

Supporting Information

On the Importance of Pb···X (X = O, N, S, Br) Tetrel Bonding Interactions in a series of tetra- and hexa-coordinated Pb(II) compounds

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Table S1. Selected (Å) and bond angles (°) for (1–5) determined by X-ray diffraction.

Compound-(1)			
Pb-N(4)	2.362(12)	Pb-N(2)	2.469(10)
Pb-O(1)	2.447(9)	Pb-N(3)	2.642(12)
N(4)-Pb-O(1)	84.1(4)	N(4)-Pb-N(3)	83.2(4)
N(4)-Pb-N(2)	83.3(4)	O(1)-Pb-N(3)	127.4(3)
O(1)-Pb-N(2)	64.8(3)	N(2)-Pb-N(3)	63.1(3)
Compound-(2)			
Pb1-N(2)	2.489(5)	Pb1-N(3)	2.612(5)
Pb1-O(1)	2.503(4)	Pb1-Br(1)	2.7687(6)
Pb-O(2)	2.932(4)		
N(2)-Pb(1)-O(1)	64.06(13)	N(2)-Pb(1)-Br(1)	80.44(10)
N(2)-Pb(1)-N(3)	63.52(15)	O(1)-Pb(1)-Br(1)	83.68(10)
O(1)-Pb(1)-N(3)	127.06(14)	N(3)-Pb(1)-Br(1)	81.03(11)
Compound-(3)			
Pb(1)-N(7)	2.436(6)	Pb(1)-O(1)	2.648(4)
Pb(1)-O(2)	2.575(4)	Pb(1)-O(3)	2.655(7)
Pb(1)-N(3)	2.644(5)	Pb(1)-N(2)	2.688(4)
N(7)-Pb(1)-O(2)	78.84(19)	N(3)-Pb(1)-O(3)	147.3(2)
N(7)-Pb(1)-N(3)	76.08(18)	O(1)-Pb(1)-O(3)	80.8(2)
O(2)-Pb(1)-N(3)	61.89(14)	N(7)-Pb(1)-N(2)	80.76(19)
N(7)-Pb(1)-O(1)	82.32(19)	O(2)-Pb(1)-N(2)	119.89(13)
O(2)-Pb(1)-O(1)	160.77(15)	N(3)-Pb(1)-N(2)	58.46(14)
N(3)-Pb(1)-O(1)	116.97(14)	O(1)-Pb(1)-N(2)	59.99(14)
N(7)-Pb(1)-O(3)	79.9(2)	O(3)-Pb(1)-N(2)	138.1(2)
O(2)-Pb(1)-O(3)	92.1(2)		
Compound-(4)			
Pb1-N(7)	2.543(13)	Pb1-N(1)	2.751(8)
Pb1-N(6)	2.593(7)	Pb1-N(2)	2.752(7)
Pb1-N(5)	2.633(6)	Pb1-S(1)	3.051(3)
Pb1-N(8)	2.766(14)		
N(7)-Pb(1)-N(6)	76.7(4)	N(6)-Pb(1)-N(2)	119.0(2)
N(7)-Pb(1)-N(5)	103.1(3)	N(5)-Pb(1)-N(2)	72.9(2)
N(6)-Pb(1)-N(5)	61.4(2)	N(8)-Pb(1)-N(2)	130.5(3)
N(7)-Pb(1)-N(8)	148.0(4)	N(1)-Pb(1)-N(2)	58.4(2)
N(6)-Pb(1)-N(8)	74.7(4)	N(7)-Pb(1)-S(1)	86.9(3)
N(5)-Pb(1)-N(8)	75.2(3)	N(6)-Pb(1)-S(1)	87.02(19)
N(7)-Pb(1)-N(1)	90.9(4)	N(5)-Pb(1)-S(1)	142.72(18)
N(6)-Pb(1)-N(1)	167.5(3)	N(8)-Pb(1)-S(1)	77.7(3)
N(5)-Pb(1)-N(1)	124.4(2)	N(1)-Pb(1)-S(1)	90.65(19)
N(8)-Pb(1)-N(1)	116.9(4)	N(2)-Pb(1)-S(1)	144.01(17)

N(7)-Pb(1)-N(2)	76.7(3)		
Compound-(5)			
Pb(1)-N(1)	2.548(6)	Pb(1)-N(5)	2.430(5)
Pb(1)-N(2)	2.638(5)	Pb(1)-S1(1)	2.9117(16)
Pb(1)-N(6)	2.921(6)		
N(5)-Pb(1)-N(2)	74.00(17)	N(1)-Pb(1)-S(1)	129.40(12)
N(1)-Pb(1)-N(2)	62.66(17)	N(2)-Pb(1)-S(1)	66.76(12)
N(5)-Pb(1)-N(1)	81.75(18)	N(5)-Pb(1)-S(1)	85.95(14)

Table S2. Relevant Hydrogen Bonding Parameters (Å, °).

D-H...A	D-H	H...A	D...A	D-H...A	Symmetry
Compound-(1)					
O2-H50...O1	1.04	1.78	2.77(2)	157	-x, -y, 1-z
C13-H13...N7	0.93	2.51	3.38(2)	155	-x, 1/2+y, 1/2-z
C14-H14...O2	0.93	2.46	3.14(2)	130	----
C34-H34...N6	0.93	2.58	3.34(3)	139	x, y, -1+z
Compound-(2)					
O2-H2A...N4	0.85	2.11	2.924(8)	161	----
O2-H2B...O1	0.87	2.28	3.138(7)	171	-x, 1-y, -1-z
C6-H6...O2	0.95	2.52	3.198(9)	128	1+x, 1+y, 1+z
Compound-(5)					
N3-H3N...N6	0.82	2.24	3.018(9)	159	1+x, y, z
N4-H41N...S3	0.86	2.58	3.407(6)	160	1+x, -y, 1/2+z
N4-H42N...N6	0.89	2.20	3.026(8)	154	1+x, y, z
C3-H3...N5	0.95	2.62	3.377(9)	136	x, 1-y, 1/2+z
C4-H4...S3	0.95	2.84	3.785(8)	172	1+x, 1-y, 1/2+z

Table S3. Geometrical parameters (Å, °) for the π -stacking interactions.

rings <i>i-j</i>	Rc ^[a]	R1v ^[b]	R2v ^[c]	α ^[d]	β ^[e]	γ ^[f]	Symmetry
Compound-(1)							
Cg(4)⋯Cg(5)	3.721 (9)	3.442(7)	3.325(7)	6.2	26.69	22.36	-x, -y, -z
Compound-(2)							
Cg(4)⋯Cg(5)	4.035(4)	3.698(3)	3.564(3)	19.1	28.00	23.61	-x, 2-y, -z
Compound-(3)							
Cg(4)⋯Cg(4)	3.858(4)	3.405(3)	3.405(3)	0.0	28.05	28.05	1-x, 1-y, 1-z
Cg(4)⋯Cg(5)	3.793(4)	3.438(3)	3.327(3)	7.4	28.68	25.00	-1+x, -1+y, z
Compound-(4)							
Cg(4)⋯Cg(4)	3.823(7)	3.606(5)	3.607(5)	0.0	19.39	19.39	1-x, -y, 2-z
Compound-(5)							
Cg(1)⋯Cg(1)	3.979(4)	3.440(3)	3.530(3)	5.0	27.45	30.16	x, 1-y, -1/2+z
Cg(1)⋯Cg(1)	3.979(4)	3.531(3)	3.440(3)	5.0	30.16	27.45	x, 1-y, 1/2+z

In **(1)**, Cg(4) and Cg(5) are the centroids of the (N3/C10–C14) and (N7/C21–C24/C26) rings respectively. In **(2)**, Cg(4) and Cg(5) are the centroids of the (N3/C2–C6) and (N4/C8–C12) rings respectively. In **(3)**, Cg(4) and Cg(5) are the centroids of the (N5/C5–C9) and (N6/C22–C26) rings respectively. In **(4)**, Cg(4) is the centroids of the (C16–C21) ring. In **(5)**, Cg(1) is the centroids of the (N1/C1–C5) ring. ^[a]Centroid distance between ring *i* and ring *j*. ^[b]Vertical distance from ring centroid *i* to ring *j*. ^[c]Vertical distance from ring centroid *j* to ring *i*. ^[d]Dihedral angle between the first ring mean plane and the second ring mean plane of the partner molecule. ^[e]Angle between centroids of first ring and second ring mean planes. ^[f]Angle between the centroid of the first ring and the normal to the second ring mean plane of the partner molecule.

Table S4. Geometrical Parameters (Å, °) for Y–X⋯ π interactions.

Y–X⋯Cg(I)	X⋯Cg	Y⋯Cg	Y–X⋯Cg	X-Perp	Symmetry
Compound-(3)					
C(27)–S(1)⋯Cg(5)	3.695(4)	5.086(9)	142	3.385	2-x, 2-y, 2-z
Compound-(4)					
C(31)–O(1)⋯Cg(1)	3.82(3)	3.64(3)	71.9(15)	3.740	-1+x, y, z
O(1)–C(31)⋯Cg(1)	3.64(3)	3.82(3)	86.6(16)	3.220	-1+x, y, z

In **(3)**, Cg(5) is the centroid of the rings generated through the atoms (N6/C22–C26). In **(4)**, Cg(5) is the centroid of the rings generated through the atoms (N1/C1–C5).

Supramolecular self-assemblies in (1-5).

In (**1**), the phenyl ring carbon atom C(34) acts as donor to the azido nitrogen atom of the partner molecule at $(x, y, -1+z)$; thus forming a centrosymmetric dimeric ring $R_2^2(18)$ (M) centered at $(0, 0, 1/2)$ (Fig. S1a). This M-ring interconnects the partner molecules and forming a one-dimensional chain that propagating along $[001]$ direction. These parallel chains are further interconnected through another C–H \cdots N hydrogen bond. The pyridine ring carbon atom C(13) acts as donor to the pyridine ring nitrogen atom N(7) of the partner molecule from nearest parallel chain structure. Thus, interconnects the parallel chains to build a two-dimensional framework in (011) plane (Fig. S1a). Again, two pyridine rings are juxtaposed through face-to-face π -stacking interaction with an intercentroid separation of $3.721(9)$ Å that leads the molecules to form a chain structure in (**1**) (Fig. S1b).

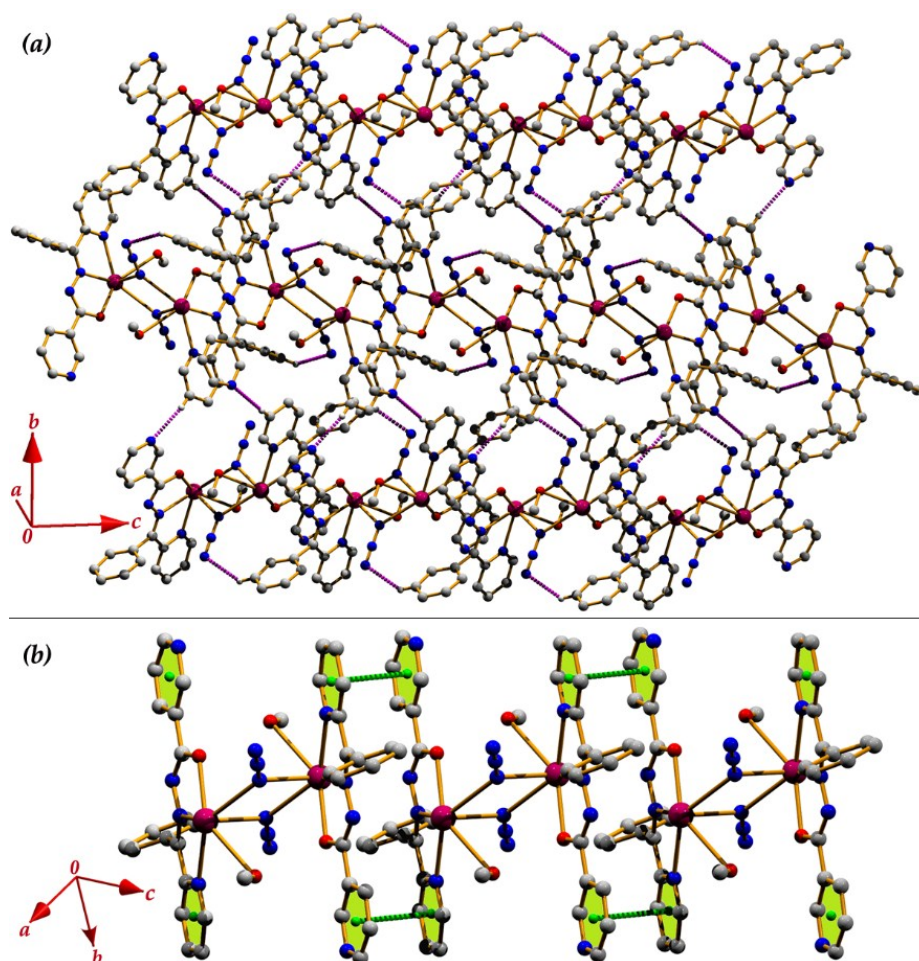


Fig. S1 (a) Formation of supramolecular network in (011) plane through C–H···N hydrogen bonds; (b) π – π stacking interaction in (**1**).

In (**2**), the solvent water molecule plays a vital role in building ring motifs. The water oxygen atom O(2) acts as double donor to the pyridine ring nitrogen atom N(4) and metal coordinated oxygen atom O(1) of the partner molecule at $(-x, 1-y, -1-z)$; thus forming a $R_4^4(18)$ ring motif (Fig. S2a). Again, another pyridine ring carbon atom C(6) from nearby partner molecule acts as donor to the water oxygen atom at $(1+x, 1+y, 1+z)$ that leads to the formation of $R_4^4(14)$ ring in (**2**). These two types of ring motifs are interlinked and generates a two-dimensional framework in (101) plane (Fig. S2a). In another substructure, the pyridine rings (N3/C2–C6) and (N4/C8–C12) are juxtaposed through π -stacking interaction with an intercentroid separation of 4.035(4)Å. Again, the pyridine ring carbon atom interconnects the nearby dimeric unit through C–H··· π interactions and leading to the formation of layered network in (**2**) (Fig. S2b).

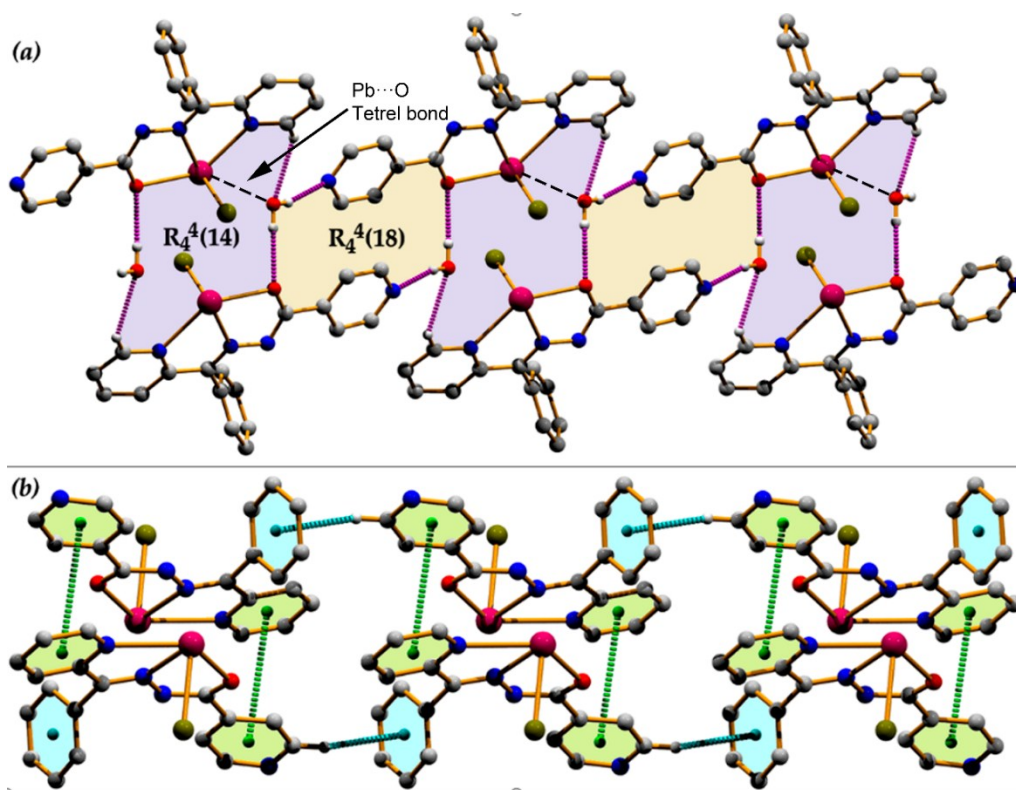


Fig. S2 (a) Formation of ring motifs and propagation of network in (101) plane with indication of the Pb···O tetrel bond involving the water molecule (black dashed line); (b) Formation of layer network through C–H··· π and π – π stacking interactions in (**2**). The C–H··· π and π – π stacking interactions are highlighted by dotted lines of turquoise and green colour respectively.

In **(3)**, the structure do not exhibit any intermolecular hydrogen bonds (Table S2). The sulfur atom S(1) of the N-coordinated pseudohalide ligand is in contact with the π -cloud of the pyridine ring (N6/C22–C26) in the molecule at (2-x, 2-y, 2-z) with a separation distance of 3.695Å (Table S4). The centroid of this pyridine ring is in contact with another pyridine ring (N5/C5–C9) of the partner molecule with an intercentroid separation distance of 3.793(4)Å (Table S3). Interestingly, the pyridine ring (N5/C5–C9) is further juxtaposed through face-to-face π -stacking interactions with an intercentroid separation of 3.858(4)Å and with a interplanar spacing of 3.405Å. Due to the self-complementarity nature, the pyridine rings are optimized through π -stacking interactions and generates the same network in opposite side of the ring. Thus, as a whole, a unique (l.p)⋯ π^+ / π^+ - π^+ / π^+ - π^+ / π^+ - π^+ / π^+ - π^+ / π^+ ⋯(l.p) network is observed in **(3)** (Fig. S3).

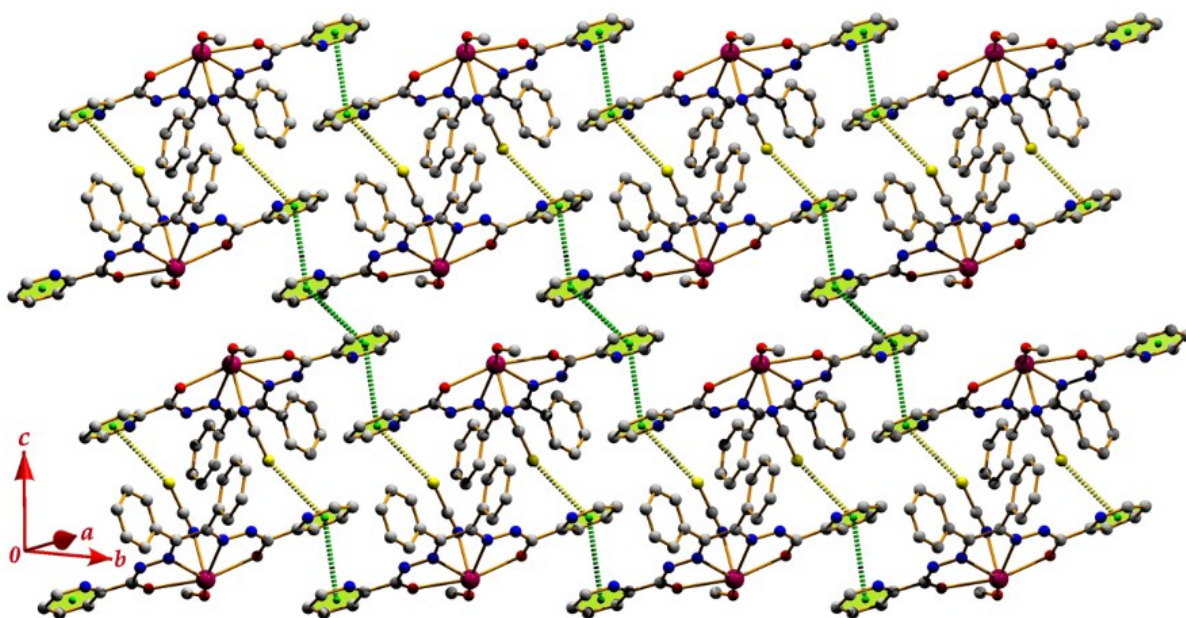


Fig. S3 Formation of layered network in **(3)** through weak noncovalent lone-pair(l.p)⋯ π and π - π stacking interactions.

Compound **(4)** do not exhibit any classical hydrogen bonding interaction in the solid-state. The molecular packing in **(4)** is such that the π - π stacking interactions between the aryl rings of adjacent partner molecules are optimized. Benzene rings (C16–C21) of the molecules at (x, y, z) and (1-x, -y, 2-z) are strictly parallel, with an interplanar spacing of 3.606Å, and a ring centroid separation of 3.823(7) Å,

corresponding to a ring offset of 1.69Å. The dimeric unit through π - π stacking interaction in (4) is depicted in Fig. S4.

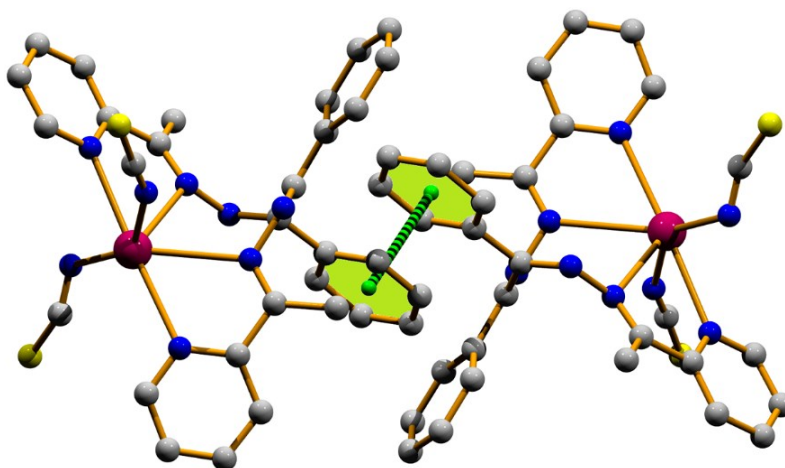


Fig. S4 Dimeric unit through π -stacking interaction in (4).

In (5), the pyridine ring carbon atom C(3) acts as donor to the nitrogen atom N(5) of the N-coordinated pseudohalide ligand in the molecule at $(x, 1-y, 1/2+z)$; thus interconnects the partner molecules and generates a one-dimensional chain along $[001]$ direction (Fig. S5a). Again, the pyridine ring carbon atom C(4) also acts as donor to the S(3) atom of the solvent pseudohalide ligand at $(1+x, 1-y, 1/2+z)$. The parallel 1D chains are further interconnected through N-H \cdots S bond. The sulfur atom S(3) acts as acceptor to the N(4) atom of the partner molecules that interconnects the chain chains and generates a two-dimensional network in (011) plane (Fig. S5a). The molecular packing in (5) is such that the π - π stacking interactions between the pyridine rings of adjacent partner molecules are optimized. The pyridine rings (N1/C1-C5) are strictly parallel, with a ring centroid separation of 3.979(4)Å. The π - π stacking interaction leading to the formation of layer architecture in (5) (Fig. S5b).

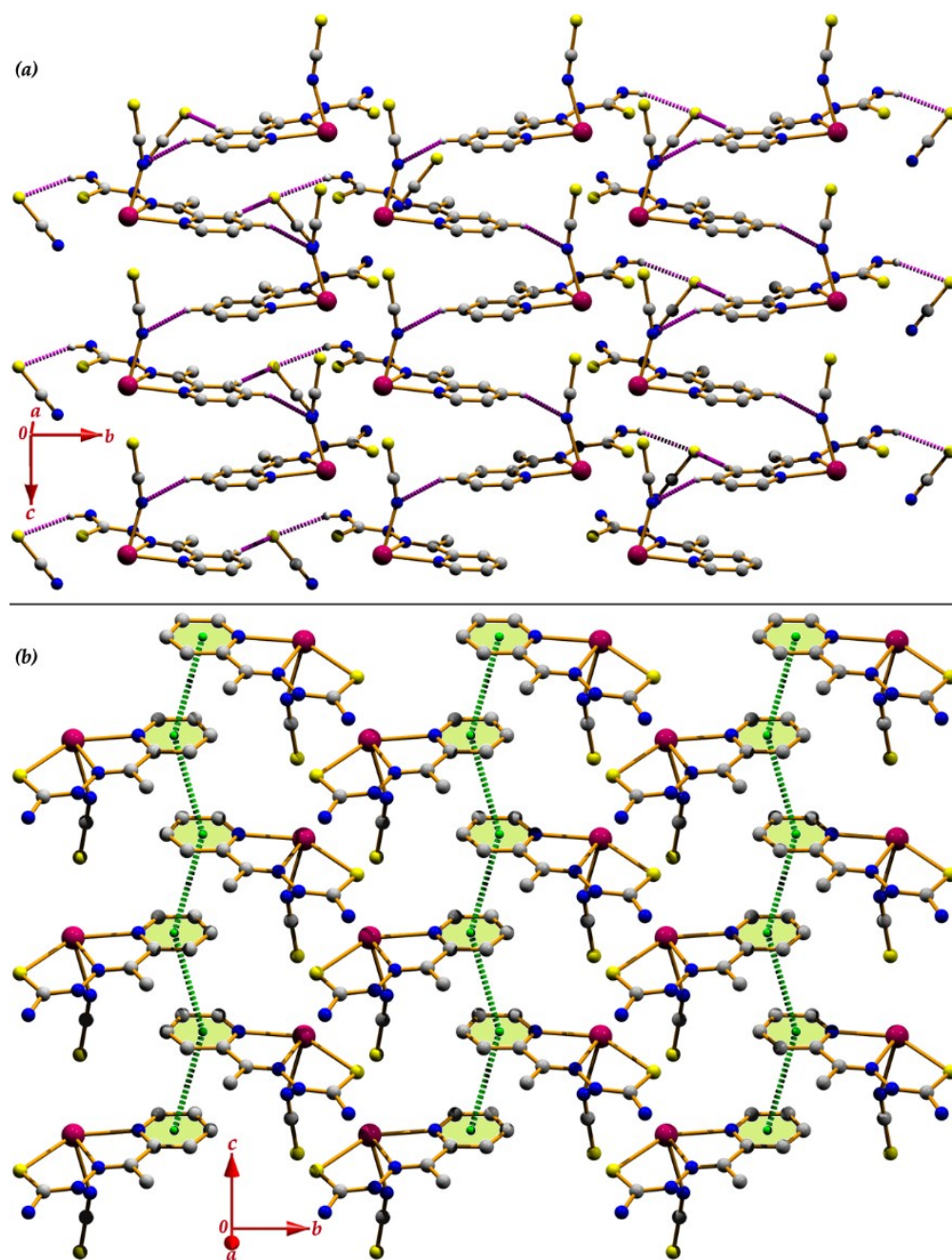


Fig. S5 (a) Formation of two-dimensional network through hydrogen bonds; (b) Supramolecular layered structure in (5).

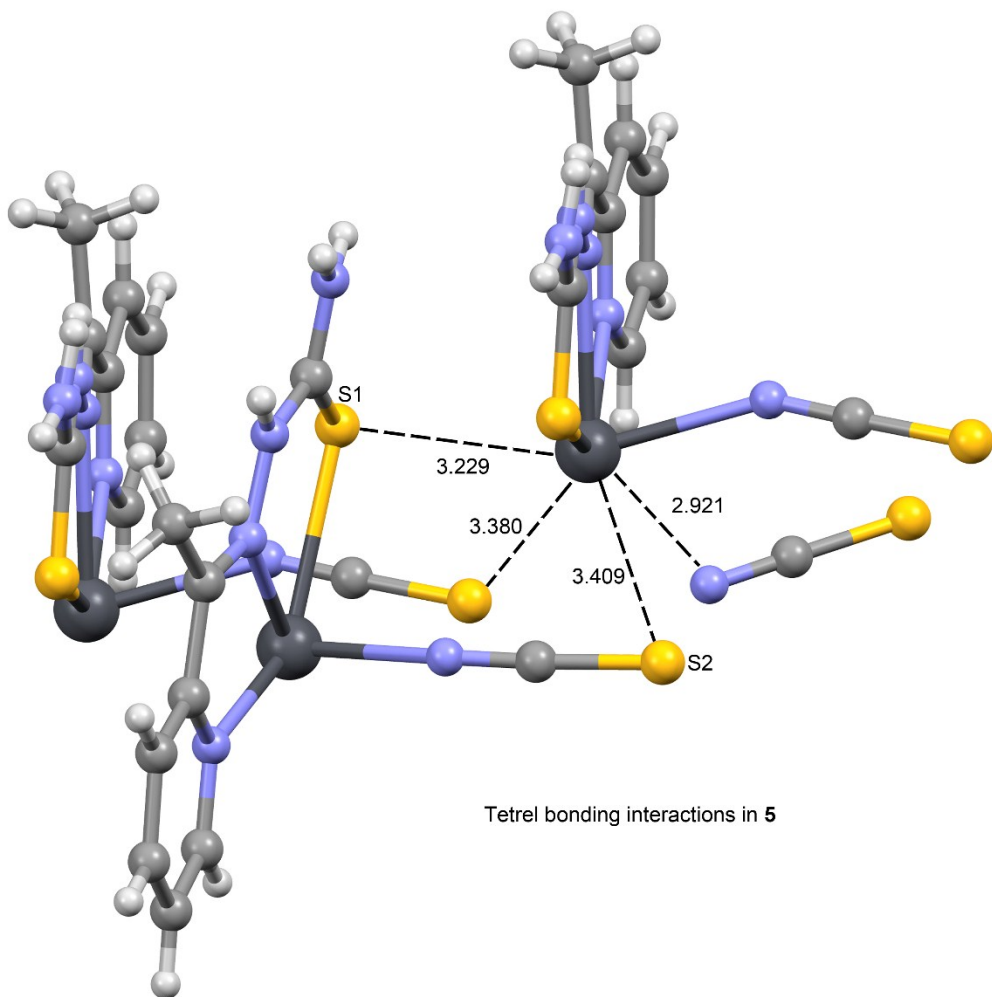


Fig. S6 Tetrel bonding interactions observed in the solid state of **5**.

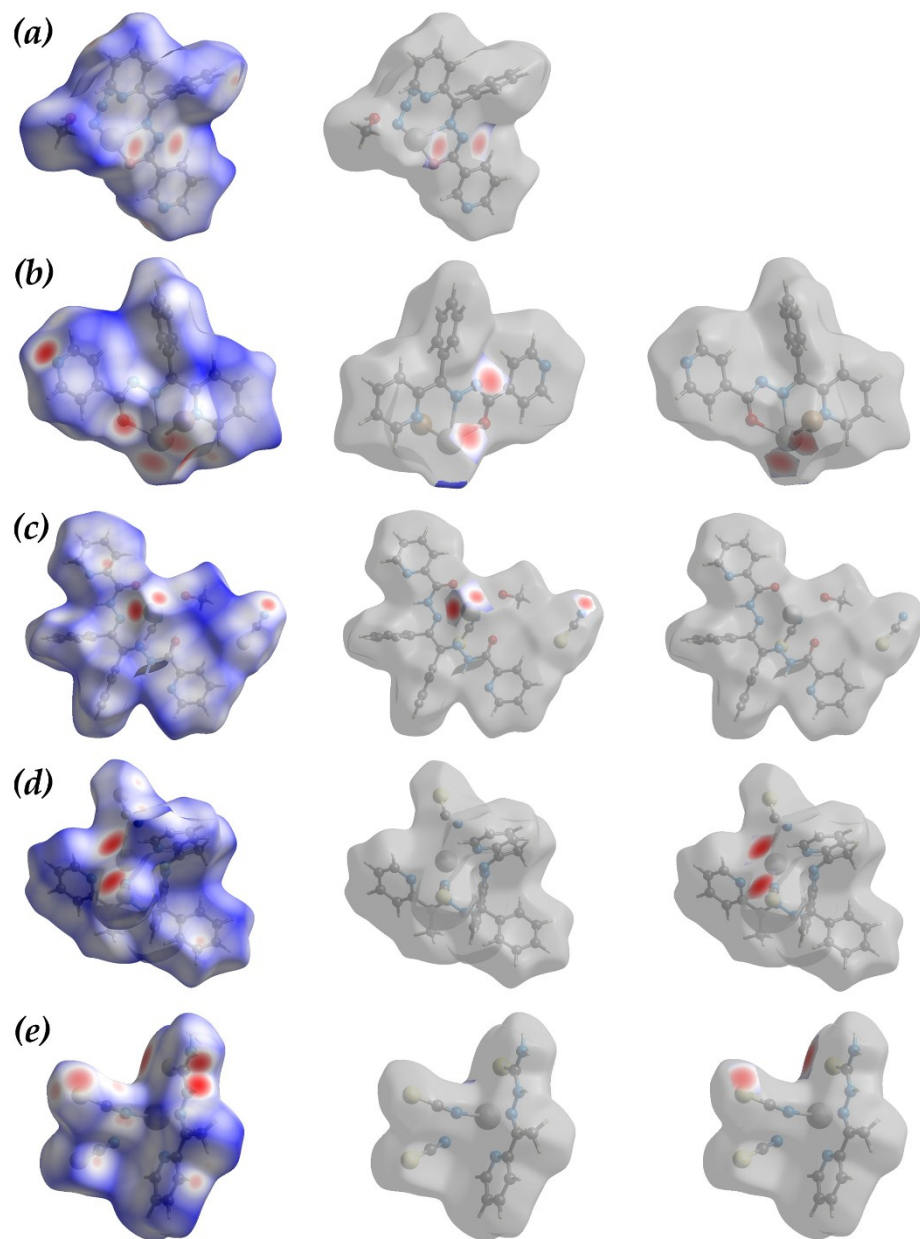


Fig. S7 Hirshfeld surfaces mapped with d_{norm} for complexes (**1–5**) and are depicted in (*a–e*) respectively. The Pb...N/N...Pb contribution to the Hirshfeld surfaces are shown in middle column whereas the right-hand column shows the Pb...Br/Br...Pb and/or Pb...S/S...Pb contacts.

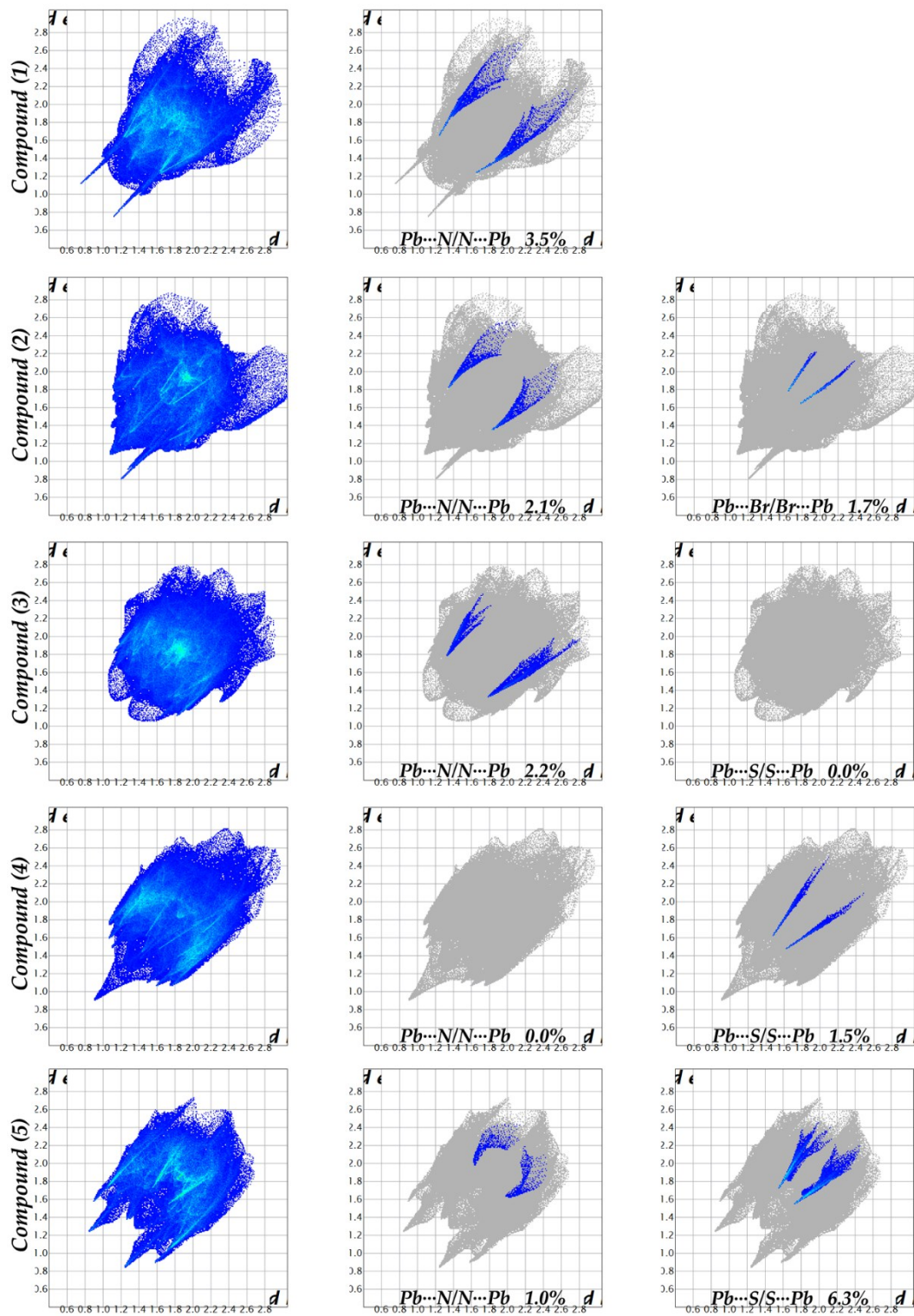


Fig. S8 Fingerprint plots of (1–5): Full (left) and resolved into tetrel bonds [Pb...N (middle) and Pb...Br and/or Pb...S (right)] showing the percentages of contacts contributed to the total Hirshfeld Surface area of molecules.