130.05(9)	O5-Mn2-N4	163.04(9)
O8-Mn1-N2	124.30(9)	O12-Mn2-N4	92.72(8)
O3-Mn1-N2	84.28(10)	O1-Mn2-N4	84.46(8)
O2-Mn1-N2	85.25(9)	O13-Mn2-N4	98.80(9)
N1-Mn1-N2	70.21(10)	N3-Mn2-N4	71.79(9)
<b>5</b>			
Mn1-O3	2.151(4)	Mn1-O5	2.187(4)
Mn1-O7	2.162(4)	Mn1-N1	2.299(4)
Mn1-O4#1	2.179(3)	Mn1-N2#2	2.367(4)
O4-Mn1#3	2.179(3)	N2-Mn1#4	2.367(4)
O3-Mn1-O7	86.94(15)	O4-Mn1-O5	87.56(14)
O3-Mn1-O4#1	99.43(15)	O3-Mn1-N1	97.9(2)
O7-Mn1-O4#1	173.35(15)	O7-Mn1-N1	91.51(15)
O3-Mn1-O5	171.42(17)	O4-Mn1-N1	89.52(13)
O7-Mn1-O5	85.94(15)	O5-Mn1-N1	87.11(18)
O3-Mn1-N2#2	91.59(16)	O7-Mn1-N2	97.67(15)
O4#1-Mn1-N2#2	80.34(13)	O5-Mn1-N2#2	84.64(13)

<sup>a</sup> Symmetry codes: a: #1, x,y,z-1; x,y,z+1; b: #1, x-1,y,z; c: #1,x,y,z-1; #2, x-1,y,z-1; #3, x,y,z+1; #4 x+1,y,z+1; d: #1, -x+1/2,y,z+1/2; #2 -x+1/2,y+1/2,z; #3 -x+1/2,y+0,z-1/2; #4 -x+1/2,y-1/2,z.

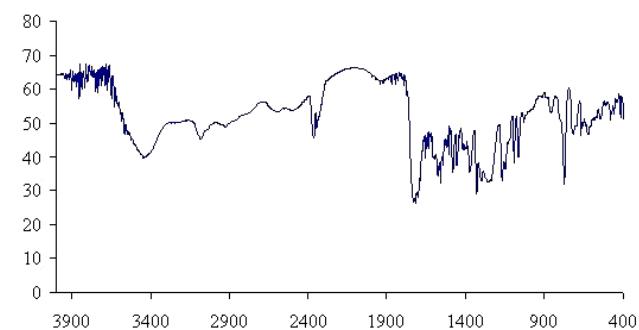
**Table S2 Parameters of hydrogen bonding interactions (Å and °) within 1and 3<sup>a</sup>**

D—H···A	d(D—H)	d(H···A)	d(D···A)	<(DHA)
<b>1</b>				
O7—H7···O2	0.83	2.21	2.771(7)	100.2
O11—H1W···O8#1	0.83	2.34	3.031(7)	140.5
O3—H3···O10#2	0.82	1.84	2.644(7)	165.9
<b>3</b>				
O10—H8W···O16	0.84	1.96	2.802(3)	177.3
O18—H16W···O15	0.84	1.96	2.802(3)	177.3
O10—H7W···O13	0.84	1.92	2.750(1)	170.4
O18—H15W···O22	0.84	1.92	2.750(1)	170.4

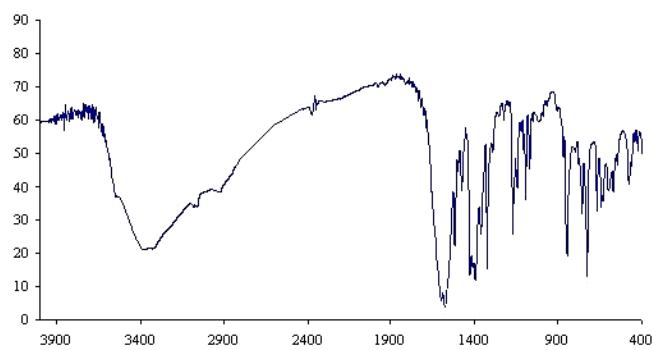
<sup>a</sup> Symmetry codes: #1 -x+1,-y+2,-z+2; #2 -x+2,-y+2,-z+2.



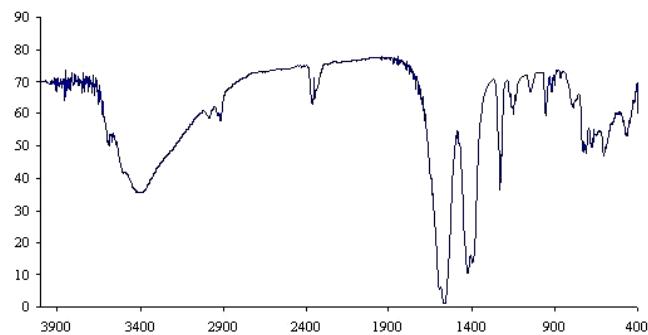
**Fig. S1** 2D layer of **3** via hydrogen-bonding synthons  $R_2^2(8)$ ,  $R_1^2(6)$  and  $R_2^2(10)$ .



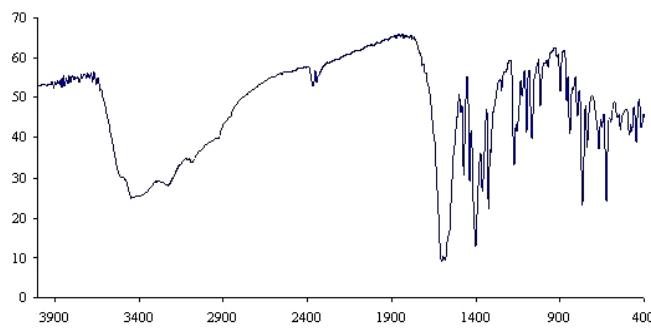
Complex **1**



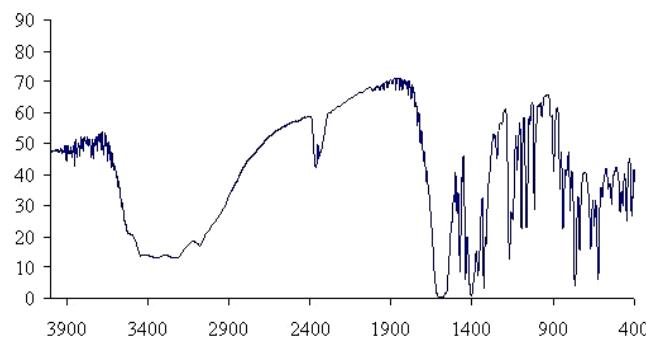
Complex **2**



Complex 3

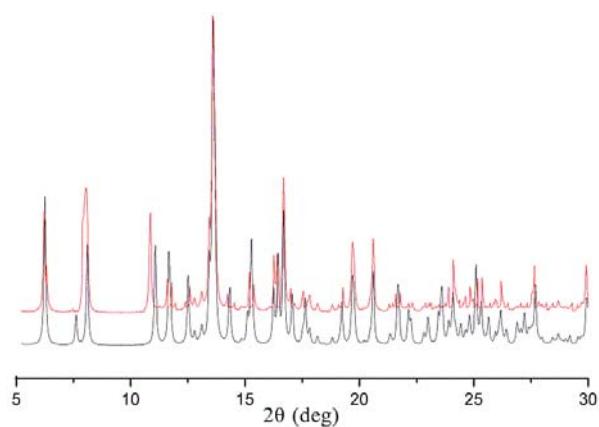


Complex 4

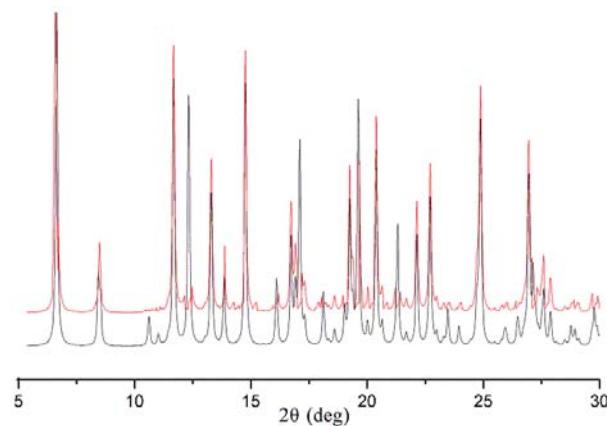


Complex 5

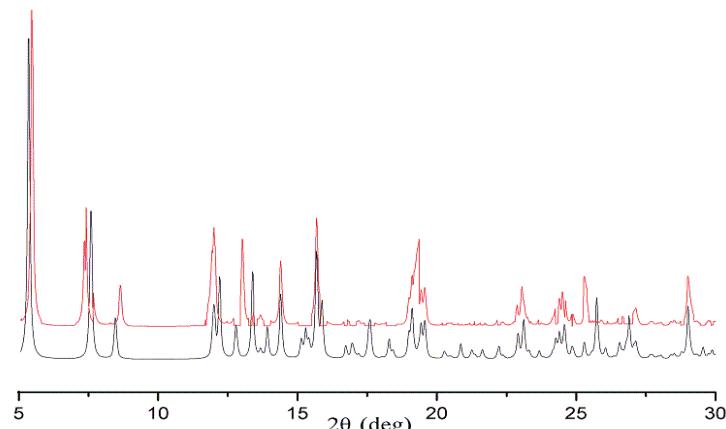
**Fig. S2** IR spectra for complexes **1-5**.



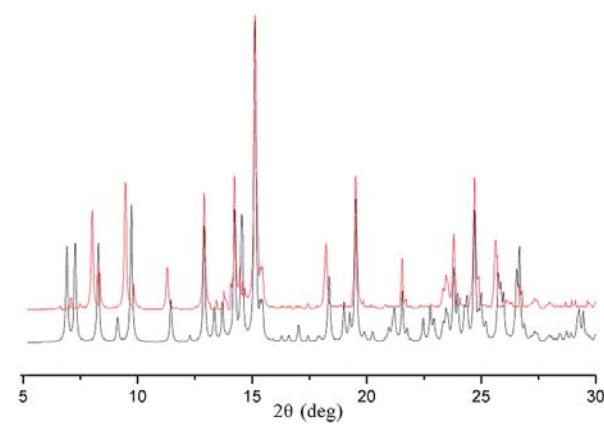
(a)



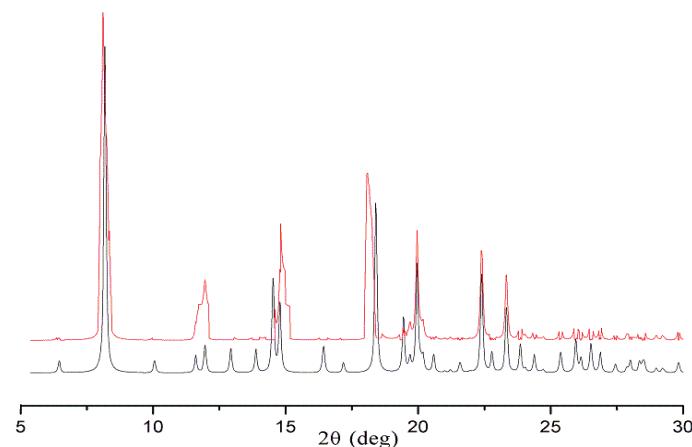
(b)



(c)

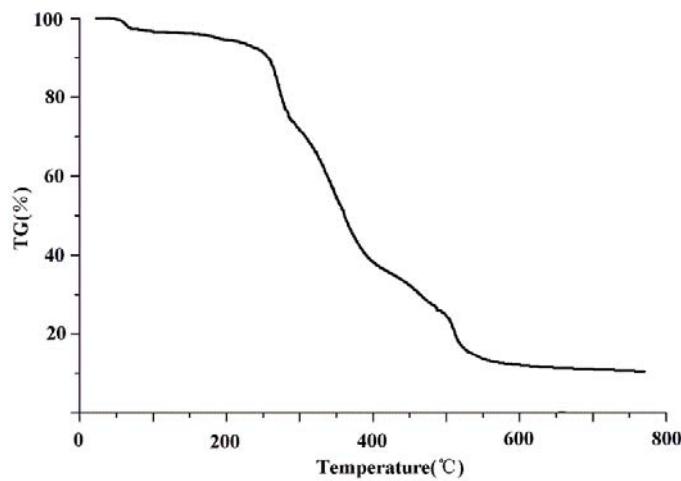


(d)

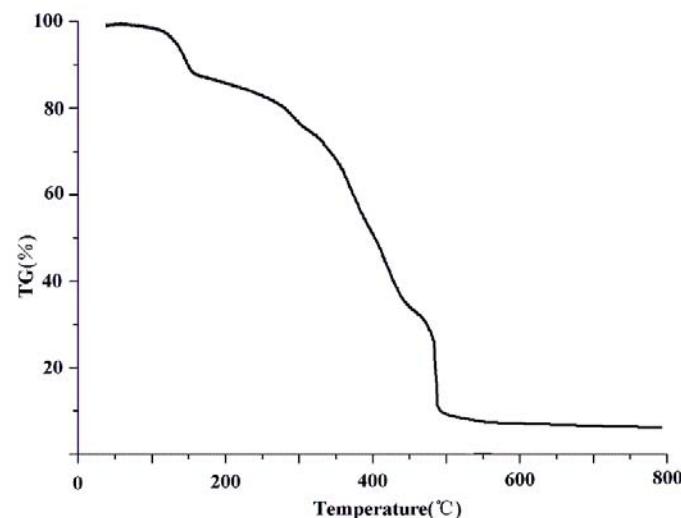


(e)

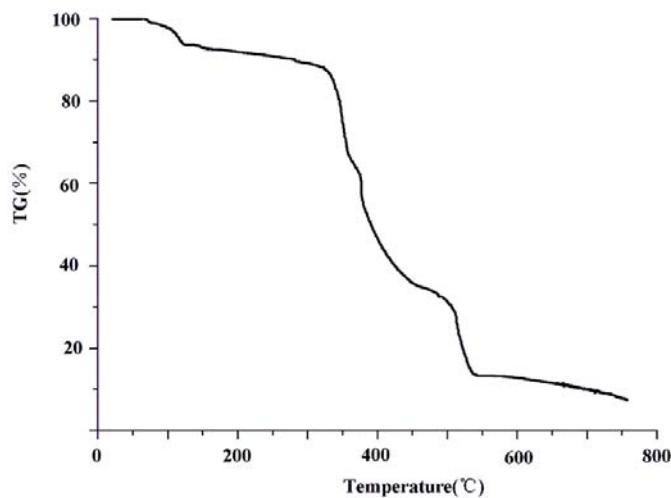
**Fig. S3** Experimental (red) and calculated (black) PXRD patterns for **1-5** (from **a** to **e**).



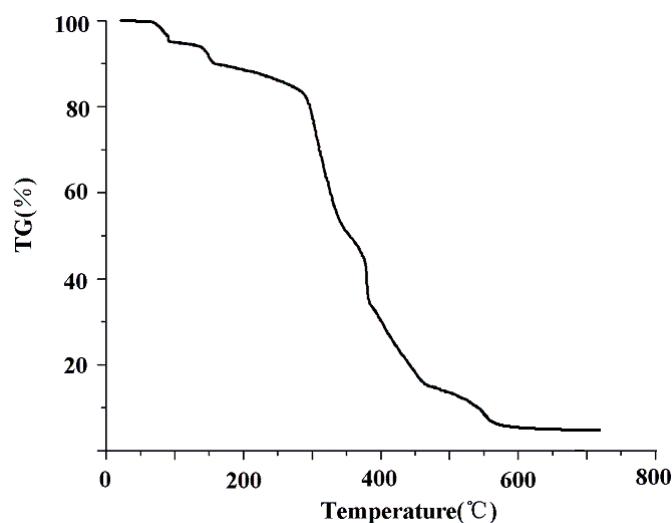
**Complex 1**



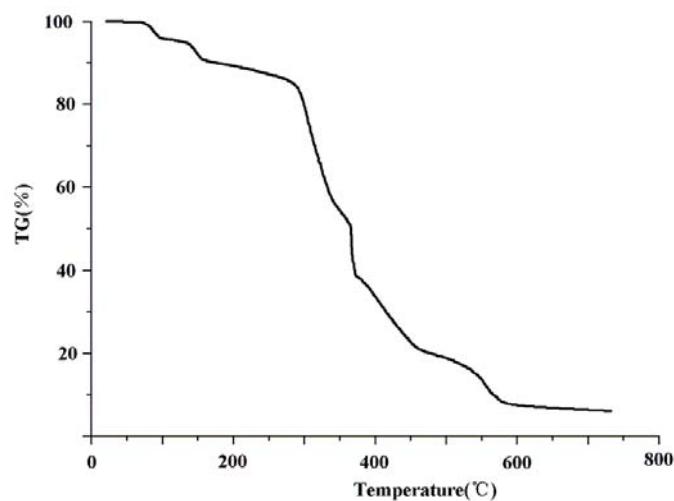
**Complex 2**



**Complex 3**



**Complex 4**



**Complex 5**

**Fig. S4** TGA curves of complexes **1-5**.