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Synthesis, X-ray characterization, DFT calculations and Hirshfeld surface analysis of M^{n+} ions (n = 2,3; M = Ni, Cd, Mn, Co and Cu): The role of secondary bonding and steric effects in complexes based on thiosemicarbazone

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Table S1. Crystal data and structure refinement for [Ni(L1)(N_3)] (**1**), [Ni(L2)(N_3)] (**2**), [Cu(L1)(μ-Cl)]$_2$[Cu(L1)Cl]$_2$ (**3**) and [Cu(L3)(μ-N_3)]$_2$ (**4**).

Compound	[Ni(L1)(N_3)]	[Ni(L2)(N_3)]	[Cu(L1)(μ-Cl)]$_2$[Cu(L1)(Cl)]$_2$	[Cu(L3)(μ-N_3)]$_2$
Empirical formula	$C_{13}H_{11}N_7NiS$	$C_{14}H_{13}N_7NiS$	$C_{52}H_{44}Cl_4Cu_4N_{16}S_4$	$C_{28}H_{22}Cu_2N_{14}S_2$
Formula weight	356.06	370.08	1417.23	745.80
Temperature / K	293	293	150	100
Wavelength / Å	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	$P\bar{1}$	$C2/c$	$P2_1/n$	$Pbca$
Unit cell dimensions				
a / Å	6.812(3)	11.0428(8)	13.2776(5)	13.7877(7)
b / Å	8.063(3)	12.3443(5)	15.4640(6)	12.9538(6)
c / Å	13.349(5)	22.9690(11)	13.4326(5)	15.6337(8)
α / º	97.10(3)	–	–	–
β / º	96.91(3)	94.927(5)	102.185(1)	–
γ / º	99.02(3)	–	–	–
Volume / Å^{-3}	711.2(5)	3119.5(3)	2695.91(18)	2790.4(2)
Z	2	8	2	4
Calc. density / Mg/m^3	1.663	1.576	1.746	1.775
Absorp. coefc. / mm^{-1}	1.517	1.387	1.966	1.725
F(000)	364	1520	1432	1512
Crystal size	0.19 × 0.15 × 0.06	0.15 × 0.10 × 0.05	0.10 × 0.06 × 0.04	0.31 × 0.15 × 0.13
θ range / º	2.82–28.88	3.76–27.00	2.03–27.14	2.52–29.13
Limiting indices / h,k,l	–9/9, –10/10, –17/17	–13/14, –15/15, –29/29	–17/16, –18/19, –15/17	–15/18, –14/17, –21/20
Refl. collect/unique (R_{int})	15636/3455 (0.0264)	11052/3395 (0.0342)	29992/5950 (0.0560)	31742/3759 (0.0325)
Completeness θ / º	97.8/28.00	99.4/27.00	99.6/27.14	100.0/29.13
Absorp. correct.	Analytical	Multi-scan	Multi-scan	Multi-scan
Max. /min. transm.	0.9145/0.7614	0.934/0.819	0.7455/0.6845	0.7459/0.6131
Data / parameters	3455/199	3395/213	5950/361	3759/209
Goodness-of-fit on F^2	1.037	0.914	1.005	1.082
Final R indices	R_1 = 0.0294, wR_2 = 0.0625	R_1 = 0.0277, wR_2 = 0.0601	R_1 = 0.0334 wR_2 = 0.0673	R_1 = 0.0226, wR_2 = 0.0689
R indices (all data)	R_1 = 0.0441, wR_2 = 0.0674	R_1 = 0.0551 wR_2 = 0.0848	R_1 = 0.0599 wR_2 = 0.0754	R_1 = 0.0341, wR_2 = 0.0733
Largest dif. peak/hole	0.242/–0.231	0.283/–0.239	0.467/–0.355	0.839/–0.318

Table S1 (cont). Crystal data and structure refinement for $[Mn(L1)_2]\cdot EtOH$ (**5**), $[Cd(L1)_2]\cdot MeOH$ (**6**) and $[Co(L2)_2]\cdot N_3$ (**7**).

Compound	$[Mn(L1)_2]\cdot EtOH$	$[Cd(L1)_2]\cdot MeOH$	$[Co(L2)_2]\cdot N_3$
Empirical formula	$C_{28}H_{28}MnN_8OS_2$	$C_{27}H_{26}CdN_8OS_2$	$C_{28}H_{26}CoN_{11}OS_2$
Formula weight	611.64	655.08	639.65
Temperature / K	100	100	273
Wavelength / Å	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*C*2/*c*	*C*2/*c*	$P2_1/c$
Unit cell dimensions			
a / Å	14.5132(9)	14.0111(11)	9.1405(4)
b / Å	18.7859(9)	19.8804(119	24.3129(12)
c / Å	11.3833(6)	10.7121(8)	15.1947(6)
α / º	–	–	–
β / º	111.460(2)	108.500(3)	120.285(4)
γ / º	–	–	–
Volume / $Å^{-3}$	2888.4(3)	2829.6(3)	2915.9(2)
Z	4	4	4
Calc. density / Mg/m^3	1.407	1.538	1.457
Absorp. coefc. / mm^{-1}	0.639	0.956	0.772
F(000)	1268	1328	1320
Crystal size	0.25 × 0.20 × 0.18	0.14 × 0.12 × 0.10	0.25 × 0.24 × 0.22
θ range / º	2.90–26.42	2.34–26.43	2.28-28.24
Limiting indices / *h,k,l*	–18/18, –23/23, –14/14	–17/17, –24/23, –13/13	–12/11, –32/29, –20/20
Refl. collect/unique (R_{int})	20205/2960 (0.0244)	19776/2907 (0.0258)	11180/6673 (0.0564)
Completeness θ / º	99.8/25.00	99.4/25.24	99.7/25.00
Absorp. correct.	Multi-scan	Multi-scan	Multi-scan
Max. /min. transm.	0.8937/0.8566	0.9106/0.8780	0.8485/0.8304
Data / parameters	2960/201	2907/182	6673/381
Goodness-of-fit on F^2	1.085	1.048	0.895
Final *R* indices	R_1 = 0.0365, wR_2 = 0.1025	R_1 = 0.0486, wR_2 = 0.1272	R_1 = 0.0462, wR_2 = 0.1056
R indices (all data)	R_1 = 0.0404, wR_2 = 0.1053	R_1 = 0.0534, wR_2 = 0.1323	R_1 = 0.1332, wR_2 = 0.1339
Largest dif. peak/hole	0.876/–0.516	2.801/–1.084	0.417/–310

Table S2. Selected bond lengths [Å] and bond angles [º] for [Ni(L1)(N_3)] (**1**), [Ni(L2)(N_3)] (**2**), [Cu(L1)(μ-Cl)]$_2$[Cu(L1)Cl]$_2$ (**3**) and [Cu(L3)(μ-N_3)]$_2$ (**4**).

Compound	**[Ni(L1)(N_3)]**	**[Ni(L2)(N_3)]**	**[Cu(L1)(Cl)]**	**[Cu(L1)(μ-Cl)]$_2$**	**[Cu(L3)(μ-N_3)]$_2$**
M-N_{azm}	1.8459(15)	1.850(2)	1.969(2)	1.967(2)	1.9596(14)
M-X	1.8773(17)	1.882(2)	2.2135(8)	2.2535(7)	2.3761(15)
M-N_{py}	1.9248(17)	1.932(2)	2.018(2)	2.019(2)	2.0379(14)
M-S	2.1507(10)	2.1480(8)	2.2502(8)	2.2628(8)	2.0210(14)[b]
M-X_p[a]				2.811397(12)	1.9600(14)
N_{azm}-M-X	176.50(7)	175.72(11)	177.49(7)	173.59 (7)	171.17(6)
N_{azm}-M- N_{py}	83.52(7)	83.42(9)	80.93(9)	80.82(9)	79.35(6)
N_{azm}-M-S	86.61(6)	86.70(7)	83.43(7)	83.08(7)	79.22(5)[b]
X-M-N_{py}	93.75(7)	94.12(10)	97.32(7)	87.65(7)	93.86(5)
X-M-S	96.14(6)	95.74(8)	98.36(3)	97.51(3)	96.29(5)[b]
N_{py}-M-S	170.10(5)	170.13(7)	164.29(7)	162.15(7)	156.25(6)[b]
N_{azm}-M-X_p				91.580(1)	90.04(5)
N_{py}-M-X_p				89.865(1)	95.62(6)
X-M-X_p				94.643(1)	82.97(6)
S-M-X_p				98.253(1)	106.88(6)[b]

*N_{azm}= azomethine atom, N_{py} = pyridine atom,; [a)] bridging ligand atom (Cl in **3** or N in **4**); [b)]N1 instead of S

Table S2 (cont.). Selected bond lengths [Å] and bond angles [º] for $[Mn(L1)_2]\cdot EtOH$ (**5**), $[Cd(L1)_2]\cdot MeOH$ (**6**) and $[Co(L2)_2]$ N_3 (**7**).

Compound	**$[Mn(L1)_2]\cdot EtOH$**	**$[Cd(L1)_2]\cdot MeOH$**	**$[Co(L2)_2]$ N_3**
M-N_{azm}	2.2427(17)	2.342(3)	1.880(3)
M-N_{py}	2.2696(17)	2.406(3)	1.969(3)
M-S	2.5092(6)	2.5675(12)	2.2156(10)
M-N_{azm}(a	2.2427(17)	2.342(3)	1.888(3)
M-N_{py}(a	2.2696(17)	2.406(3)	1.955(3)
M-S(a	2.5092(6)	2.5675(12)	2.2274(10)
N_{azm}-M- N_{py}	72.88(6)	69.89(11)	82.21(11)
N_{azm}-M-S	75.40(4)	74.57(8)	86.07(8)
N_{azm}-M-N_{azm}(a	160.37(9)	157.96(16)	179.46(11)
N_{azm}-M-N_{py}(a	92.72(6)	93.39(11)	97.88(12)
N_{azm}-M-S(a	118.58(4)	120.66(8)	93.68(8)
N_{py}-M-S	148.21(4)	144.45(9)	168.02(9)
N_{py}-M-N_{azm}(a	92.72(6)	93.39(11)	97.62(12)
N_{py}-M-N_{py}(a	87.27(8)	83.75(15)	90.18(11)
N_{py}-M- S(a	96.37(4)	97.81(8)	91.14(8)
S-M-N_{azm}(a	118.58(4)	120.65(8)	94.11(8)
S-M-N_{py}(a	96.37(4)	97.81(8)	88.95(8)
S-M-S(a	96.80(3)	100.78(6)	92.10(4)
N_{azm}(a-M-N_{py}(a	72.88(6)	69.89(11)	82.64(12)
N_{azm}(a-M-S(a	75.40(4)	74.57(8)	85.81(9)
N_{py}(a-M-S(a	148.21(4)	144.45(9)	168.44(9)

a)In **5** and **6**, symmetry transformation used to generate equivalent atoms: -x, y, -z+1/2. In **7**, second ligand molecule.

Table S3. Hydrogen bond parameters [Å, º] for [Ni(L1)(N_3)] (**1**), [Ni(L2)(N_3)] (**2**), [Cu(L1)(μ-Cl)]$_2$ [Cu(L1)Cl]$_2$ (**3**) and [Cu(L3)(μ-N_3)]$_2$ (**4**), [Mn(L1)$_2$]·EtOH (**5**), [Cd(L1)$_2$]·MeOH (**6**) and [Co(L2)$_2$]N_3 (**7**).

Compound	**D–H···A***	**D–H**	**H···A**	**D···A**	**∠DHA**
[Ni(L1)(N_3)]	N_{ta}-H···N_{az}^{t}	0.86	2.19	3.041(3)	173.4
t: -x+1, -y, -z+1					
[Ni(L2)(N_3)]	N_{ta}-H···N_{az}^{t}	0.84	2.23	3.058(4)	167.0
	C7-H7B···S1[a]	0.96	2.86	3.735(3)	152.0
t: -x+1, -y, -z+1; a: x-1/2, y+1/2, z					
[Cu(L1)(μ-Cl)]$_2$[Cu(L1)Cl]$_2$	N_{ta}-H···S1[a]	0.88	2.77	3.570(2)	151.2
	N_{ta}-H···S2[b]	0.88	2.63	3.508(2)	172.3
	C2-H2···Cl2[b]	0.95	2.82	3.579(3)	137.0
	C2-H2···S2[b]	0.95	2.93	3.780(1)	149.0
	C15-H15···Cl1[a]	0.95	2.92	3.613(1)	131.3
a: x, y, z+1; b: x, y, z-1;					
[Cu(L3)(μ-N_3)]$_2$	C14-H14B···S1[a]	0.98	2.99	3.871(1)	149.7
a: -x, y+1/2, -z+1/2					
[Mn(L1)$_2$]·EtOH	N_{ta}-H···S2[a]	0.86	2.60	3.368(2)	149.4
	C4-H4A···S2[b]	0.95	2.95	3.625(4)	129.5
	C14-H14B···N_{hz}[c]	0.99	2.67	3.615(12)	158.6
a: -x, -y+1, -z; b: x+1/2, -y+1/2, z+1/2; c: x, y, z+1					
[Cd(L1)$_2$]·MeOH	N_{ta}-H···S1[a]	0.88	2.82	3.472(4)	132.0
	C6-H6A···O10[b]	0.95	2.60	3.485(9)	154.8
	C13-H13A···S1[c]	0.95	2.99	3.884(5)	158.0
	C1-H1A···O10[d]	0.95	2.57	3.497(9)	164.2
a: -x+1, -y+1, -z+1; b:-x+1, y, -z+3/2; c: x, -y+1, z-1/2; d: -x+1/2, -y+1/2, -z+2					
[Co(L2)$_2$]·N_3	N_{ta}-H4A···N_{az}	0.86	2.06	2.915(5)	171.8
	N_{ta}-H8···N_{az}^{t}	0.86	2.18	2.950(6)	149.0
t: x, -y+1/2, z+1/2					

*N_{ta} = thioamide atom, N_{az}^{t} = azide terminal atom, N_{hz} = hydrazine atom,

Table S4. Intermolecular interaction parameters (Å, º)

Compound	*π···π interactions*	**Cg(I)···Cg(J)**	**α**
[Ni(L1)(N$_3$)]	Cg(1)···Cg(1)^a	3.608(2)	0
	Cg(1)···Cg(1)^b	3.576(2)	0
	Cg(1)···Cg(2)^a	3.535(2)	0.34
	Cg(1)···Cg(2)^b	3.671(2)	0.34
	Ring-metal interactions	**Cg(I)···Ni(J)**	**β**
	Cg(1)···Ni(1)^a	3.574	18.34
	Cg(1)···Ni(1)^b	3.994	33.51
Cg(1): ring (Ni1/S3/C3/N2/N1); Cg(2): ring (Ni1/N1/C11/C12/N113) a = 1-*x, 1-y, 1-z;* b = *2-x, 1-y, 1-z*			
	π···π interactions	**Cg(I)···Cg(J)**	**α**
[Ni(L2)(N$_3$)]	Cg(1)···Cg(1)^a	3.576(1)	0
	Cg(1)···Cg(2)^a	3.735(1)	0.42
	Cg(1)···Cg(3)^b	3.624(2)	0.44
	Cg(2)···Cg(2)^b	3.578(2)	0
	Cg(2)···Cg(3)^b	3.651(2)	0.08
	Ring-metal interactions	**Cg(I)···Ni(J)**	**β**
	Cg(1)···Ni(1)^a	3.775	23.02
	Cg(3)···Ni(1)^b	3.863	27.60
Cg(1): ring (Ni1/S1/C8/N3/N2); Cg(1): ring (Ni1/N1/C5/C6/N2); Cg(3): ring (N1/C1/C2/C3/C4/C5) a = 1/2-*x, 1/2-y, 1-z;* b = *1-x, 1-y, 1-z*			
	π···π interactions	**Cg(I)···Cg(J)**	**α**
[Cu(L1)(μ-Cl)]$_2$[Cu(L1)Cl]$_2$	Cg(3)···Cg(5)^a	3.554(2)	3.51
	Cg(4)···Cg(5)^a	3.550(2)	3.33
	Cg(4)···Cg(9)^b	3.813(2)	4.62
	Cg(5)···Cg(7)^c	3.323(2)	7.68
	Cg(6)···Cg(5)^c	3.775(1)	6.00
	Cg(7)···Cg(9)^d	3.619(2)	1.19
	Cg(8)···Cg(9)^d	3.739(2)	1.45
	Ring-metal interactions	**Cg(I)···Cu(J)**	**β**
	Cg(5)···Cu(1)^c	3.688	33.96
	Cg(5)···Cu(2)^e	3.943	31.90

	Cg(9)···Cu(1)[f]	3.767	27.61

Cg(3): ring (Cu2/N7/C21/C22/N8); Cg(4): ring (N8/C22/C23/C24/C25/C26); Cg(5): ring (C14/C15/C16/C17/C18/C19);
Cg(6): ring (Cu1/S1/C7/N2/N3); Cg(7): ring (Cu1/N3/C8/C9/N4); Cg(8): ring (N4/C9/C10/C11/C12/C13);
Cg(9): ring (C1/C2/C3/C4/C5/C6)
a = *3/2-x, -1/2+y, 3/2-z;* b = *2- x, -y, 1-z;* c = *2-x, 1-y, 1-z*; d = *3/2-x, 1/2+y, 1/2-z*; e = *3/2-x, 1/2+y, 3/2-z*; f = *3/2-x, -1/2+y, 1/2-z*

[Cu(L3)(μ-N_3)]$_2$	*π···π interactions*	**Cg(I)···Cg(J)**	**α**
	Cg(4)···Cg(5)[a]	3.822(1)	18.59
	Ring-metal interactions	**Cg(I)···Cu(J)**	**β**
	Cg(6)···Cu(1)[a]	3.700	42.98

Cg(4): ring (S1/C1/N1/C8/C13); Cg(5): ring (N4/C3/C4/C5/C6/C7); Cg(6): ring (C8/C9/C10/C11/C12/C13)
a = *1/2-x, -1/2+y, z*

Cg(I)···Cg(J): Distance between ring centroids; α: Dihedral angle between planes I and J; β: Angle vector and normal to plane I.

Table S4 (cont.). Intermolecular interaction parameters (Å, º)

Compound	*π···π interactions*	**Cg(I)···Cg(J)**	**α**
	Cg(2)···Cg(5)[a]	3.769(2)	3.44
	Cg(4)···Cg(5)[b]	3.769(2)	3.44
	Cg(5)···Cg(5)[a]	3.784(1)	0
[Mn(L1)$_2$]·EtOH	*C-H···π-ring interactions*	**Cg(I)···H**	**γ**
	C1-H1A···Cg(2)[c]	2.95	17.19
	C1-H1A···Cg(3)	2.95	17.19
	C3-H3A···Cg(6)[d]	2.82	18.12
Cg(2): ring (Mn1/N1/C5/C6/N2); Cg(3): ring (Mn1/S2a/C7a/N3a/N2a); Cg(4): ring (Mn1/N1a/C5a/C6a/N2a); Cg(5): ring (N1/C1/C2/C3/C4/C5); Cg(6): ring (C8/C9/C10/C11/C12/C13)			
a = 1/2-*x, 1/2-y, 1-z;* b = *-1/2+x, 1/2-y, -1/2+z;* c = *-x, y, 1/2-z;* d = 1/2-x, -1/2+y, 1/2-z			
	π···π interactions	**Cg(I)···Cg(J)**	**α**
[Cd(L1)$_2$]·MeOH	Cg(2)···Cg(5)[a]	3.785(2)	2.73
	Cg(4)···Cg(5)[b]	3.785(2)	2.73
	Cg(5)···Cg(5)[a]	3.647(2)	0
Cg(2): ring (Cd1/N1/C5/C6/N2); Cg(4): ring (Cd1/N1a/C5a/C6a/N2a); Cg(5): ring (N1/C1/C2/C3/C4/C5)			
a = 3/2-*x, 1/2-y, 2-z;* b = *-1/2+x, 1/2-y, -1/2+z*			
	C-H···π-ring interactions	**Cg(I)···H**	**γ**
	C1-H1···Cg(2)	2.94	25.39
[Co(L2)$_2$]·N$_3$	C1-H1···Cg(4)	2.85	20.51
	C15-H15···Cg(1)	2.87	21.70
	C15-H15···Cg(3)	2.89	22.06
Cg(1): ring (Co1/S1/C8/N3/N2); Cg(2): ring (Co1/S2/C22/N7/N6); Cg(3): ring (Co1/N1/C5/C6/N2); Cg(4): ring (Co1/N5/C19/C20/N6)			
Cg(I)···Cg(J): Distance between ring centroids; α: Dihedral angle between planes I and J; β: Angle vector and normal to plane I.			

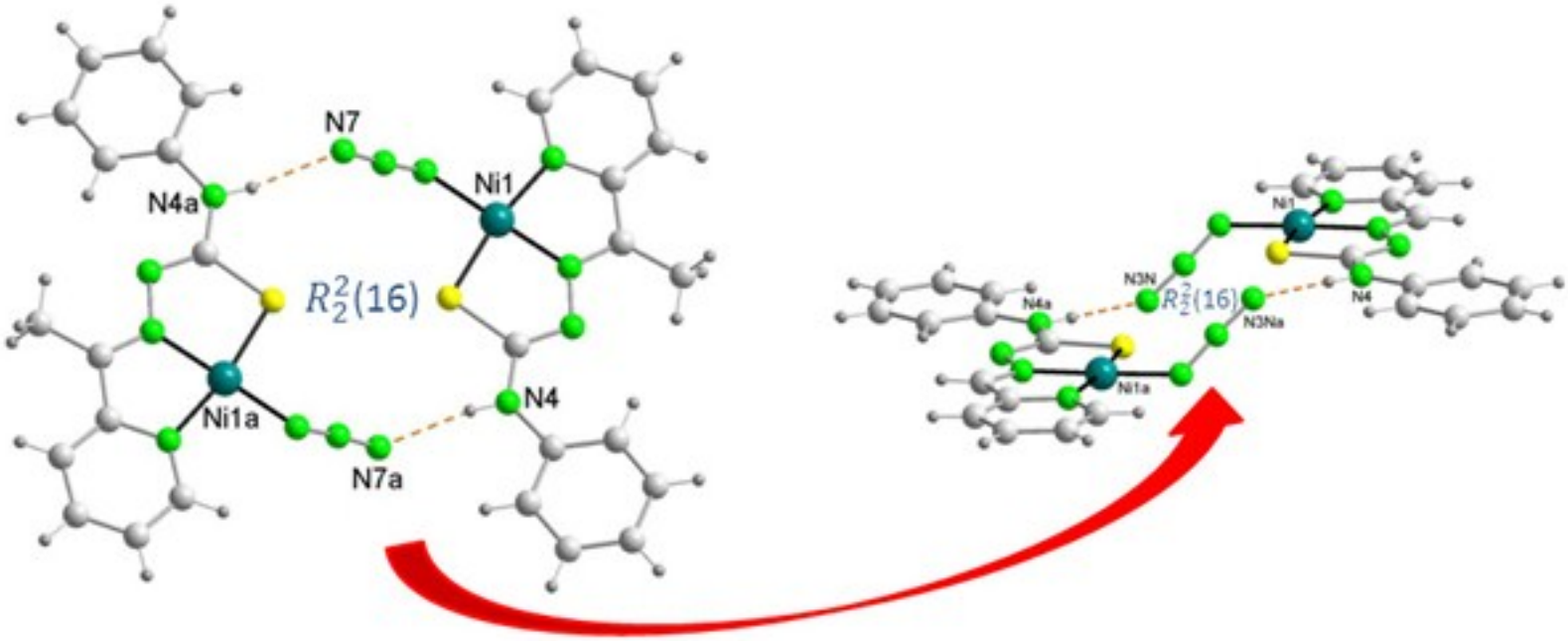

Fig. S1. Molecular pairing for the compounds **1** (right) and **2** (left) showing the intermolecular hydrogen bonding.

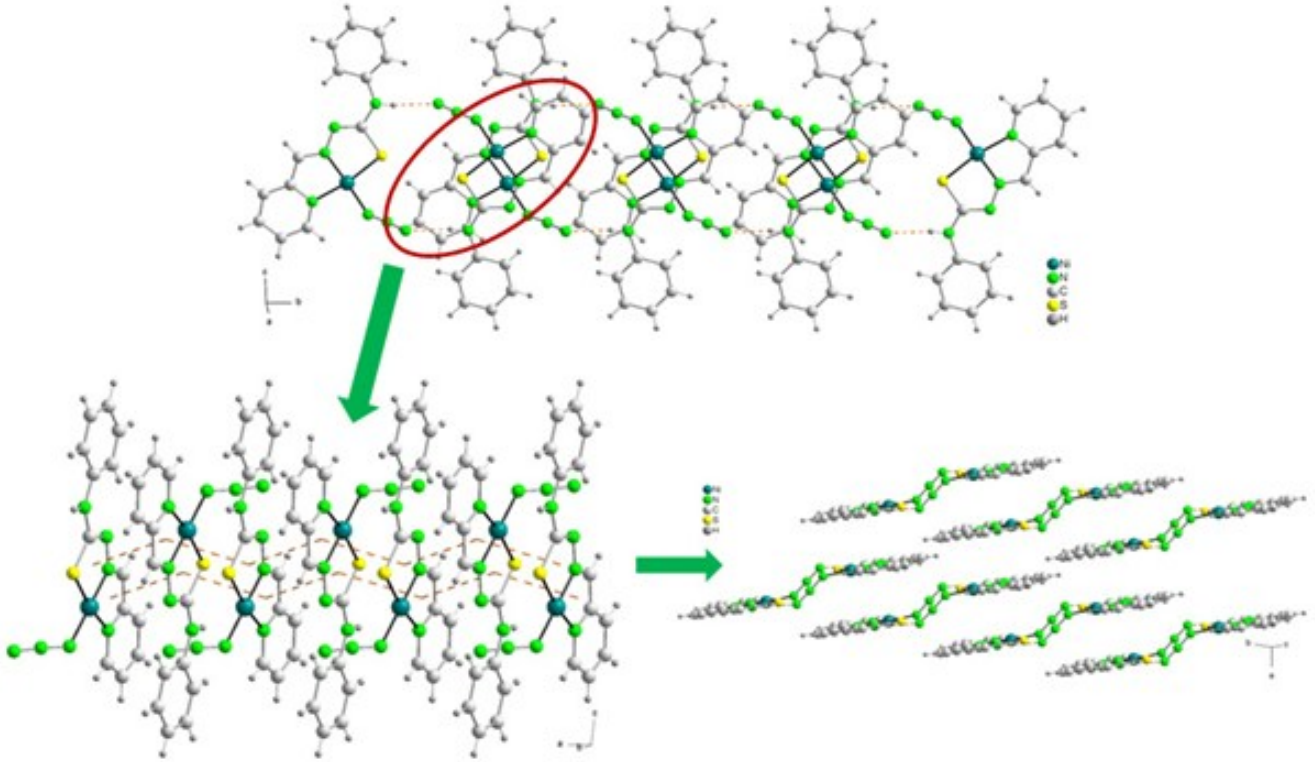

Fig. S2. Crystal packing diagram for the compound **1** showing the intermolecular π-π stacking.

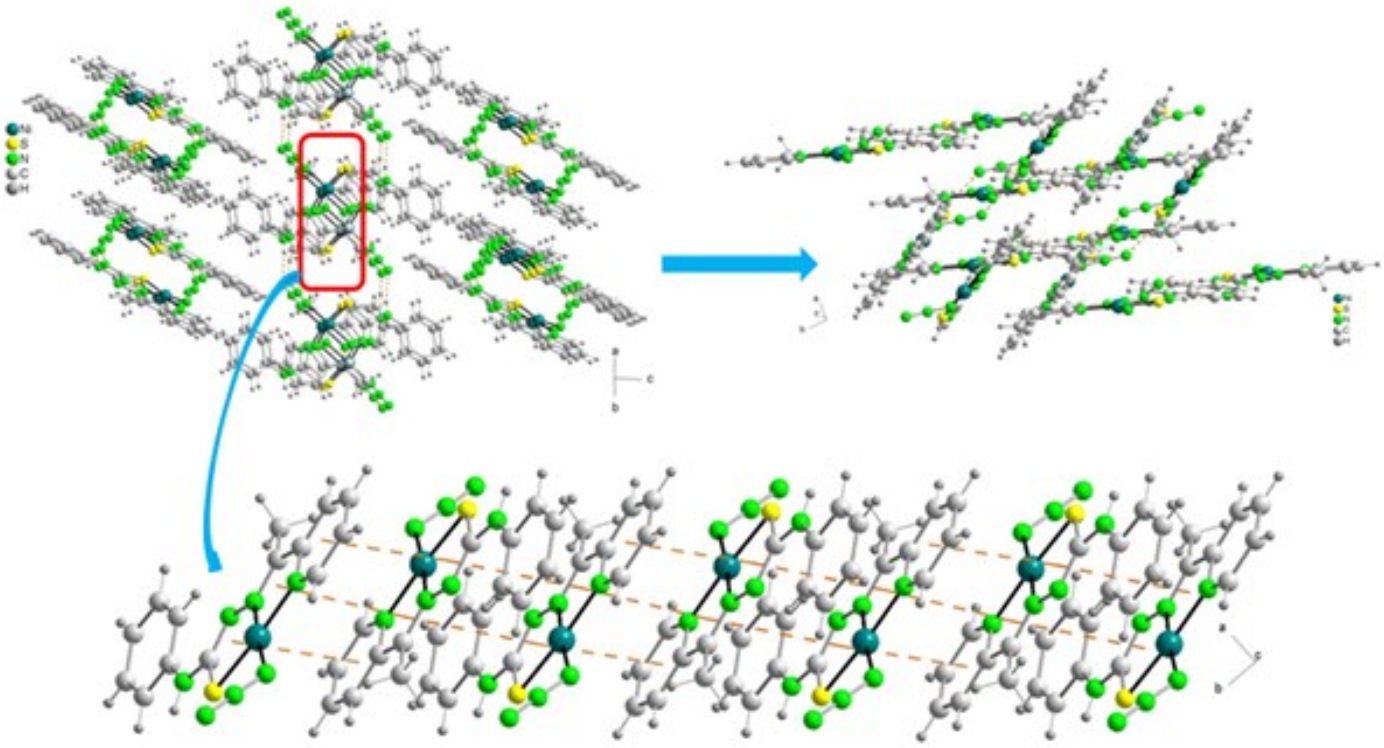

Fig. S3. Crystal packing diagram for the compound 2 showing the π-π stacking interactions.

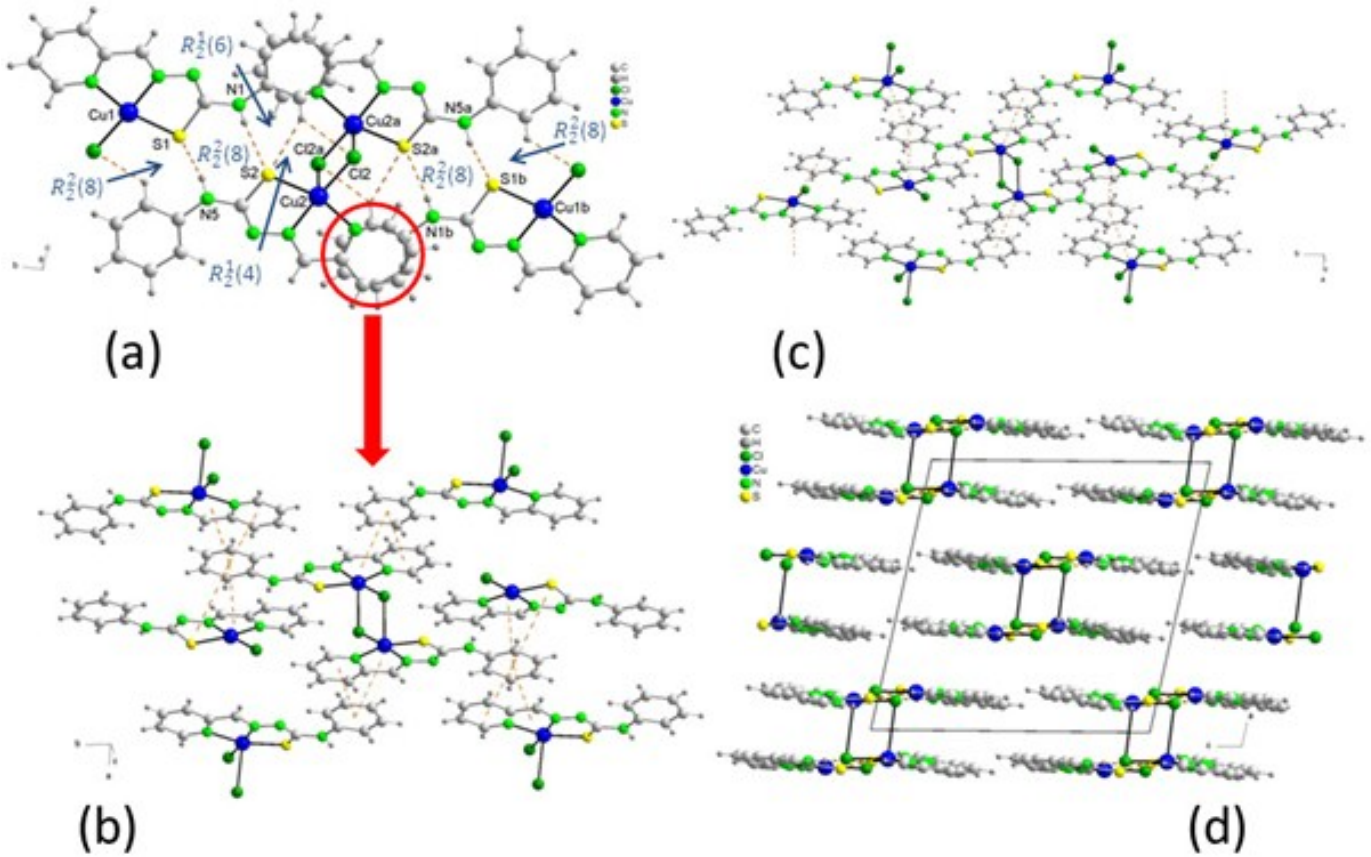

Fig. S4. Crystal packing diagram for compound 3 showing the intermolecular interactions and the supramolecular synthons.

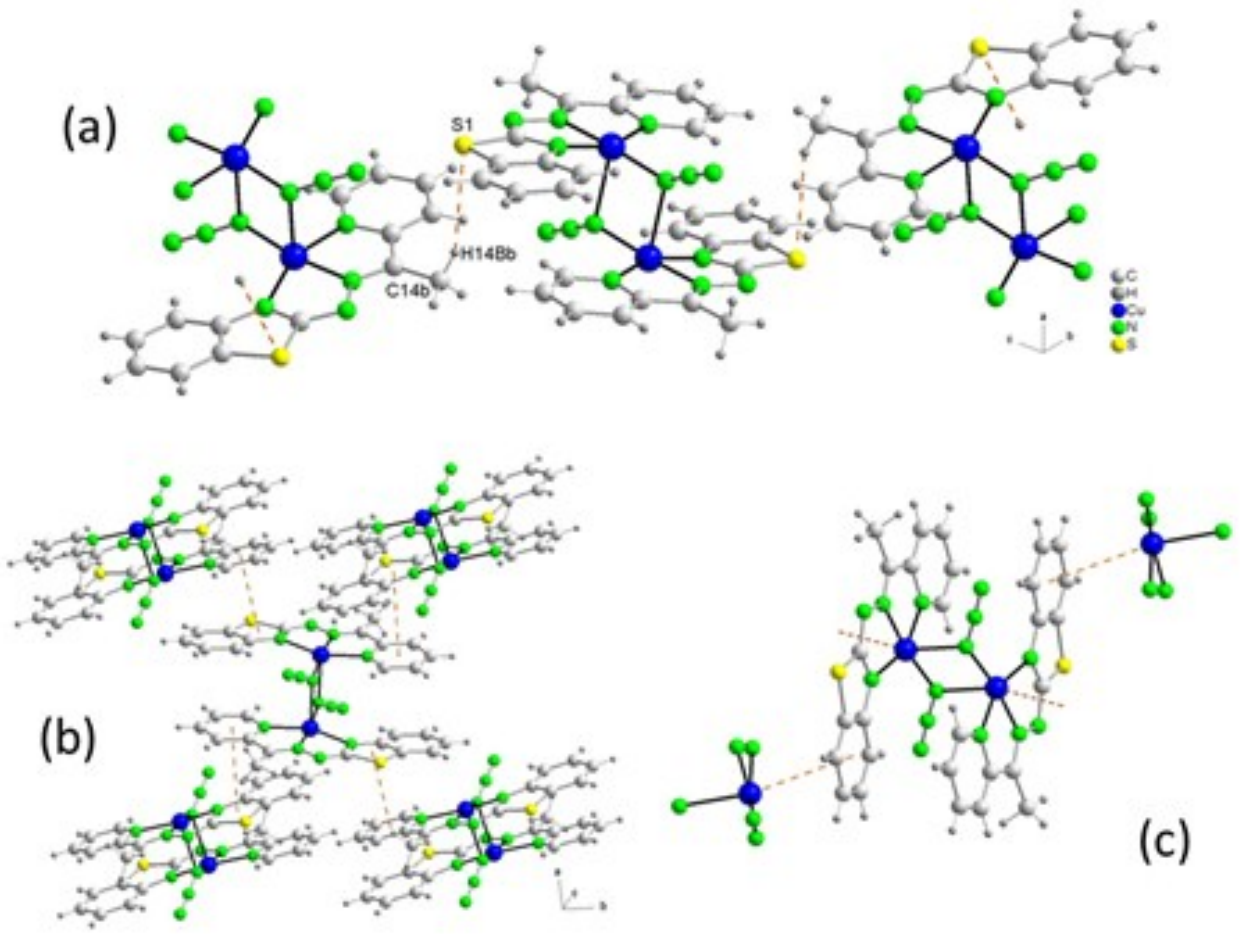

Fig. S5. Crystal packing diagram for compound **4** showing: a) no classical hydrogen bonds, b) π-π stacking interactions and c) intermolecular interactions between the phenyl ring and the copper atom.

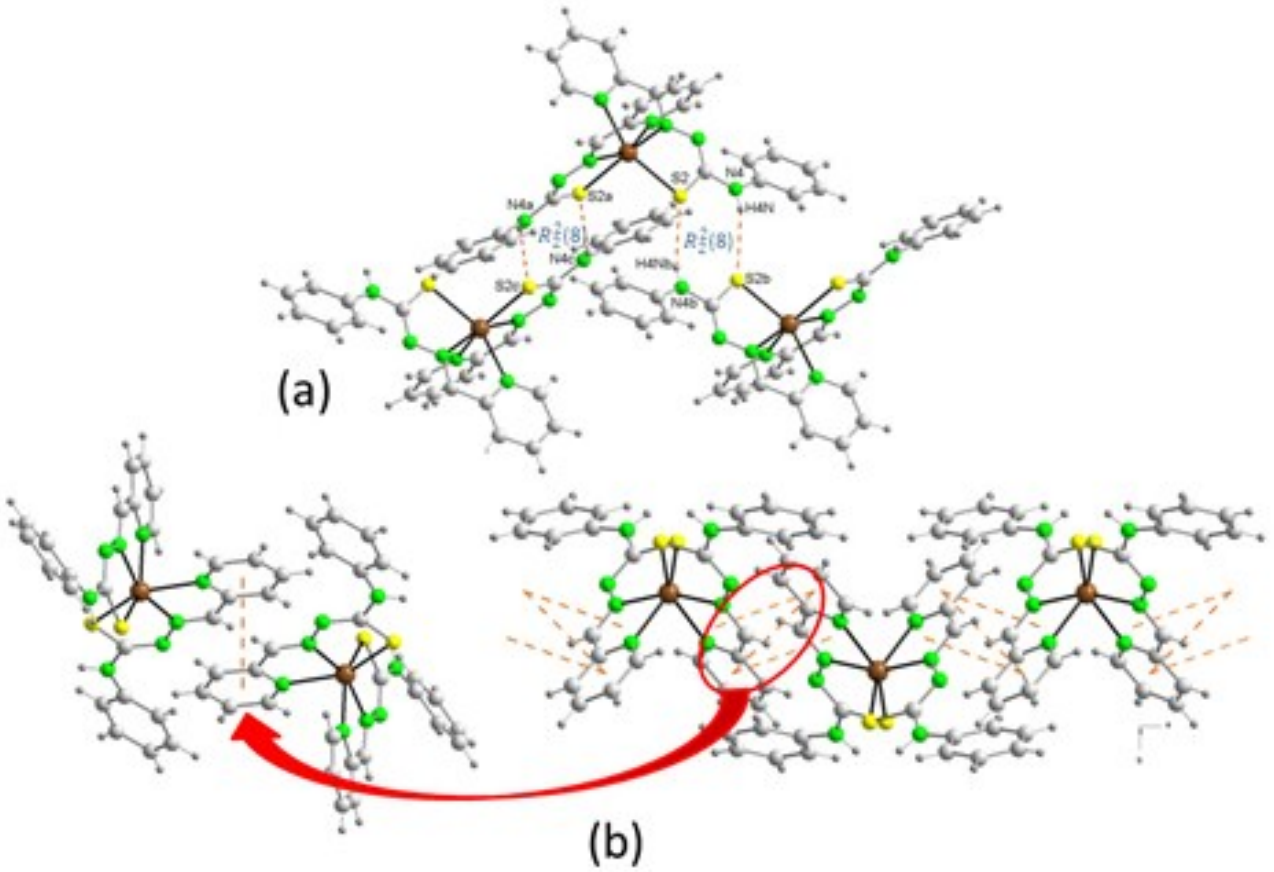

Fig. S6. Crystal packing of the molecules in **5**: a) detail of the chains viewed along the *c* axis, including supramolecular heterosynthons of $R_2^2(8)$ motif and b) view along *a* axis showing the π-π stacking interactions and detail of interactions between the pair of pyridine rings.

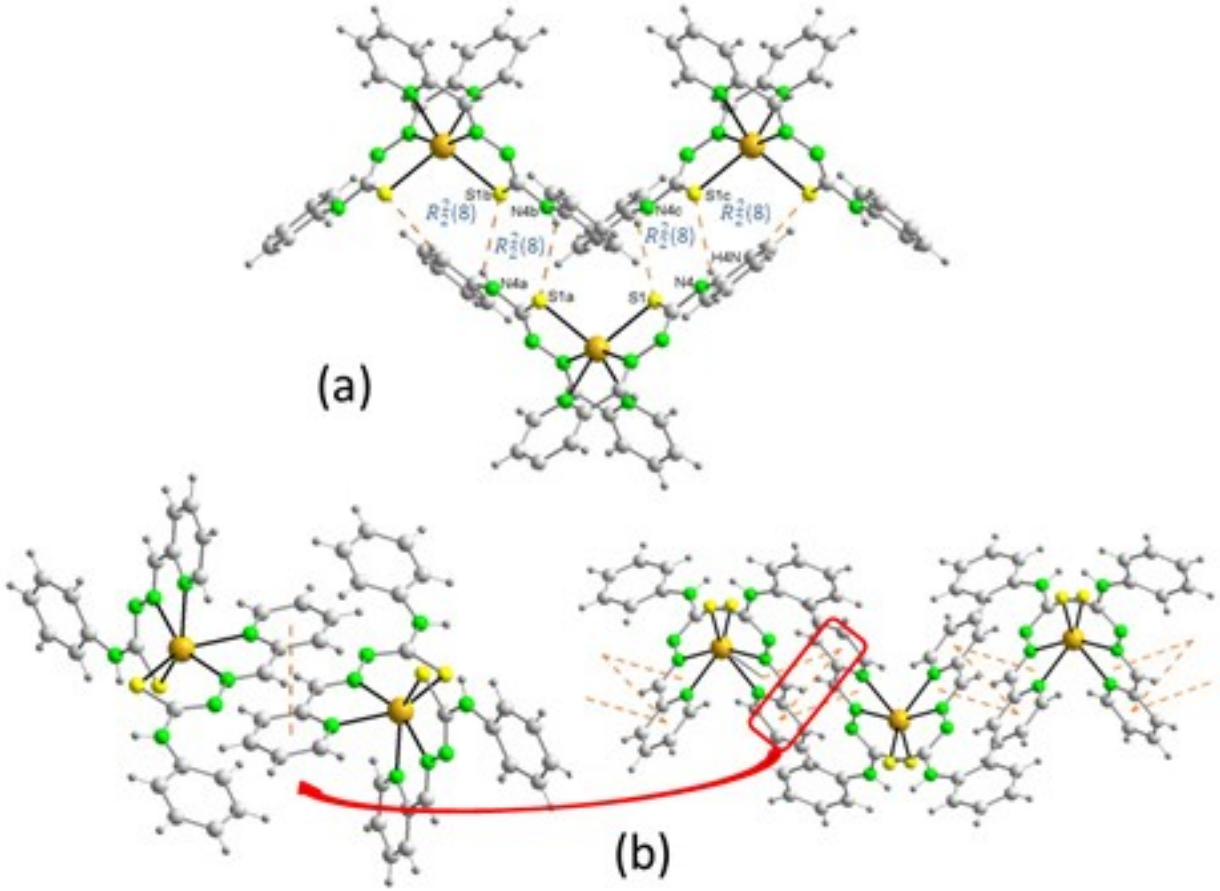

Fig. S7. Crystal packing of the molecules in **6**: a) detail of the chains viewed along the *c* axis, including supramolecular heterosynthons of $R_2^2(8)$ motif and b) view along *a* axis showing the π-π stacking interactions and detail of interactions between the pair of pyridine rings.

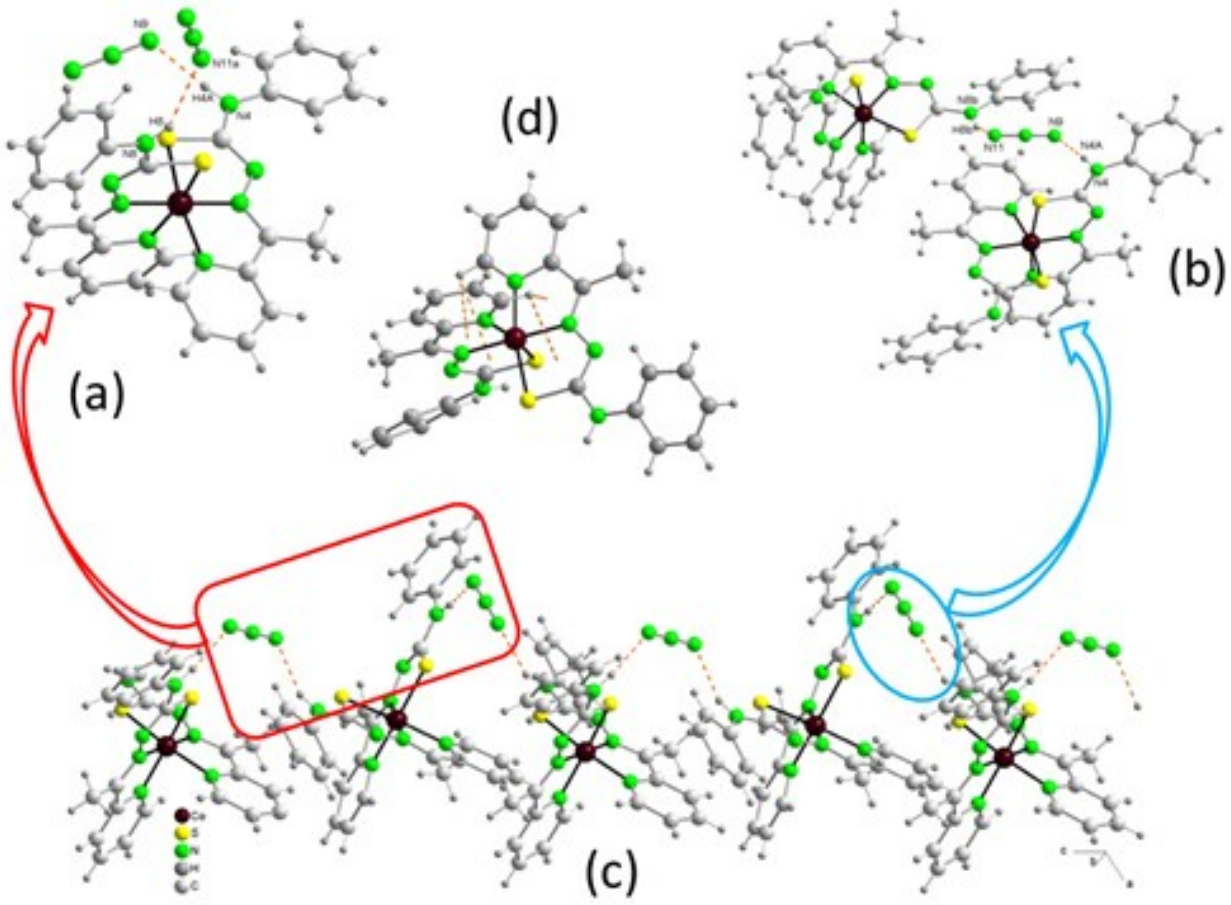

Fig. S8. Crystal packing of 7: a) details of anion-cation-anion hydrogen bonds interactions, b) details of cation-anion-cation hydrogen bonds interactions, c) view of infinite one-dimensional chains along the c axis and d) details on the C–H···chelate ring interactions.

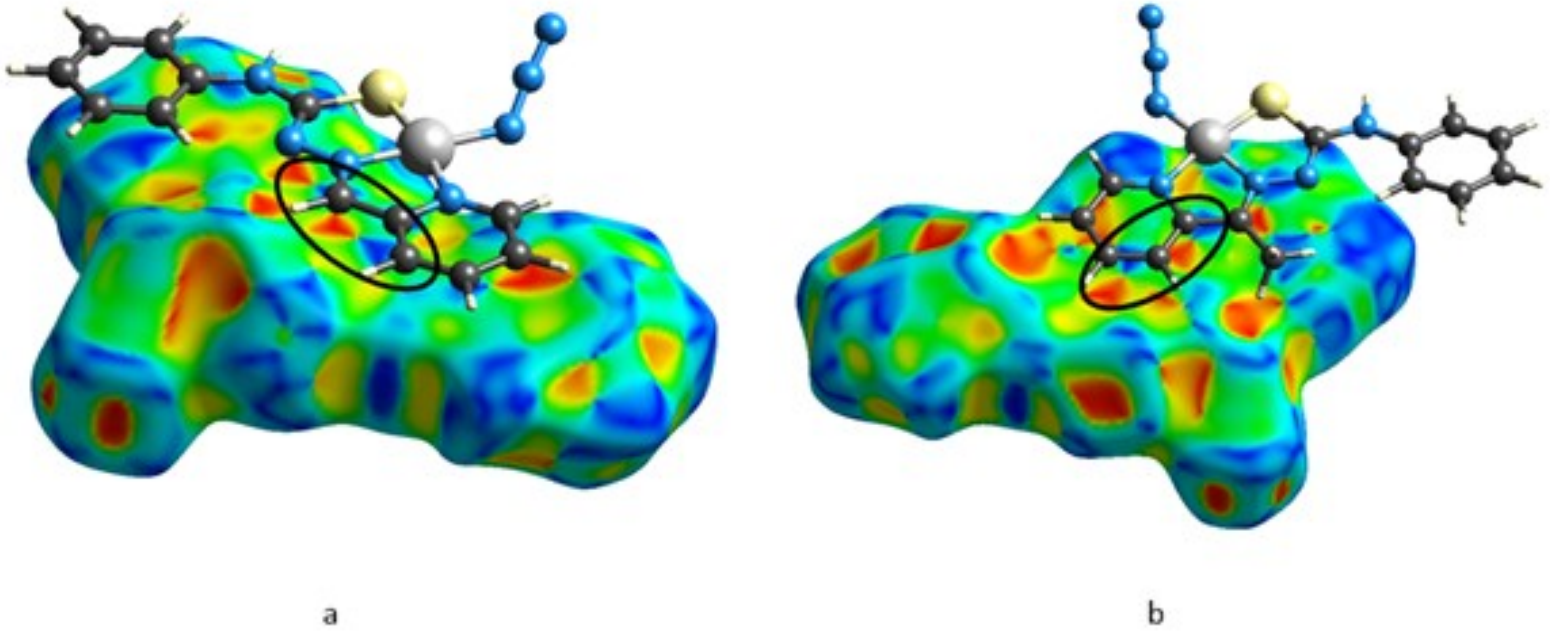

Fig. S9. Hirshfeld surface of **1** (a) and **2** (b) mapped with shape index function. Areas marker with ovals indicate stacking interactions

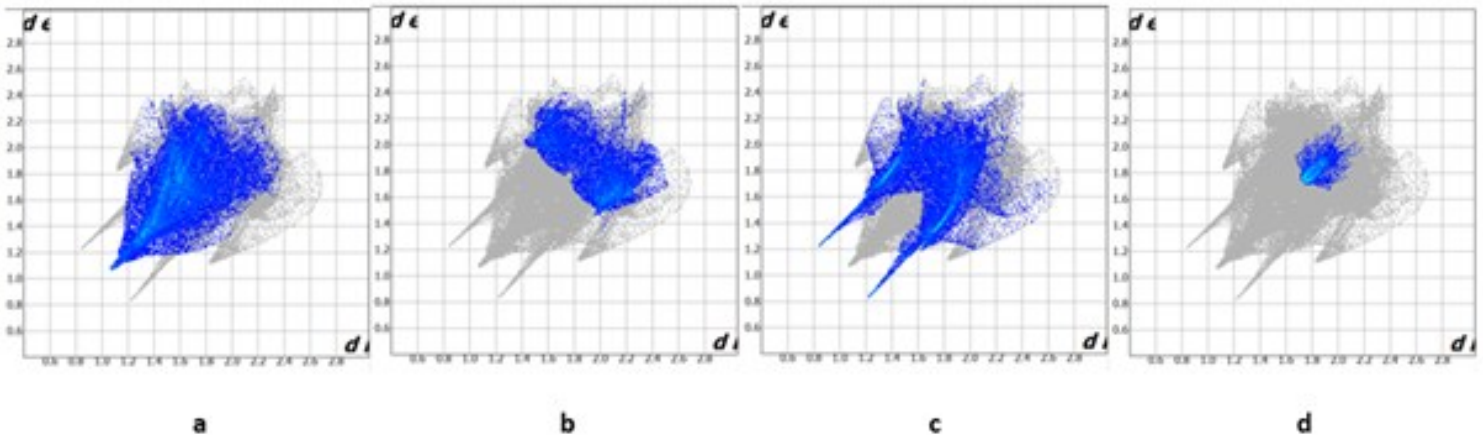

Fig. S10. Decomposed fingerprint plots of **1**: a) H···H, b) H···C, c) H···N and d) C···C.

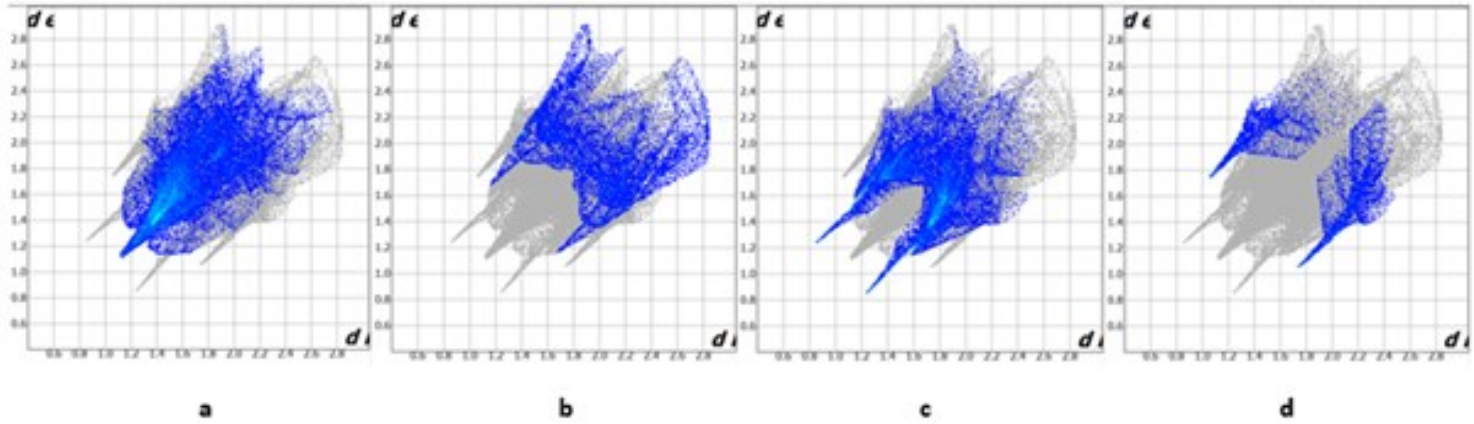

Fig. S11. Decomposed fingerprint plots of **2**: a) H···H, b) H···C, c) H···N and d) H···S.

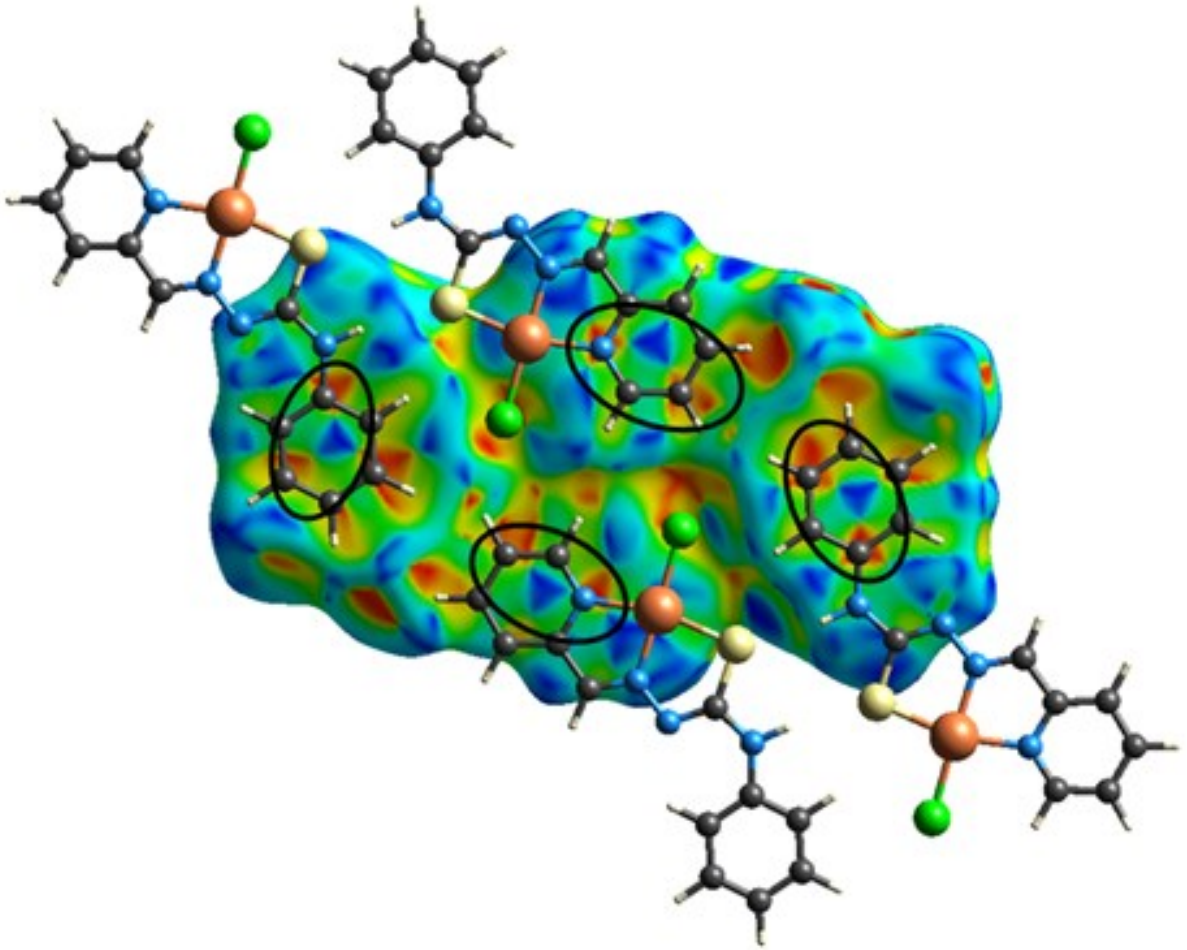

Fig. S12. Hirshfeld surface of **3** mapped with shape index function. Areas marked with ovals indicate stacking interactions.

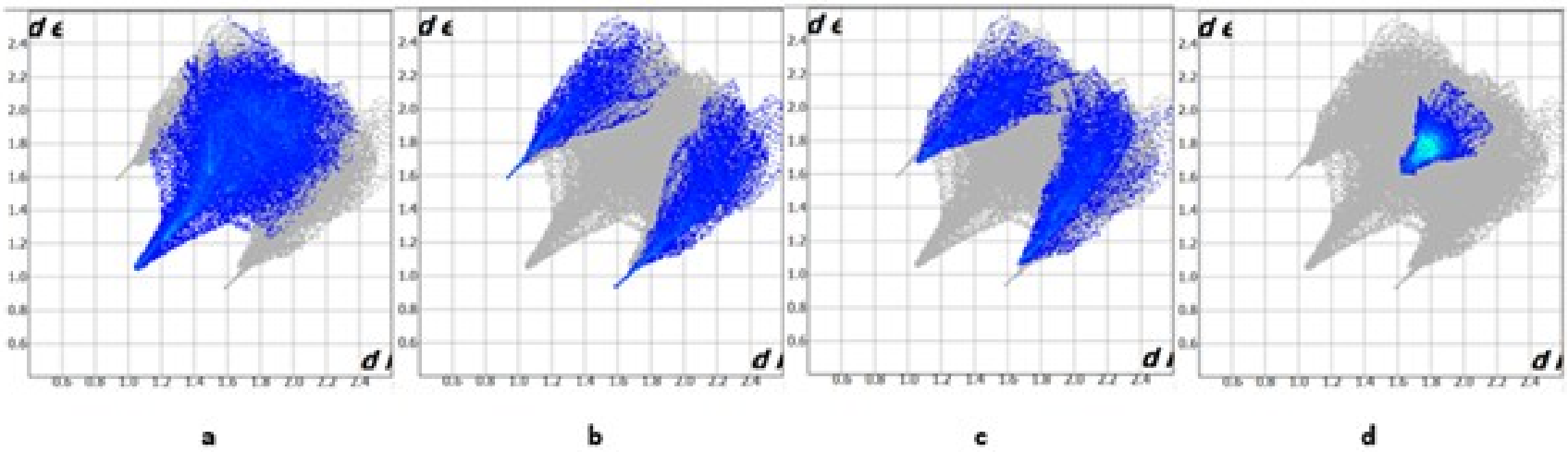

Fig. S13. Decomposed fingerprint plots for **3**: a) H···H, b) H···S, c) H···Cl and d) C···C.

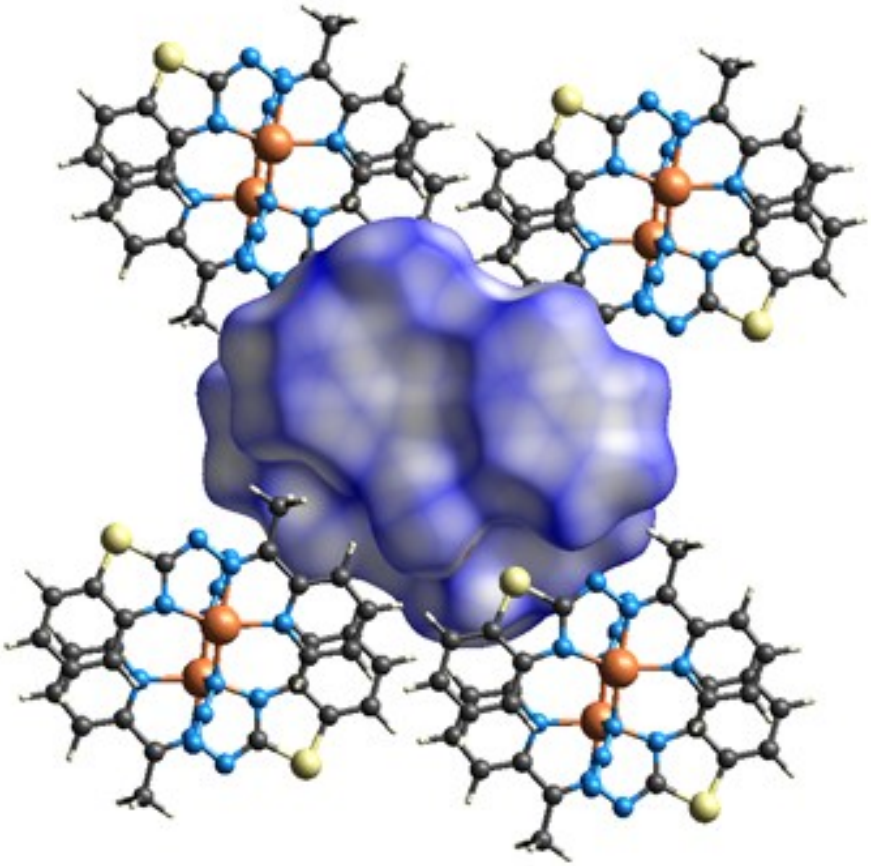

Fig. S14. Hirshfeld surface of **4** mapped with d_{norm} function.

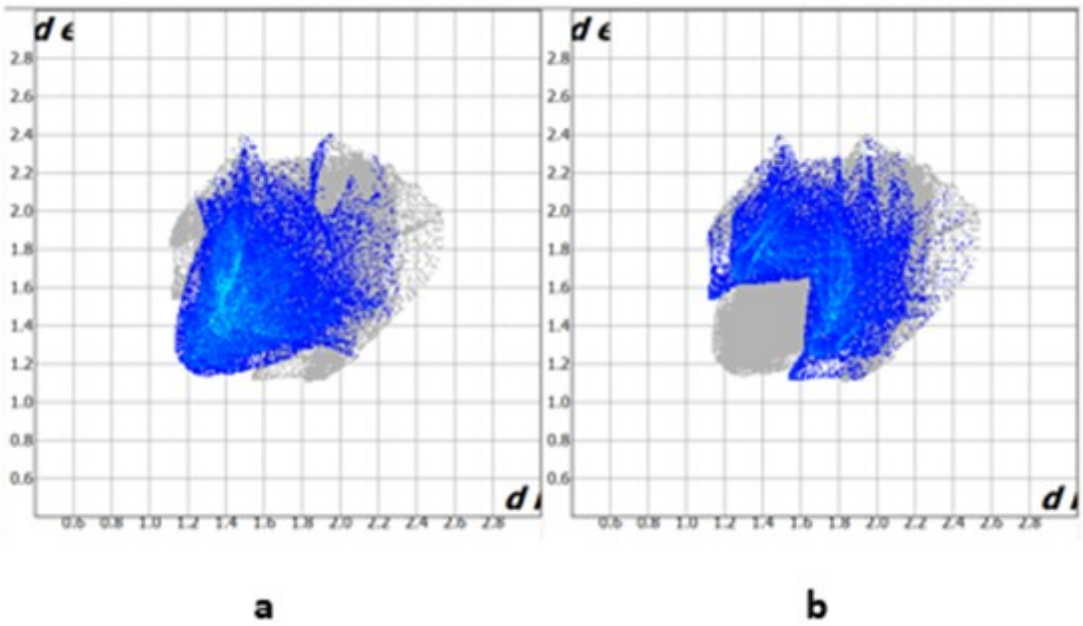

Fig. S15. Decomposed fingerprint plots of **4**: a) H···H and b) H···C.

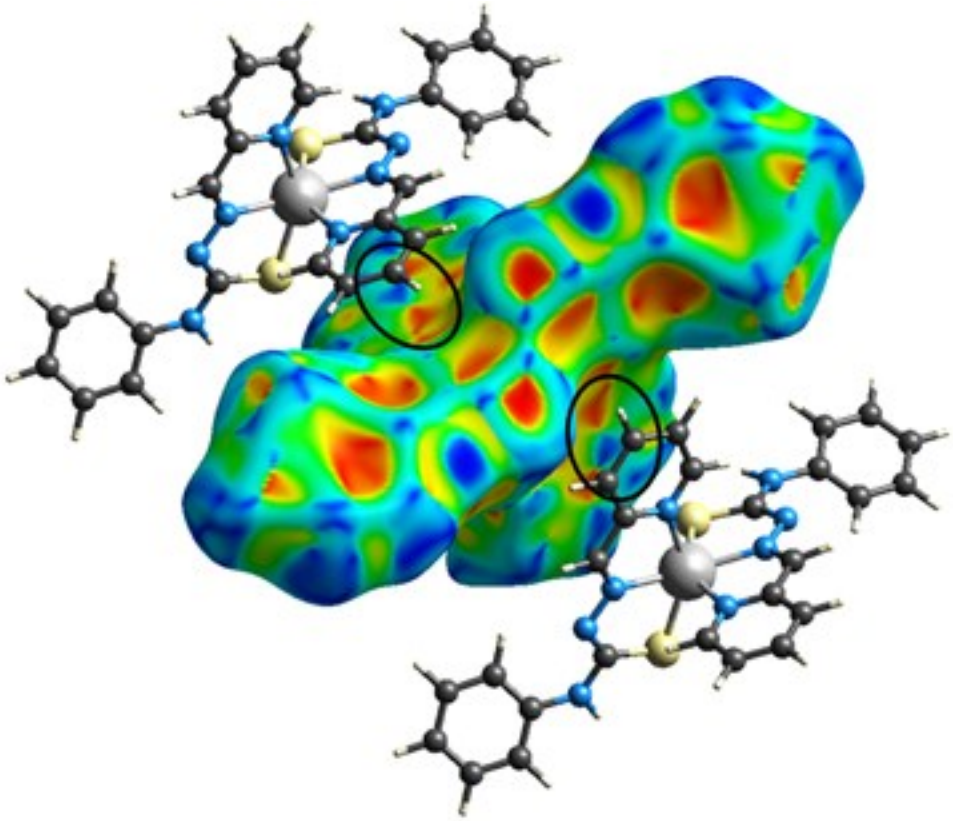

Fig. S16. Hirshfeld surface of **5** mapped with shape index function. Ovals indicate stacking interactions

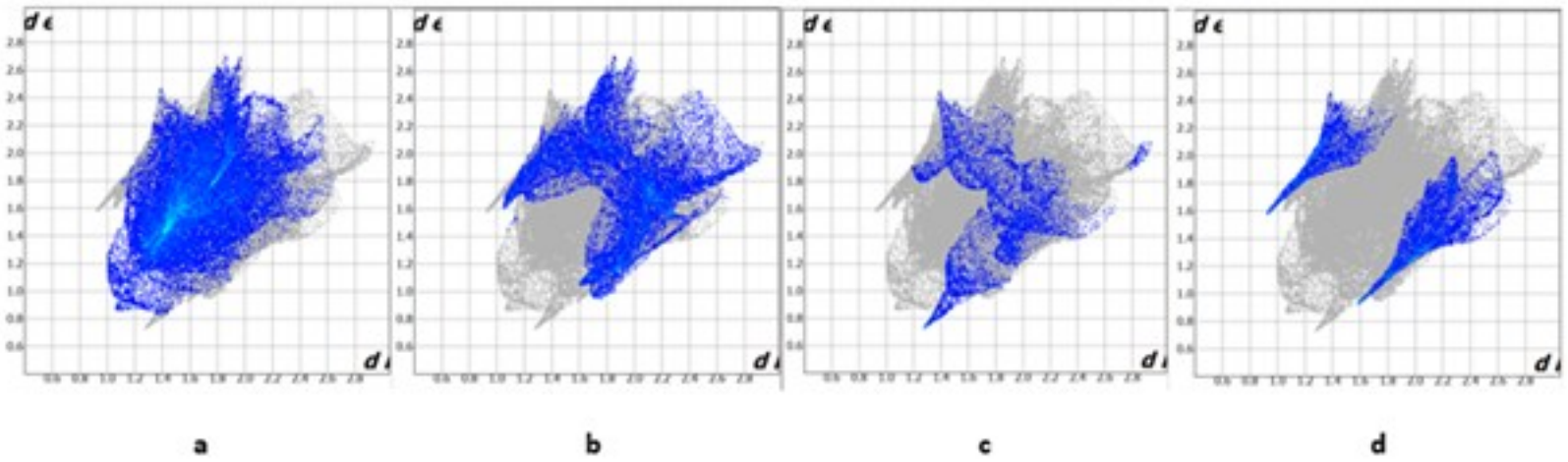

Fig. S17. Decomposed fingerprint plots of **5**: a) H···H, b) H···C, c) H···N and d) H···S.

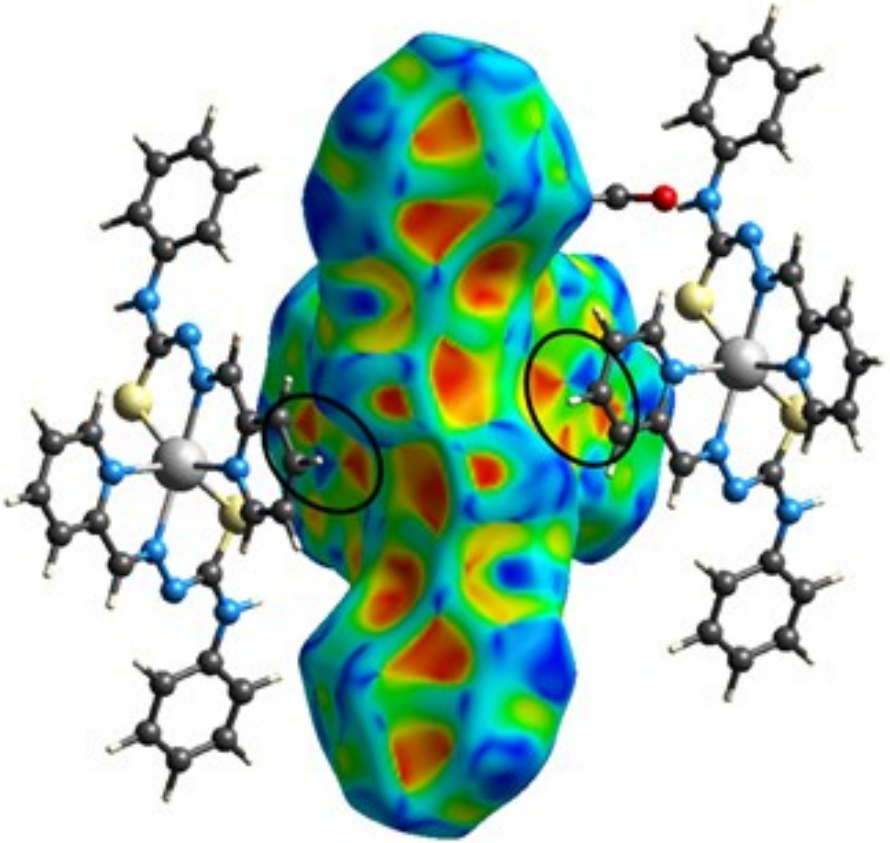

Fig. S18. Hirshfeld surface of **6** mapped with shape index function. Ovals indicate stacking interactions.

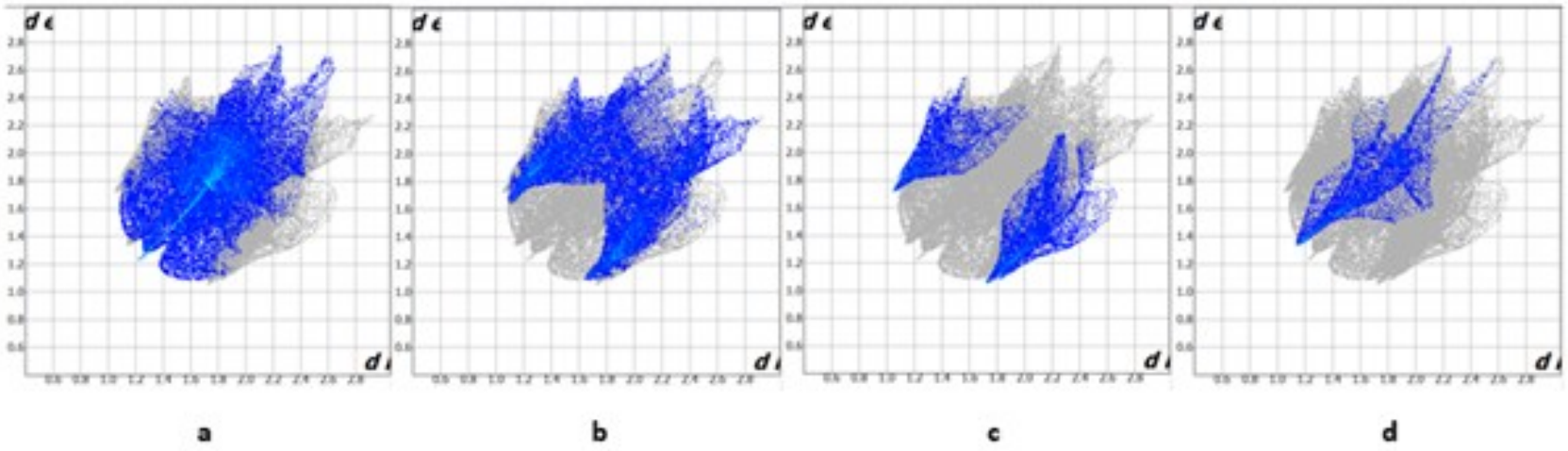

Fig. S19. Decomposed fingerprint plots of **6**: a) H···H, b) H···C, c) H···S and d) H···O.

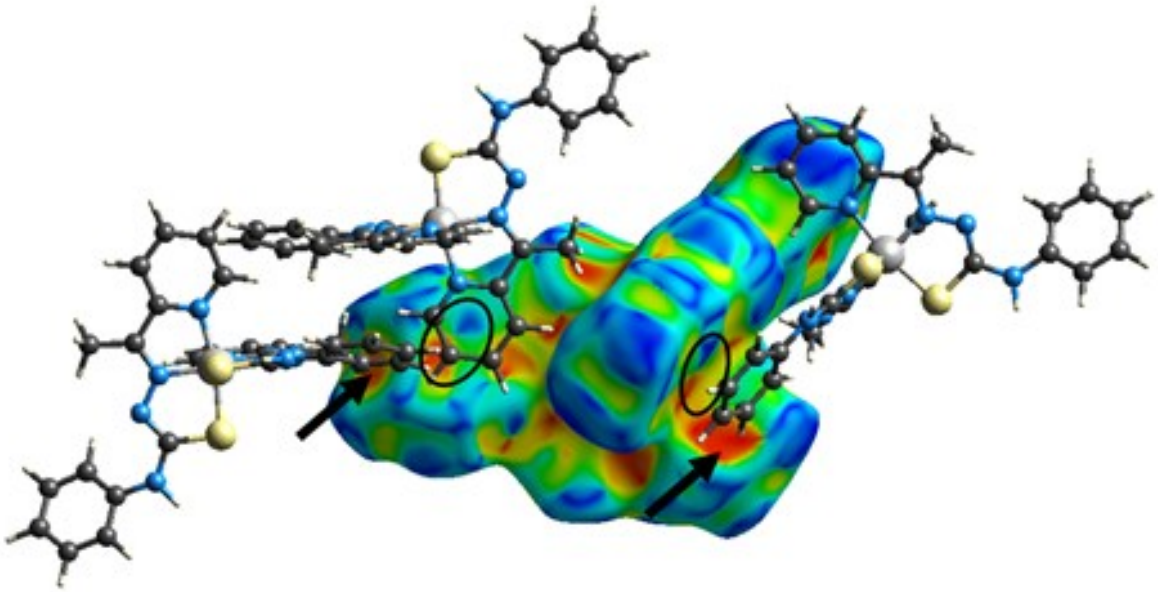

Fig. S20. Hirshfeld surface of **7** mapped with shape index function. Ovals indicate stacking interactions, while arrows indicate C-H···π interactions

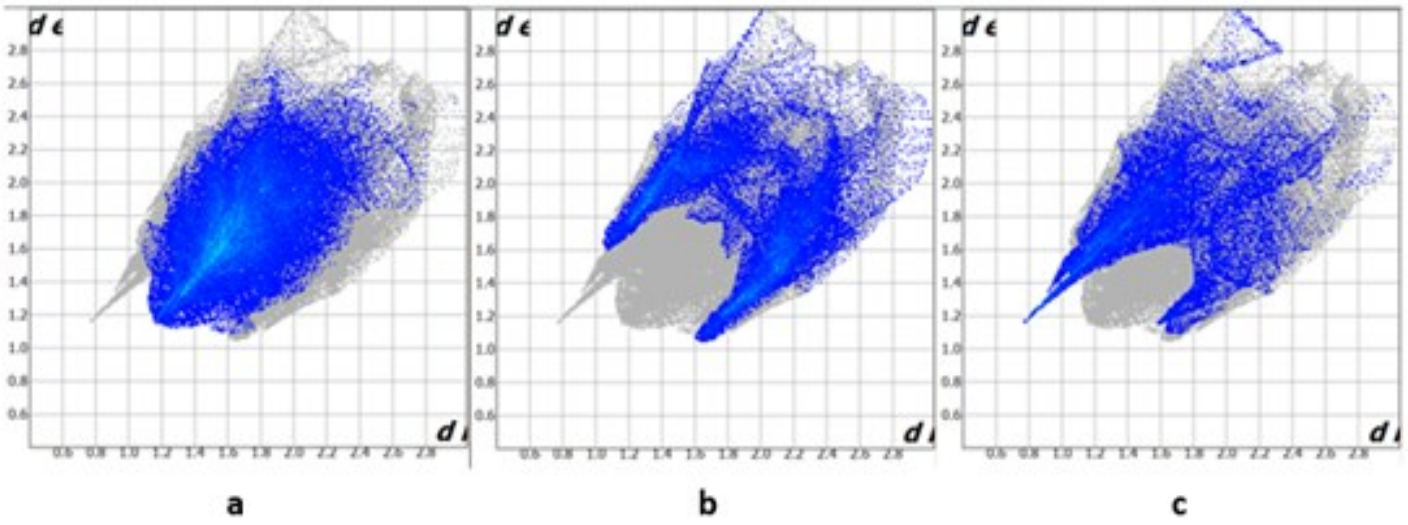

Fig. S21. Decomposed fingerprint plots of **7**: a) H···H, b) H···C and c) H···N