Electronic Supplementary Information

Methylene spacer regulated distortion from planarity of manganese(III) complexes with tetradentate N_2O_2 donor Schiff bases: Estimation of energy associated with self assembled supra-molecules

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Descriptions of Structures

[Mn(L[1])(N$_3$)(DMSO)] (2), [Mn(L[2])(NCS)(DMSO)] (3) and [Mn(L[3])(NCS)(DMSO)] (4)

The X-ray crystal structure determinations reveal that complexes **3** and **4** crystallize in monoclinic space groups $P2_1/n$, whereas complex **2** crystallizes in orthorhombic space group $P2_12_12_1$. Perspective views of complexes **2- 4** with selective atom-numbering schemes are shown in Figures S1–S2, respectively. manganese(III) in each complex assumes distorted octahedral geometry. The coordination sphere around manganese(III) centre in each complex comprises of two imine nitrogen atoms [N(19) and N(23)] and two phenoxo oxygen atoms [O(11) and O(31)] of the respective N_2O_2 donor Schiff base ligand occupying equatorial positions. Axial sites of each complexes are coordinated by a nitrogen atom, N(1) of thiocyanate (for **3** and **4**) or azide (for **2**) moiety and an oxygen atom, O(41), of a DMSO molecule. Mn-N_{imine} bond lengths fall within the

range 2.016-2.036 Å and Mn-O_{phenol} bond lengths fall in the range 1.884-1.892 Å. These values are typical of such complexes and corroborate the deprotonation of ligands.[1]

In each of complexes **2-4**, the saturated six membered chelate ring, [Mn(1)–N(19) ··· N(23)], has an intermediate conformation between chair and half chair, with puckering parameters q = 0.547(3) Å, θ = 161.7(3)°, φ = 1.0(10)°{for **2**}; q = 0.543(4) Å, θ = 162.9(4)°, φ = 3.7(14)°{for **3**} and q = 0.551(2) Å, θ = 23.20(2)°, φ = 182.7(5)°{for **4**}.[2]

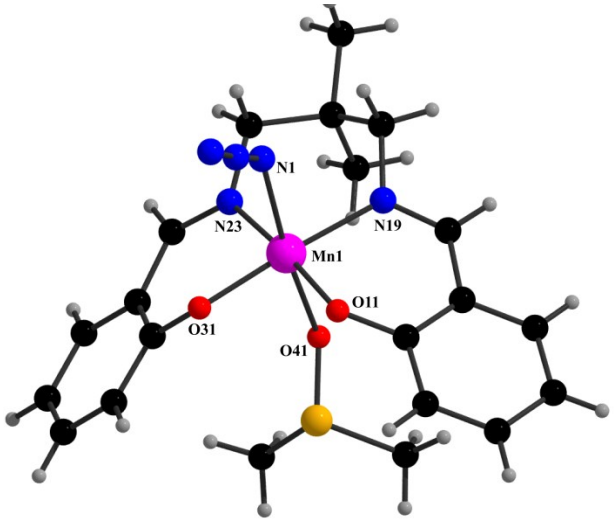

Figure S1: Perspective view of complex **2** with selective atom numbering scheme.

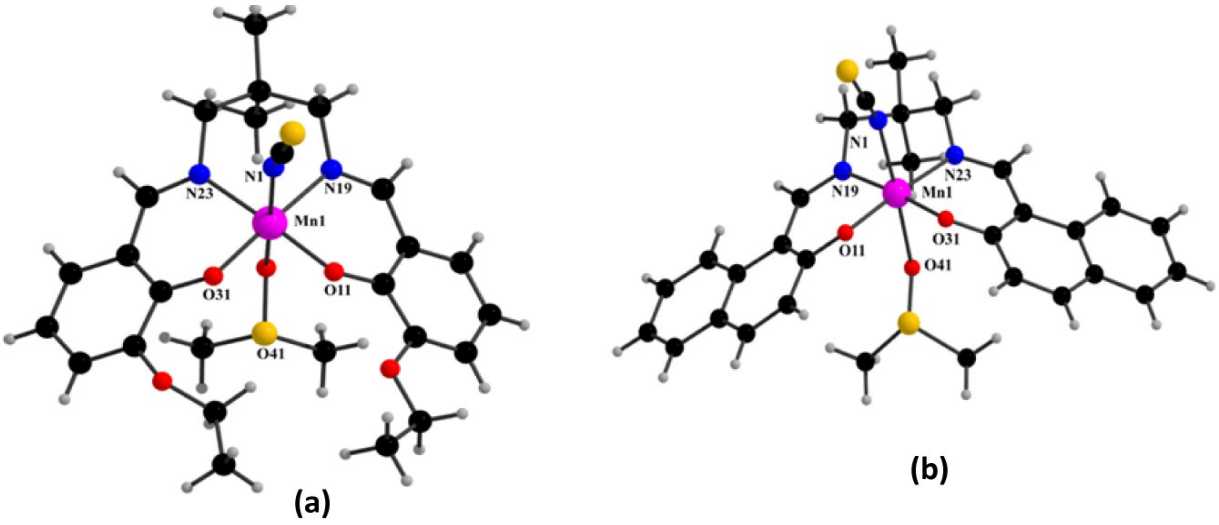

Figure S2: Perspective view of (**a**) complex **3** and (**b**) complex **4** with selective atom numbering scheme.

[Mn(L^4)(DMSO)(H$_2$O)]ClO$_4$ (6)

X-ray crystallographic data shows that complex **6** crystallizes in monoclinic space group *C*2/m. Perspective view of complex **6** with selective atom-numbering scheme is shown in Figure S3. Manganese(III) in this complex attains six coordinated distorted octahedral geometry being bonded to two phenoxo oxygen atoms, O(11) and O(11)^b (^{b} = x,1-y, z), and two imine nitrogen atoms, N(19) and N(19)^b of a deprotonated tetradentate Schiff base ligand, one oxygen atom, O(41) from a water and one oxygen atom O(1_2) from a DMSO moiety. Mn-N_{imine} and Mn-O_{phenol} bond lengths are similar to those observed in complexes **1-5** and other related complexes.[1] The five membered saturated chelate ring**,** [Mn(1)-N(19)-C(9)-C(9)^b-N(19)^b] have puckering parameters q = 0.755(7) Å, θ = 90.0(5)$^\circ$,φ =67.6(4)$^\circ$.[2]

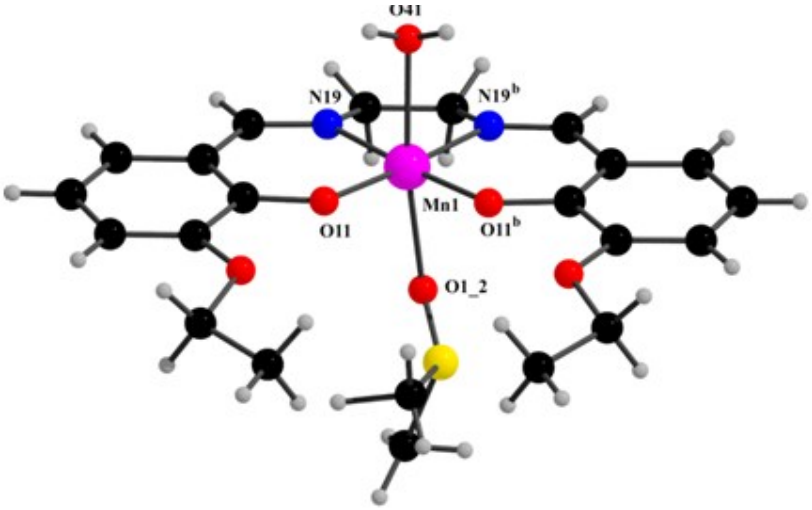

Figure S3: Perspective view of **6** with selective atom numbering scheme. The perchlorate ion is not shown for clarity.

The hydrogen atoms, H(1) and H(1)^{b} (^{b} = x,1-y, z), attached with the oxygen atom, O(41), form bifurcated hydrogen bonds with symmetry related oxygen atoms, O(11)^{a}, O(2)^{a} (^{a} = 1-x,1-y,1-z) and O(11)^{c}, O(2)^{c} (^{c} =1-x,y,1-z) respectively to form a well isolated supramolecular dimer (Figure S4). Details of hydrogen bonding interactions are given in Table S4.

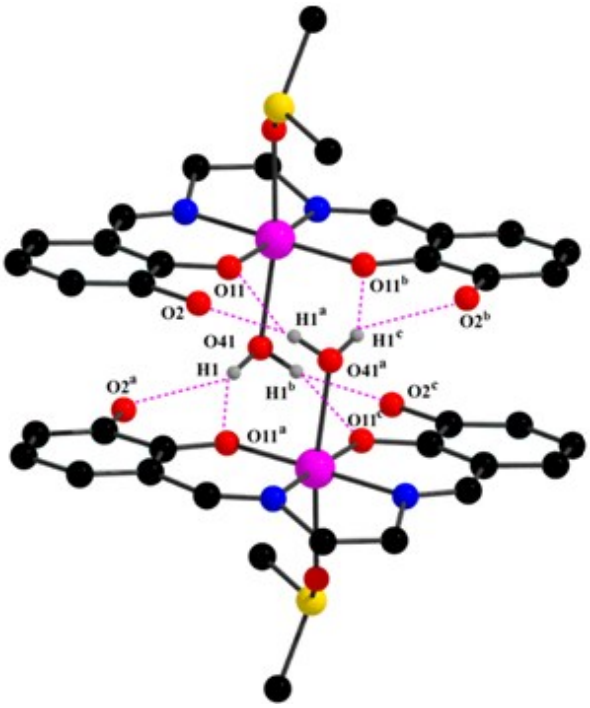

Figure S4: Hydrogen bonded dimeric structure of complex **6**. Symmetry transformations [a] = 1-x,1-y,1-z; [b] = x,1-y, z; [c] =1-x,y,1-z. Only the relevant atoms have been labeled. Ethyl groups attached to oxygen atoms and hydrogen atoms have been omitted for clarity.

IR, electronic spectra and magnetic property

In the IR spectra of all seven complexes, distinct bands within 1596–1620 cm^{-1} region are observed which are characteristic of the $\bar{\nu}_{C=N}$ stretching vibrations of manganese-bound imine functionalities.[3]Complexes **1**, **3**, **4** and **7** show strong and sharp bands within 2058-2068 cm^{-1} region due to presence of nitrogen bonded thiocyanate group.[4] Strong band at ~2049 cm^{-1} in complex **2**, indicates the presence of azide group.[5] Similarly, a strong and sharp band at ~ 2073 cm^{-1} proves the presence of nitrogen bonded selenocyanate moiety in complex **5**.[1a] These above mentioned peaks are due to symmetric stretching frequencies of the thiocyanate/azide/selenocyanate moieties (~ 2049-2073 cm^{-1}). Peaks in the region of ~ 1300-1365 cm^{-1} and ~ 605-653 cm^{-1} are also observed which correspond to the asymmetric stretching

vibrations [$\nu_{as(NCS)}$/ $\nu_{as(NNN)}$/ $\nu_{as(NCSe)}$] and bending vibrations of the thiocyanate/azide/selenocyanate groups.[6] A broad band at ~3435 cm^{-1} in complex **6** is attributed to the presence of hydrogen bonded H_2O.[7]

The electronic absorption spectra of all seven complexes in DMSO display intense absorption bands within 226-274 nm region which are assigned to intra-ligand $\pi \rightarrow \pi^*$ transitions. Bands around 326-371 nm region are due to $n \rightarrow \pi^*$ transitions. Absorption bands within the ranges of 400-492 nm are assigned to ligand to metal charge transfer bands (LMCT). Absorption bands with shoulders within 501-659 nm regions are due to spin allowed d–d transition.[8-10]

Formulations of all seven complexes as manganese(III) complexes are supported by the room temperature solid state magnetic moment values in the region 4.95-5.15μ_B. These values are expected for discrete, high-spin (S = 2), magnetically non-coupled manganese(III) complexes having four unpaired electrons.[11-13]

Powder X-ray diffraction

The experimental XRD patterns of the powdered bulk products matched well with the simulated XRD patterns, calculated from CIFs using the CCDC Mercury software (Figure S5, Supporting Information file). This indicated the purity of the bulk products.

AIM analysis of complex 4

The Bader's theory of AIM has been used to characterize the π–π and hydrogen bonding noncovalent interactions in complex **4**. A bond critical point (CP) and a bond path connecting two atoms is an unambiguous evidence of interaction. The AIM distributions of critical points and bond paths computed for the self-assembled dimer of complex **4** is shown in Figure S5. The distribution reveals two interesting aspects which have not been previously noted. The first one is the existence of two intramolecular C–H···π interactions since the distribution of CPs shows the

presence of two bond CPs (red sphere) and a bond path connecting two hydrogen atoms of the DMSO to the naphthalene moiety. This interaction likely stabilizes the distorted geometry observed in **4**. The second interesting aspect is that the π–π interaction involves the manganese six-membered chelate ring (highlighted using a light blue color). It can be clearly observed that three bond CPs and bond paths connect the chelate ring of one molecule to the naphthalene ring of the other ring and vice versa. Therefore, this π-stacking interaction can be defined as chelate ring···π interaction. This supramolecular assembly is further characterized by ring and cage CPs (yellow and green spheres, respectively) that are generated due to the formation of supramolecular rings and cages.

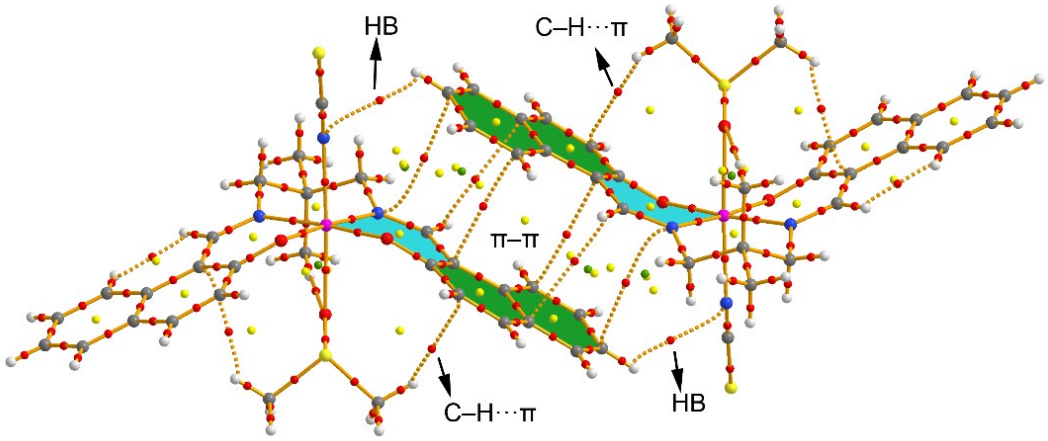

Figure S5: Distribution of bond, ring and cage critical points (red, yellow and cage spheres, respectively) and bond paths for the self-assembled dimer of **4**.

The AIM theory has been also used to characterize the noncovalent interactions in the π–π assemblies of **7**. The distribution of critical points and bond paths is shown in Figure S6. Each hydrogen bonding interaction is characterized by a bond CPs (red sphere) and a bond path connecting the nitrogen/oxygen/sulfur donor atom to the corresponding hydrogen atom. Moreover,

the $(\pi–\pi)_1$ interaction is characterized by four bond CPs (red spheres) and bond paths inter-connecting four aromatic carbon atoms of the naphthalene rings (see Figure S6a). In addition, the $(\pi–\pi)_2$ interaction is characterized by three bond CPs (red spheres) and bond paths connecting three aromatic carbon atoms of naphthalene ring to three carbon atoms of the phenyl ring (see Figure S6b).

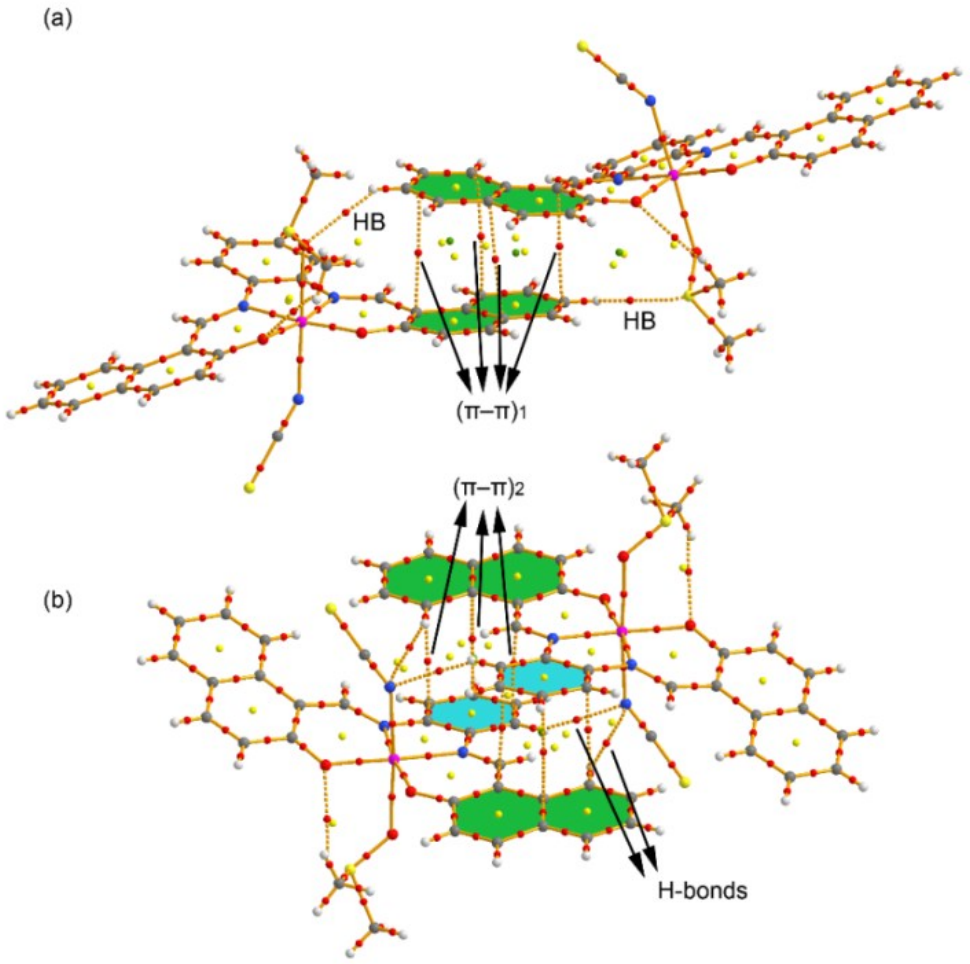

Figure S6: Distribution of bond, ring and cage critical points (red, yellow and cage spheres, respectively) and bond paths for the $(\pi–\pi)_1$ (a) and $(\pi–\pi)_2$ (b) assemblies.

Finally, the AIM theory has been used to characterize the noncovalent interactions in the C–H···π/π–π/π···H–C assembly of **3**. The distribution of critical points and bond paths is shown

in Figure S7. Each hydrogen bonding interaction is characterized by a bond CPs (red sphere) and a bond path connecting the carbon atom of the SCN donor moiety to the corresponding aromatic hydrogen atom. Moreover, the π–π interaction is characterized by four bond CPs (red spheres) and bond paths inter-connecting four aromatic carbon atoms of the phenyl rings and exo cyclic C=N bonds. The interaction is further characterized by the formation of several ring and cage CP (yellow and green spheres, respectively). The intramolecular C–H···π interaction is characterized by one bond CP (red sphere) and bond path connecting one aromatic carbon atom to one hydrogen atom of the DMSO (see Figure S7), thus confirming the existence of the interaction and formation of the C–H···π/π–π/π···H–C assembly.

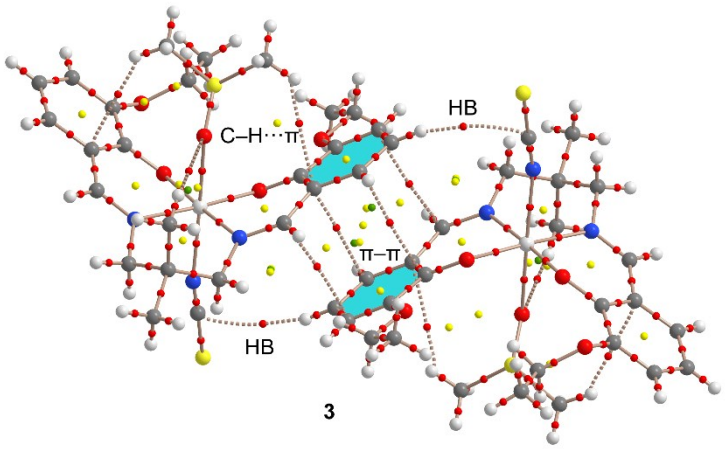

Figure S7: Distribution of bond, ring and cage critical points (red, yellow and cage spheres, respectively) and bond paths for the C–H···π/π–π/π···H–C assembly in **3**.

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Table S1: Crystal data and refinement details for complexes **1 -7**

Complex	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Formula	$C_{22}H_{26}MnN_3O_3S_2$	$C_{21}H_{26}MnN_5O_3S$	$C_{26}H_{34}MnN_3O_5S_2$	$C_{30}H_{30}MnN_3O_3S_2$	$C_{46}H_{62}Mn_2N_6O_{13}SSe_2$	$C_{22}H_{30}MnN_2O_{10}SCl$	$C_{31}H_{24}MnN_3O_3S_2$
Formula Weight	499.54	483.48	587.64	599.63	1238.93	604.93	605.59
Crystal System	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Triclinic	monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_12_12_1$	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$C2/m$	$P2_1/n$
a(Å)	13.8991(4)	9.8670(3)	12.5031(6)	15.6204(7)	11.0249(4)	15.3576(1)	13.3075(2)
b(Å)	11.8029(4)	12.1265(5)	14.6639(7)	11.7065(5)	11.9113(5)	17.1311(1)	10.9780(1)
c(Å)	14.2659(5)	18.8346(7)	15.1065(8)	15.7573(7)	11.9381(5)	12.1008(8)	18.002(2)
α (°)	_	–	–	–	114.8490(10)	(90)	(90)
β(°)	92.954(3)	(90)	90.903(4)	97.221(2)	106.7730(10)	123.884(2)	91.781(4)
γ(°)	_	–	–	–	95.7180(10)	–	(90)
V(Å^3)	2337.21(1)	2253.60(1)	2769.4(2)	2858.5(2)	1317.29(9)	2642.9(3)	2628.6(5)
Z	4	4	4	4	1	4	4
$d_{(calc)}$ [g/cm^3]	1.420	1.425	1.409	1.393	1.562	1.520	1.530
μ [mm^{-1}]	0.772	0.711	0.668	0.644	2.007	0.897	0.702
F(000)	1040	1008	1232	1248	634	1256	1248
Total Reflections	10750	15036	12742	28327	14450	21283	68640
Unique Reflections	6541	6532	7761	5179	4799	3147	4806
Observed data[I > 2 σ(I)]	5434	4921	4169	4262	4114	2835	4312
R(int)	0.025	0.069	0.074	0.059	0.034	0.056	0.070
R1, wR2 (all data)	0.0543, 0.1043	0.0828, 0.0880	0.1621, 0.1282	0.0478, 0.0750	0.0373,0.0662	0.0479, 0.1075	0.0439, 0.1050
R1, wR2 ([I > 2 σ(I)]	0.0423, 0.0982	0.0566, 0.0800	0.0827, 0.1056	0.0338, 0.0705	0.0281,0.0630	0.0427, 0.1056	0.0383, 0.1002

Table S2: Bond lengths (Å) of complexes **1 -7**

Complex	1	2	3	4	5	6	7
Mn(1)-O(11)	1.8895(1)	1.889(3)	1.884(3)	1.8919(14)	1.8774(18)	1.8600(19)	1.8971(2)
Mn(1)-O(31)	1.8840(1)	1.884(3)	1.888(3)	1.8850(15)	1.8839(17)	_	1.9050(2)
Mn(1)-O(41)	2.2665(1)	2.267(3)	2.267(3)	2.2598(14)	2.2998(19)	2.258(3)	2.2780(2)
Mn(1)-N(1)	2.1956(2)	2.179(3)	2.217(3)	2.2135(18)	2.277(2)	_	2.2461(2)
Mn(1)-N(19)	2.0274(2)	2.029(3)	2.026(3)	2.0162(17)	1.985(2)	1.973(2)	1.9808(2)
Mn(1)-N(23)	2.0360(2)	2.029(4)	2.022(3)	2.0186(17)	1.984(2)	_	1.9700(2)
Mn(1)-O(1_2)	_	_	_	_	_	2.252(4)	_

Table S3: Selected bond angles (°) of complexes **1 - 7**.

Complex	1	2	3	4	5	6	7
O(11)-Mn(1)-O(31)	88.89(6)	87.87(1)	89.31(1)	88.77(6)	93.85(8)	_	96.24(7)
O(11)-Mn(1)-O(41)	89.96(5)	89.73(1)	91.38(1)	88.52(6)	92.07(7)	91.95(9)	87.74(6)
O(11)-Mn(1)-N(1)	94.67(6)	96.76(1)	94.24(1)	89.96(6)	95.86(8)	_	91.00(7)
O(11)-Mn(1)-N(19)	88.85(6)	90.04(1)	89.68(1)	88.74(7)	91.55(8)	92.37(9)	91.38(7)
O(11)-Mn(1)-N(23)	175.28(6)	173.90(1)	176.60(1)	176.05(7)	173.31(8)	_	173.21(7)
O(31)-Mn(1)-O(41)	89.18(5)	91.46(1)	91.77(1)	88.20(6)	90.59(7)	_	87.44(6)
O(31)-Mn(1)-N(1)	91.88(6)	96.07(1)	94.67(1)	93.67(7)	91.71(7)	_	88.55(7)
O(31)-Mn(1)-N(19)	175.69(7)	176.55(1)	176.33(1)	175.81(7)	174.07(9)	_	171.65(7)
O(31)-Mn(1)-N(23)	89.49(6)	89.52(1)	89.25(1)	88.31(7)	91.73(8)	_	90.42(7)
O(41)-Mn(1)-N(1)	175.28(6)	170.22(1)	171.50(1)	177.57(6)	171.58(8)	_	175.64(7)
O(41)-Mn(1)-N(19)	87.15(6)	85.78(1)	84.73(1)	88.37(6)	86.76(8)	86.97(9)	89.44(6)
O(41)-Mn(1)-N(23)	85.59(5)	84.83(1)	85.60(1)	88.74(6)	84.17(8)	_	91.22(7)
N(1)-Mn(1)-N(19)	91.96(6)	86.90(1)	88.92(1)	89.70(7)	90.18(8)	_	94.76(7)
N(1)-Mn(1)-N(23)	89.81(6)	88.99(1)	88.94(1)	92.87(7)	87.66(8)	_	90.52(7)
N(19)-Mn(1)-N(23)	92.48(6)	92.29(1)	91.57(1)	94.02(7)	82.73(9)	_	81.90(8)
O(1_2) -Mn(1)-O(11)	_	_	_	_	_	95.77(1)	_
O(1_2)-Mn(1)-O(41)	_	_	_	_	_	172.04(9)	_
O(1_2)-Mn(1)-N(19)	_	_	_	_	_	94.66(1)	_

O(1_2)-Mn(1)-O(11)[b]	–	–	–	–	–	85.86(1)	–
O(1_2)-Mn(1)-N(19)[b]	–	–	–	–	–	85.48(1)	–
O(11)-Mn(1)-O(11)[b]	–	–	–	–	–	91.80(9)	–
O(11)-Mn(1)-N(19)[b]	–	–	–	–	–	175.73(9)	–
O(41)-Mn(1)-N(19)[b]	–	–	–	–	–	86.97(9)	–
O(11)[b]-Mn(1)-O(41)	–	–	–	–	–	91.95(9)	–
N(19)-Mn(1)-N(19)[b]	–	–	–	–	–	83.45(1)	–
O(11)[b]-Mn(1)-N(19)[b]	–	–	–	–	–	92.37(9)	–

Symmetry transformation: [b] = x,1-y, z.

Table S4: Hydrogen bond distances (Å) and angles (◦) for **4** and **5**:

Complex	D–H···A	D-H	H···A	D···A	∠D-H···A
4	O(1S)-H(1S)···O(14)[a]	0.80	2.29	2.963	142
	O(1S)-H(1S)···O(15)[a]	0.80	2.29	3.006	150
	O(1S)-H(2S)···O(1)[a]	0.80	2.21	2.879	143
	O(1S)-H(2S)···O(2)[a]	0.80	2.32	3.022	148
5	O(1W)-H(1W)···O(1)[a]	0.81	2.20	2.900	144
	O(1W)-H(1W)···O(2)[a]	0.81	2.19	2.897	145

Symmetry transformation: [a] = 1-x,1-y,1-zD = donor; H = hydrogen; A = acceptor.

Table S5: Distortion angles (α_1 and α_2) between the plane of phenyl ring(s) of salpn (propane diamine based) type ligand and the equatorial plane of manganese(III) complexes.

Complex (CCDC code)	α_1	α_2	Name of the diamine	Ref
YUHBAF	19.71	22.14	Propanediamine	14a
BEWWEH	28.36	32.32	Propanediamine	14b
BOFLOZ	20.38	25.45	Propanediamine	4a
CEKRUH	35.20	3.40	Propanediamine	14c
CEKSAO	24.20	23.53	Propanediamine	14c
COXQIP	22.71, 19.23	22.62, 13.22	Propanediamine	15a
COXQOV	36.30	39.52	Propanediamine	15a
EDANOO	13.21, 12.35	12.95, 32.53	Propanediamine	15b
ELUKIF	24.10	20.73	Propanediamine	16a
FOFWIH	36.70, 30.04	29.41, 37.73	Propane-1,2-diamino-1-ol	16b
GIJWED01	21.42	26.32	Propanediamine	16c
HERDEO	12.89	15.16	Propanediamine	16d
HIWBEV	30.42	30.42	Propanediamine	16e
HIWBUL	33.40	19.98	Propanediamine	16e
HIWCAS	42.85	37.77	Propanediamine	16e
IKERAR	4.61, 36.03	18.26, 38.28	Propanediamine	17a
JATGEQ	7.84	17.29	Propanediamine	17b
JIYSOZ	32.41	24.43	Propanediamine	18a
JUGWAJ	21.47	26.44	Propanediamine	18b
KAMSOI	24.14	12.55	Propanediamine	18c
KAMSUO	29.71	29.18	2,2-dimethylpropane-1,3-diamine	18c
LEHSIB	28.53	28.53	Propanediamine	18d
LUDCOD	21.57	22.85	2,2-dimethylpropane-1,3-diamine	19a
LUCOD01	23.16	21.61	2,2-dimethylpropane-1,3-diamine	19b
MAWKIG	12.67	26.16	1-ethylpropane-1,3-diamine	19c
MAWKOM	24.80	31.45	1-ethylpropane-1,3-diamine	19c

MAWKUS	25.17	21.19	2,2-dimethylpropane-1,3-diamine	19c
MAWKUS01	20.70	25.25	2,2-dimethylpropane-1,3-diamine	20a
OKOYUI	31.03	33.18	Propanediamine	20b
OKOYUI01	31.19	32.75	Propanediamine	20b
QARPIJ	16.61	15.53	Propanediamine	20c
RUKTUN	29.85	41.09	Propanediamine	20d
RUKVID	26.5	39.5	Propanediamine	20d
RUPZAE	27.45	33.96	Propanediamine	20d
SOZMOJ	38.47	33.18	Propanediamine	21a
TAKYOT	16.44	17.47	Propanediamine	21b
VERKIM	22.31, 21.48	28.24, 13.49	Propanediamine	21c
VOFKIK	36.80	36.03	Propane-1,2-diamino-1-ol	21d
VOLBOP	35.59	32.04	2,2-dimethylpropane-1,3-diamine	22a
WAQDEX	14.91	20.06	Propanediamine	22b
XIXHAN	26.44	27.52	Propanediamine	22c
XOKQEV	33.82, 8.71	36.51, 9.87	Propanediamine	22d
XOKQIZ	15.91, 20.52, 19.03	24.74, 14.39, 5.41	Propanediamine	22d
XUCHOT	24.02	17.68	Propanediamine	23a
XUGJIT	36.11	36.11	Propanediamine	23b
YUHBAF	21.94	19.71	Propanediamine	23c
(Complex **1**)	33.45	31.80	2,2-dimethylpropane-1,3-diamine	This work
(Complex **2**)	30.38	32.95	2,2-dimethylpropane-1,3-diamine	This work
(Complex **3**)	31.94	30.39	2,2-dimethylpropane-1,3-diamine	This work
(Complex **4**)	26.03	31.66	2,2-dimethylpropane-1,3-diamine	This work

Table S6: Distortion angles (α_1 and α_2) between the plane of phenyl ring(s) of salen (ethylene diamine based) type ligand and the equatorial plane of manganese(III) complexes.

(CCDC code)	**α_1**	**α_2**	**Diamine used**	**Ref**

HIJZOR	8.79	11.6	Ethylenediammine	24a
PULGAG	13.15	22.43	Cyclohexane-1,2-diamine	24b
PULGEK	22.54	25.88	Cyclohexane-1,2-diamine	24b
EBEFAU02	15.80	18.93	Ethylenediammine	24c
ASERUM	19.01	18.11	1,1,2,2-tetramethylethylenediamine	24d
CONMEZ	2.71	10.34	Phynelendiamine	25a
DUPWER	3.88	2.77	Phynelendiamine	25b
DEVMOH01	10.49	12.50	Ethylenediammine	24c
HOVFUU	11.59	14.11	Ethylenediammine	25c
RADNER	10.89	17.05	Ethylenediammine	26a
RAFNET	19.19	26.44	1-methylethylene-1,2-diamine	26b
RANDUH	22.14	19.43	1-methylethylene-1,2-diamine	26c
TOMDAB	18.84	14.95	Cyclohexane-1,2-diamine	26d
VUZLAD	13.58	20.66	Ethylenediammine	27a
YUHBEJ	15.52	12.24	Ethylenediammine	27b
EBEFAU	19.15	16.13	Ethylenediammine	27c
EBEFIC	16.54	10.53	Ethylenediammine	27c
EBEFIC01	9.95	8.46	Ethylenediammine	27c
GIMFOY	13.30	7.12	Ethylenediammine	28a
QETSEO	21.83	21.29	Ethylenediammine	28b
QETSEO01	21.29	21.94	Ethylenediammine	28c
BOFLIT	6.21, 10.29	7.38, 11.02	Ethylenediammine	28d
ABIJUS	8.36	20.55	Cyclohexane-1,2-diamine	29a
ABIKAZ	22.66	7.35	Cyclohexane-1,2-diamine	29a
AFAXIO	23.22	14.13	Ethylenediammine	29b
AJIMAI	11.17	7.88	Ethylenediammine	29c
AJOZEE01	19.47, 31.61	5.78, 5.59	Ethylenediammine	29d
AJOZEE02	5.96, 5.46	31.33, 19.12	Ethylenediammine	29d
ASEROG	1.25	4.75	Phynelendiamine	29e
AXUZAV	10.08	19.68	Cyclohexane-1,2-diamine	30a
AYOQUA	13.21, 14.70	15.70, 29.97	Ethylenediammine	30b
AYORAH	14.73	9.10	Ethylenediammine	30b
BANFOM	1.95	12.36	Phynelendiamine	30c
BANFOM01	1.86	12.36	Phynelendiamine	30d
BARTUL	15.67	15.44	1,1,2,2-tetramethylethylenediamine	31a
BARVAT	7.88	17.48	Ethylenediammine	31a
BAXNIZ	11.00	11.14	1,1,2,2-tetramethylethylenediamine	31b
BEQCUX	9.97	10.22	Ethylenediammine	31c
BEWVEG	10.16	15.28	1-methylethylene-1,2-diamine	31d
BEWVIK	18.87	13.48	1-methylethylene-1,2-diamine	31d
BEWVOQ	15.07	7.10	1-methylethylene-1,2-diamine	31d

BEWVUW	19.75, 18.94	11.86, 13.56	1-methylethylene-1,2-diamine	31d
BEZSOQ	12.36	12.64	Ethylenediammine	32a
BEZZEN	12.09	16.09	Ethylenediammine	32a
BILQAP	8.01	8.66	Phynelendiamine	32b
BIZBES	9.99	12.14	Phynelendiamine	32c
BIZQIL	10.62	9.22	1-methylethylene-1,2-diamine	33a
BOFLIT	11.02, 6.21	10.29, 7.38	Ethylenediammine	4a
BOLJOD	4.33	1.40	1,2-dimethylethylenediamine	33b
BOLJUJ	8.75	15.55	Ethylenediammine	33b
BOLKAQ	21.83	16.74	Ethylenediammine	33b
BOLKIY	5.52	9.07	Ethylenediammine	33b
BOLKOE	13.06	17.57	1-methylethylene-1,2-diamine	33b
BOLKUK	9.75	5.73	1,2-dimethylethylenediamine	33b
BOQXOV	10.69	17.54	Ethylenediammine	33c
BOVGID	6.15	4.55	Phynelendiamine	33d
BUTYAR	19.81	18.33	Ethylenediammine	34a
CEDCEU	17.90	10.43	Ethylenediammine	34b
CEJQEO	3.47	6.66	Phynelendiamine	34c
CEWBOW	12.57	15.70	*cis-syn*-3,4-diaminocyclopentane carboxylate	34d
COLCEN	10.89	4.37	Ethylenediammine	35a
COLDIS	14.05	15.60	Ethylenediammine	35a
CONLUO	3.05	6.68	Ethylenediammine	35b
CONMEZ	2.71	10.60	Phynelendiamine	35b
COPZIS	16.0	15.19	1,2-dimethylethylenediamine	35c
COQLIF	8.42	2.66	Phynelendiamine	35b
COVLIJ	16.45	26.26	Cyclohexane-1,2-diamine	36a
COVLOP	25.87	17.46	Cyclohexane-1,2-diamine	36a
CUDFUD	5.08	5.59	Cyclohexane-1,2-diamine	36b
DACFAQ	17.66	22.87	Cyclohexane-1,2-diamine	36c
DACFEU	28.77	17.55	Cyclohexane-1,2-diamine	36c
DAPPEQ	16.70	16.70	Ethylenediammine	36d
DATMOB	6.49	6.49	Ethylenediammine	36d
DAVGOX	2.30	5.65	Phynelendiamine	37a
DEVMOH	12.79	11.03	Ethylenediammine	37b
DEVNEY	4.71	2.68	1-methylethylene-1,2-diamine	37c
DEXYEM	9.88	8.72	Ethylenediammine	37d
DIHDUV	12.53	7.15	2,3-diaminotoluene	38a
DUBROH	11.91	11.91	Cyclohexane-1,2-diamine	38b
EDAMOL	10.50	20.03	Ethylenediammine	38c
EDANII	16.03	17.84	Ethylenediammine	15b
EDOVAV	2.79	4.72	Ethylenediammine	39a

ERIBIR	10.47	15.15	Ethylenediammine	39b
ESUMIP	3.04	3.59	Phynelendiamine	39c
EVADUA	12.21	17.03	Ethylenediammine	39d
EVAFAI	10.52	15.84	Ethylenediammine	39d
ZIRNUL	8.17	5.66	Ethylenediammine	24c
ZIRPEX	11.62	11.62	Ethylenediammine	24c
(Complex **5)**	11.48	11.04	Ethylenediammine	This work
(Complex **6)**	3.93	3.93	Ethylenediammine	This work
(Complex **7)**	5.21	18.10	Phynelendiamine	This work

Table S7: Proportions of all possible interactions for complexes **1-7** excluding complex **6**.

Interactions (%)	**1**	**2**	**3**	**4**	**5**	**7**
H···H	54.8	57.3	59.6	49.5	47.8	42.1
C···H/H···C	16.9	14.5	13.1	23.5	16.4	20.9
N···H/H···N	3.1	18.1	2.7	2.6	3.5	5.9
O···H/H···O	7.3	7.3	9.6	5.9	12.8	6.1
S···H/H···S	14	3.1	12.2	12.8	_	12.2

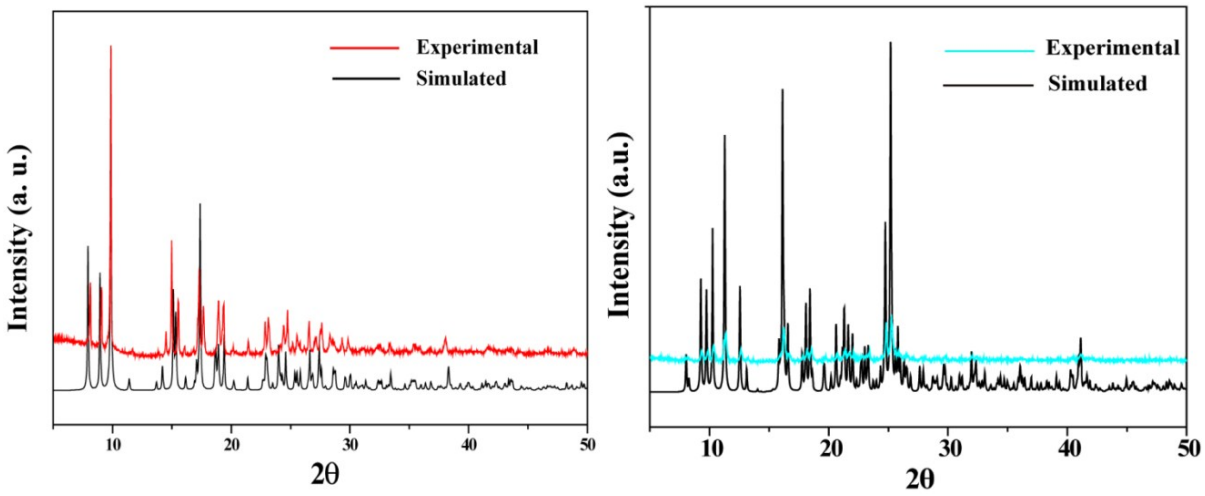

Figure S8: Experimental and simulated PXRD patterns of complexes **4** and **7.**

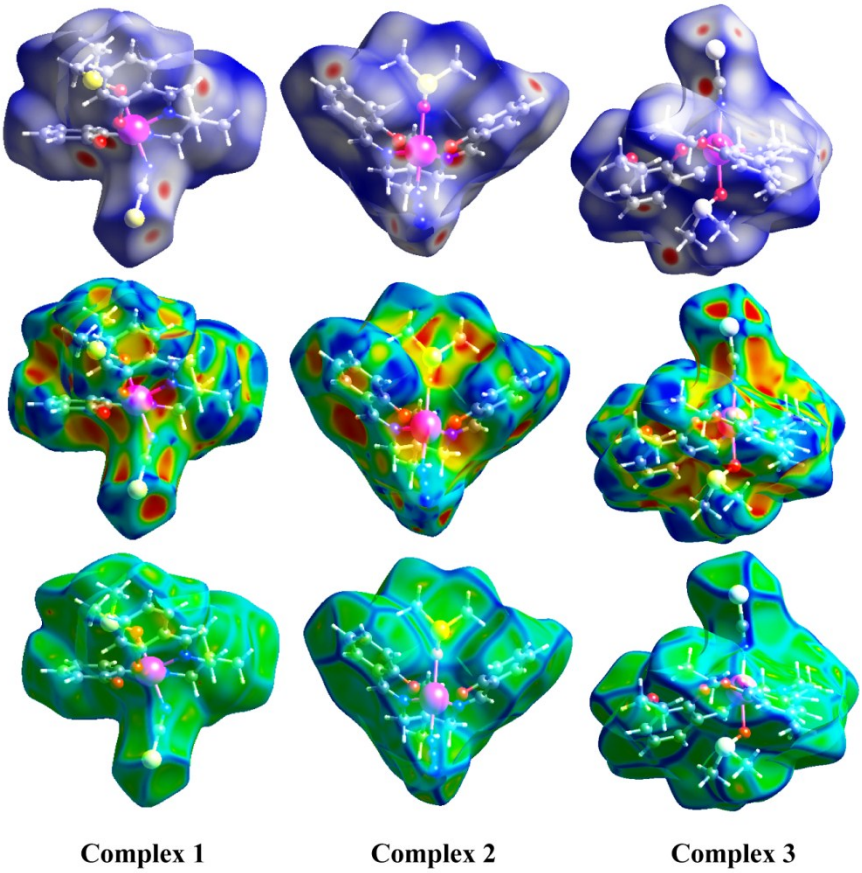

Figure S9: Hirshfeld surface analysis plots of complexes **1-3**

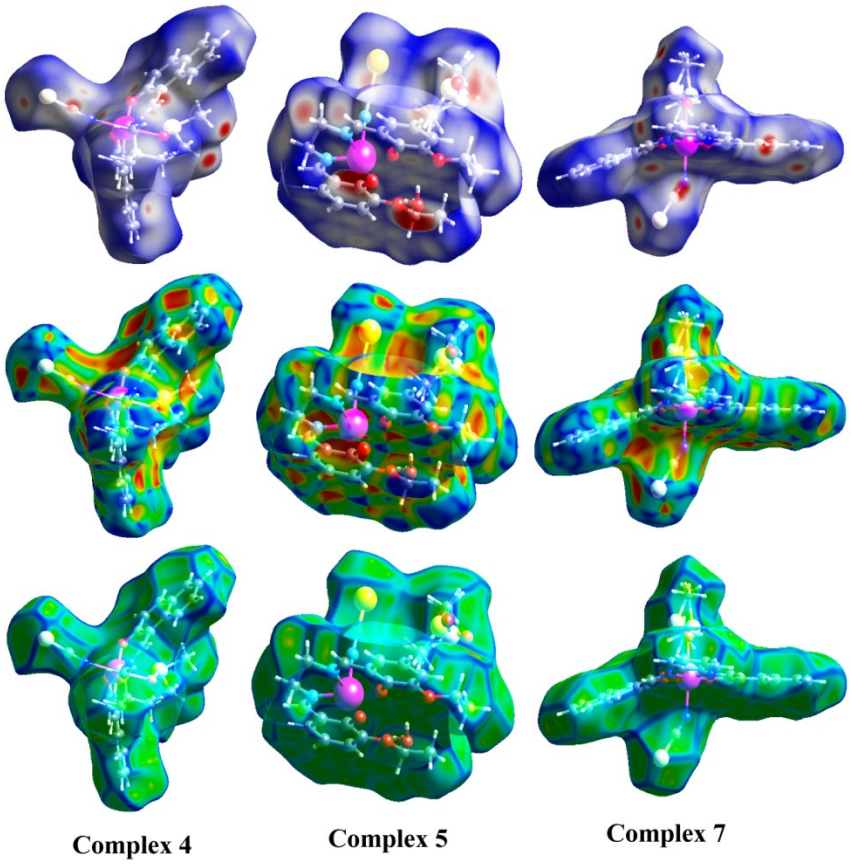

Figure S10: Hirshfeld surface analysis plots of complexes **4**, **5** and **7**.

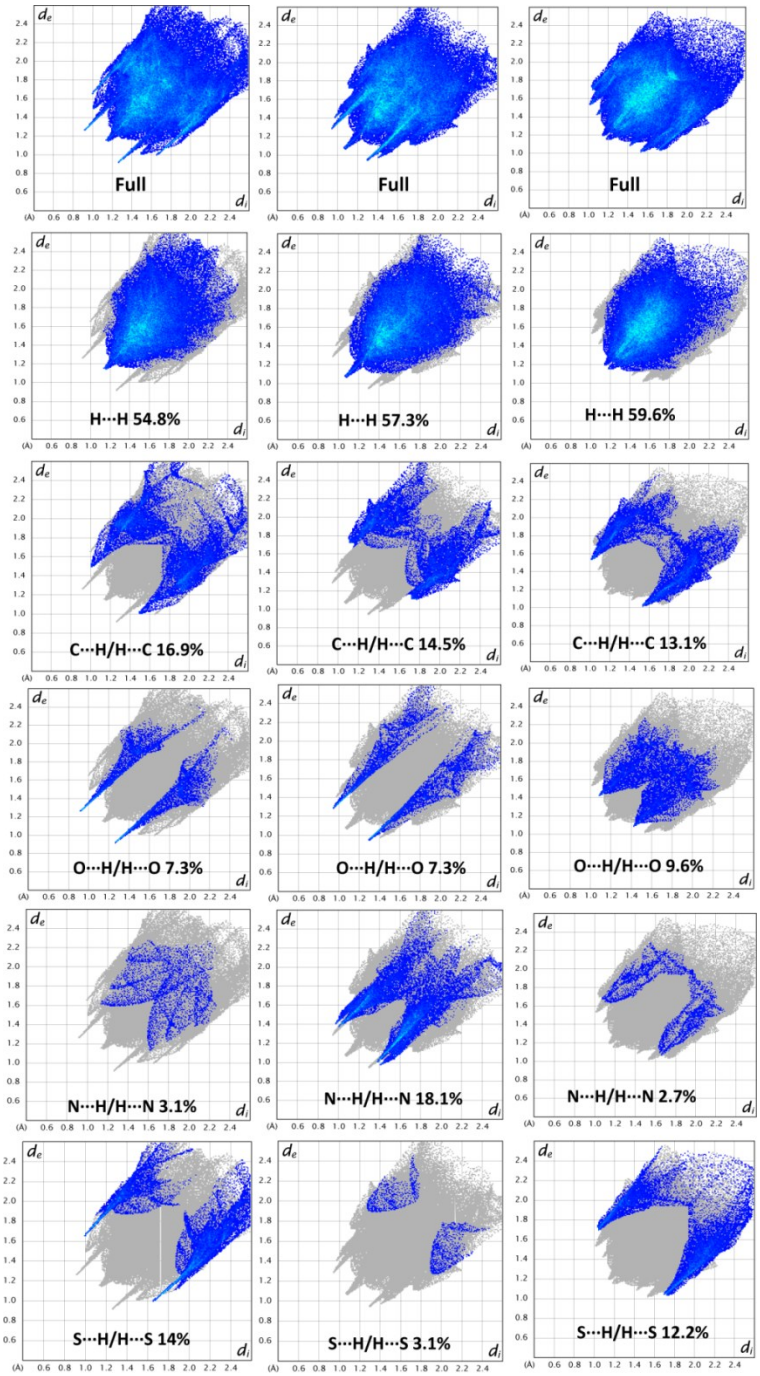

Figure S11: 2D Finger print plot of complexes **1** (left), **2** (middle) and **3** (right)

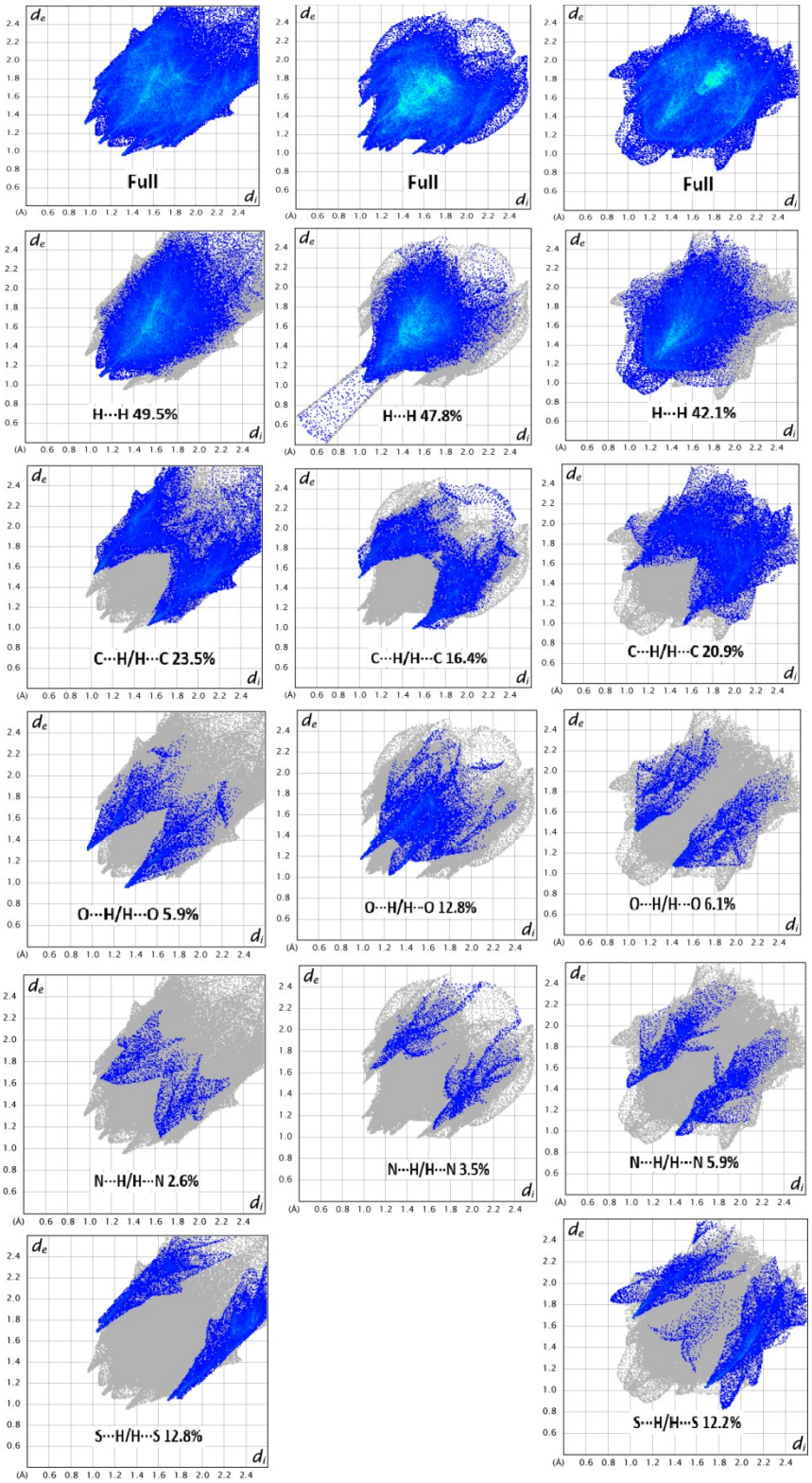

Figure S12: 2D Finger print plot of complexes **4** (left), **5** (middle) and **7** (right)

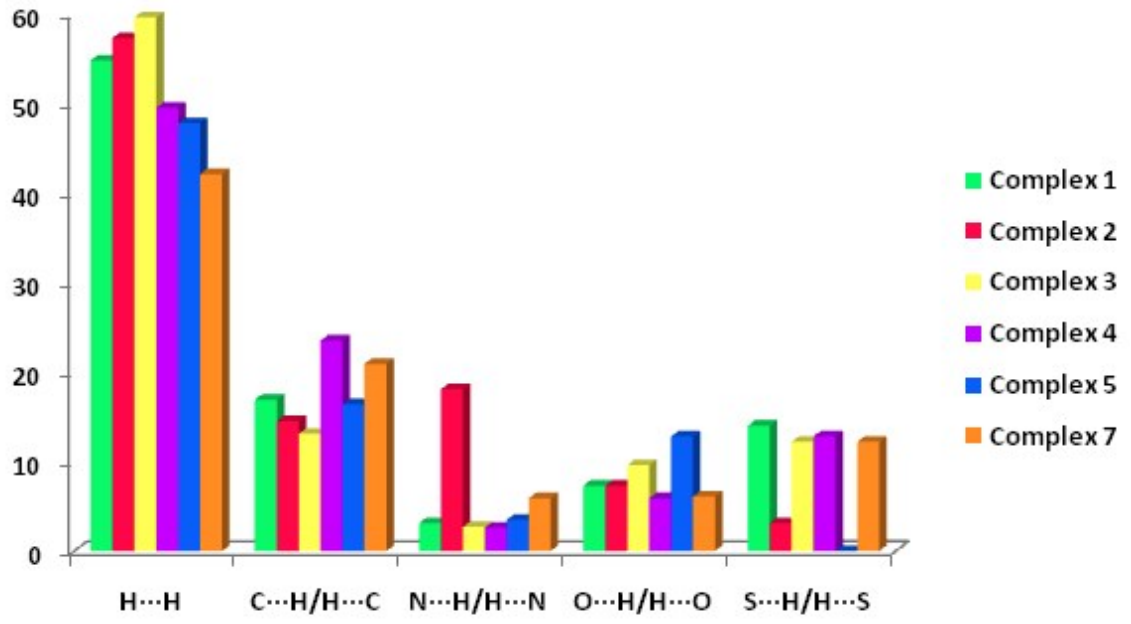

Figure S13: The contributions of all type interactions overlapping in the 2D finger print plots for complexes **1-5** and **7**.