Are fluorine-based contacts predictable? A case study in three similar coordination compounds

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1. Experimental:

1.1. Synthesis of *N*-(2,5-diFluorophenyl)-2-pyrazinecarboxamide. The ligand was prepared according to previous procedure. [1]

1.2. Synthesis of [HgCl$_2$L$^{2,5\text{-}F}$]$_n$ (1). HgCl$_2$ (27 mg, 0.1 mmol) was dissolved in 5 ml of methanol and then add to a solution of L$^{2,5\text{-}F}$ (235 mg, 0.1 mmol) in methanol (5 ml). The mixture was heated at 50 °C with stirring simultaneously for about 30 minutes and then was filtered. Suitable single crystal structures were obtained upon slow evaporation in room temperature. Also experimental X-ray powder diagram of **1** is shown in Figure S1(a). The thermal stability of **1** has been determined on single-crystalline samples between 30-800 °C in an air atmosphere with a heating rate of 10 °C/min by thermogravimetric analysis (TGA), Figure S2. The TGA curve shows that compound **1** decomposed in one step. According to TGA curve, chemical decomposition starts at about 200 °C and ends around 300 °C.

Anal. Calcd for [HgCl$_2$L$^{2,5\text{-}F}$]$_n$ ($C_{11}H_7Cl_2F_2HgN_3O$): C, 26.07; H, 1.39; N, 8.30. Found: C, 26.10; H, 1.44; N, 8.33. FT-IR (KBr pellet, cm^{-1}): 3370s, 2927s, 1707s, 1633s, 1548s, 1468s, 1397w, 1274m, 1155m, 870s, 796s, 728s, 642s.

1.3. Synthesis of [HgBr$_2$L$^{2,5\text{-}F}$]$_n$ (2). To a solution of HgBr$_2$ (36mg, 0.1mmol) in methanol (5ml), a solution of L$^{2,5\text{-}F}$ (235 mg, 0.1 mmol) in methanol (5 ml) was added. The resulted solution was then heated and stirred similar to synthesis of **1**. Colorless single crystals were obtained upon slow evaporation in room temperature. Also experimental X-ray powder diagram of **2** is shown in Figure S1(b). The thermal stability of **2** has been determined on single-crystalline samples between 30-800 °C in an air atmosphere with a heating rate of 10 °C/min by thermogravimetric analysis (TGA), Figure S2. The TGA curve shows that compound **1** decomposed in one step. According to TGA curve, chemical decomposition starts at about 200 °C and ends around 285 °C.

Anal. Calcd for [HgBr$_2$L$^{2,5\text{-}F}$]$_n$ ($C_{11}H_7Br_2F_2HgN_3O$): C, 22.18; H, 1.19; N, 7.06. Found: C, 22.20; H, 1.24; N, 7.09. FT-IR (KBr pellet, cm^{-1}): 3344s, 3059m, 1699s, 1627s, 1545s, 1481s, 1242m, 1162m, 870s, 811s, 765s, 692s.

1.4. Synthesis of [$Hg_3I_6(L^{2,5\text{-}F})_4$] (3). HgI_2 (45 mg, 0.1 mmol) was dissolved in 5 ml of methanol and then added to a solution of $L^{2,5\text{-}F}$ (235 mg, 0.1 mmol) in methanol (5 ml). By similar method suitable single crystals of **3** were obtained. Using 4:3 molar ratios of ligand and HgI_2, resulted in the same product as when using 1:1 molar ratio. Also experimental X-ray powder diagram of **3** is shown in Figure S1(c). The thermal stability of **3** has been determined on single-crystalline samples between 30-800 °C in an air atmosphere with a heating rate of 10 °C/min by thermogravimetric analysis (TGA), Figure S2. The TGA curve shows that compound **3** decomposed in one step. According to TGA curve, chemical decomposition starts at about 220 °C and ends around 310 °C.

Anal. Calcd for [$Hg_3I_6(L^{2,5\text{-}F})_4$] ($C_{44}H_{28}F_8Hg_3I_6N_{12}O_4$): C, 22.94; H, 1.22; N, 7.30. Found: C, 22.97; H, 1.26; N, 7.33. FT-IR (KBr pellet, cm^{-1}): 3337s, 3085m, 1699s, 1627s, 1540s, 1481s, 1255s, 1162m, 1017s, 890s, 811s, 724s, 645s.

1.5. Computational. Interaction energy calculations were performed by ORCA program. [2] At Density Functional Theory-Dispersion (DFT-D3) [3-4] level using B3LYP function and TZVP basis set. The data corrected for basis set superposition error (BSSE) using the counterpoise correction of Boys and Bernardi.[5] Scalar relativistic effects were taken into account by using the zeroth-order regular approximation (ZORA).[6] Electrostatic potential of molecules were computed on the 0.001 a.u isodensity surface using Surface Analysis Suite software.[7]

2. Synthesis and Crystal Structure Descriptions:

2.1. Synthesis. The ligand *N*-(2,5-difluorophenyl)-2-pyrazinecarboxamide, $\mathbf{L^{2,5\text{-}F}}$, was synthesized through a condensation reaction between pyrazinecarboxylic acid and 2,5-difluoroaniline in 1:1 molar ratio in triphenyl phosphite as the catalyst and pyridine as the solvent.[8] The equimolar amount of ligand and HgX_2 salts (X = Cl, Br and I) were then simply mixed in methanol to prepare corresponding polymeric complexes [$HgCl_2L^{2,5\text{-}F}$]$_n$, **1**, and [$HgBr_2L^{2,5\text{-}F}$]$_n$, **2**, and trinuclear complex of [$Hg_3I_6(L^{2,5\text{-}F})_4$], **3**. The suitable single crystals of **1-3** grew by slow evaporation of solvent after several weeks. It should be noted that using 4:3 molar ratio of ligand and HgI_2, resulted in the same product as when using 1:1 molar ratio. The crystallographic data for compounds **1**, **2** and **3** are presented in Table S1. Selected bond distances and angles are also summarized in Table S2. The complexes 4, 5 and 6 are synthesized according to our previous paper [1].

2.2. Structural analysis of complexes, $[HgCl_2L^{2,5\text{-}F}]_n$, 1, $[HgBr_2L^{2,5\text{-}F}]_n$, 2 and $[Hg_3I_6(L^{2,5\text{-}F})_4]$ complex, 3. All three complexes were crystalized in primitive unit cells with $P2_1/c$, *Pbca* and $P\bar{1}$ space groups for **1**, **2** and **3**, respectively, Table S1. The asymmetric units of complexes **1** and **2** are similar and include one crystallographically independent Hg^{+2} ion which is surrounded by one amide ligand, $L^{2,5\text{-}F}$, as well as two halide anions, terminated and bridged one, Figures S3(a) and S3(b). The coordination geometry around metal ion exhibit a seesaw structure with four-coordinated index[9] of τ_4 = 0.67, and 0.69 for **1** and **2**, respectively, in which amide ligand is coordinated *via* N_2 atom of pyrazin ring. Selected bond distance and angles are listed in Table S2. As depicted in Figures S4(a) and S5(a), both compounds have polymeric structure. Within the asymmetric unit of **1**, two of the chlorine atoms bridge two adjacent metal centers to generate a 1D double chain motif in the *b*-direction, which have strengthened *via* head to head $\pi_{pyz}...\pi_{pyz}$ and $\pi_F...\pi_F$ stacking, Table S3, Figure S3(a). In addition, Hg…Cl secondary bonding with distance of 3.223(7) Å which is shorter than the sum of van der Waals radii[10] is detected along chains, Figure S3(a), Table S4. The adjacent polymeric chains are paired with each other in a head to tail manner *via* C–F…Cl–Hg halogen contact, Table 1, in order to generate double chains, Figure S3(b). As shown in Figure S3(c), the double chains are linked through head to tail Hg…Cl secondary bonding with distance of 3.307(7) Å to make 2D sheets parallel to *ac*-plane. At last, the overall 3D structure is formed by C–F1…F1–C interaction, Table 1, Figure S3(c). In the crystal structure of complex **2**, 1D chains are created along *a*-axis *via* Br–Hg–Br bridge as well as Hg…Br secondary bonding with distance of 3.488(2) Å, Figure S4(a), Table S4. As shown in Figure S4(b), mentioned coordination chains interlock with each other through head to tail π_F...amide interactions to form 2D sheets in *ac*-plane, Table S3. Ultimately, the 3D crystal structure is constructed *via* C–F….O=C interaction with distance of 2.98(2) Å that is observed between the adjacent sheets, Table 1, Figure S4(b).

In complex **3**, the asymmetric unit contains one and a half crystallographycally independent Hg^{+2} ion, three iodide ions and two $L^{2,\ 5\text{-}F}$ ligand. In this compound the Hg2 atom lies on an inversion centre. As depicted in Figure S5(a), this compound is a three-centered complex with two different Hg^{+2} ions, Hg1 and Hg2. Coordination environment around Hg1 ion is seesaw with τ_4 = 0.70.[9]. On the other hand, Hg2 ion has a pseudo square-planar geometry with two iodide ions that have coordinated to metal center, while two $L^{2,5\text{-}F}$ ligands interact with metal centres along with secondary bonding where Hg…N distance is 2.843(2) Å. This distance is 8.3% less than sum of the van der walls radii and is quite in compliance with previous reports.[10] As displayed in Figure S5(a), these three-centered complexes have become more stable *via* head to head π_F…π_F and π_{pyz}…π_{pyz} stacking between coordinated and non-coordinated $L^{2,5\text{-}F}$ ligands, Table S3. According to the Figure S5(b), adjacent three-centered units are linked through C–F…C=O interaction among non-coordinated $L^{2,5\text{-}F}$ with distance of 3.03(2) Å to form 1D ribbon, Table 1. In this compound, 2D sheets are formed by head to tail π_{pyz}…π_F stacking of neighboring ribbons in *b*-axes, Table S3, Figure S5(b). These 2D sheets held together across C_{pyz}–H…O=C with distance of 2.64 and 2.46 Å, Table S5, also C-F…F-C short interactions with distance of 2.86(2) and 2.74(2) Å to build up 3D crystal structure, Table 1, Figure S5(c).

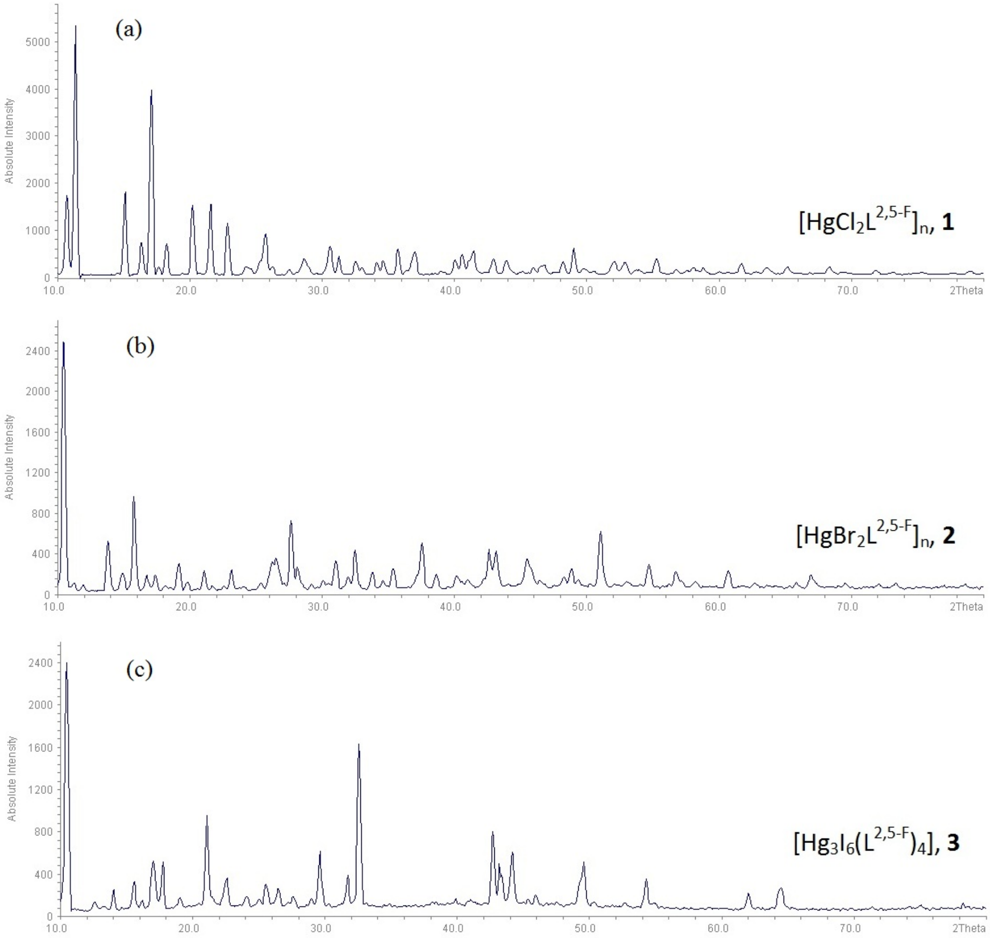


Figure S1. Experimental X-ray powder diagram of $[HgCl_2L^{2,5-F}]_n$, 1, (a), $[HgBr_2L^{2,5-F}]_n$, 2, (b) and $[Hg_3I_6(L^{2,5-F})_4]$ complex, 3, (c).

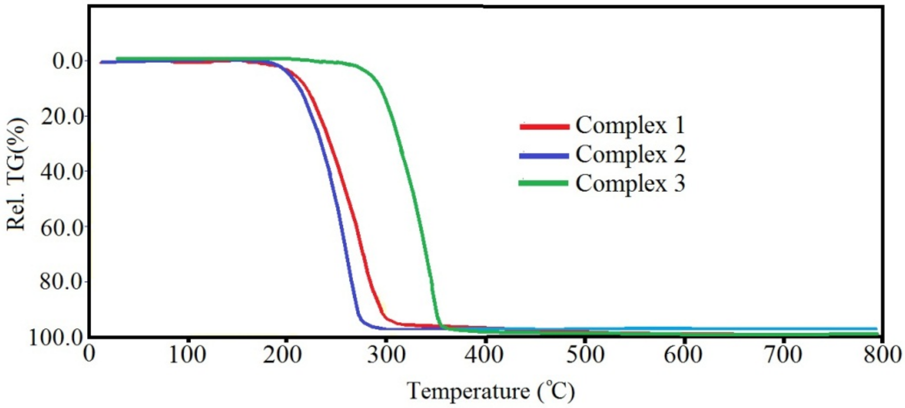
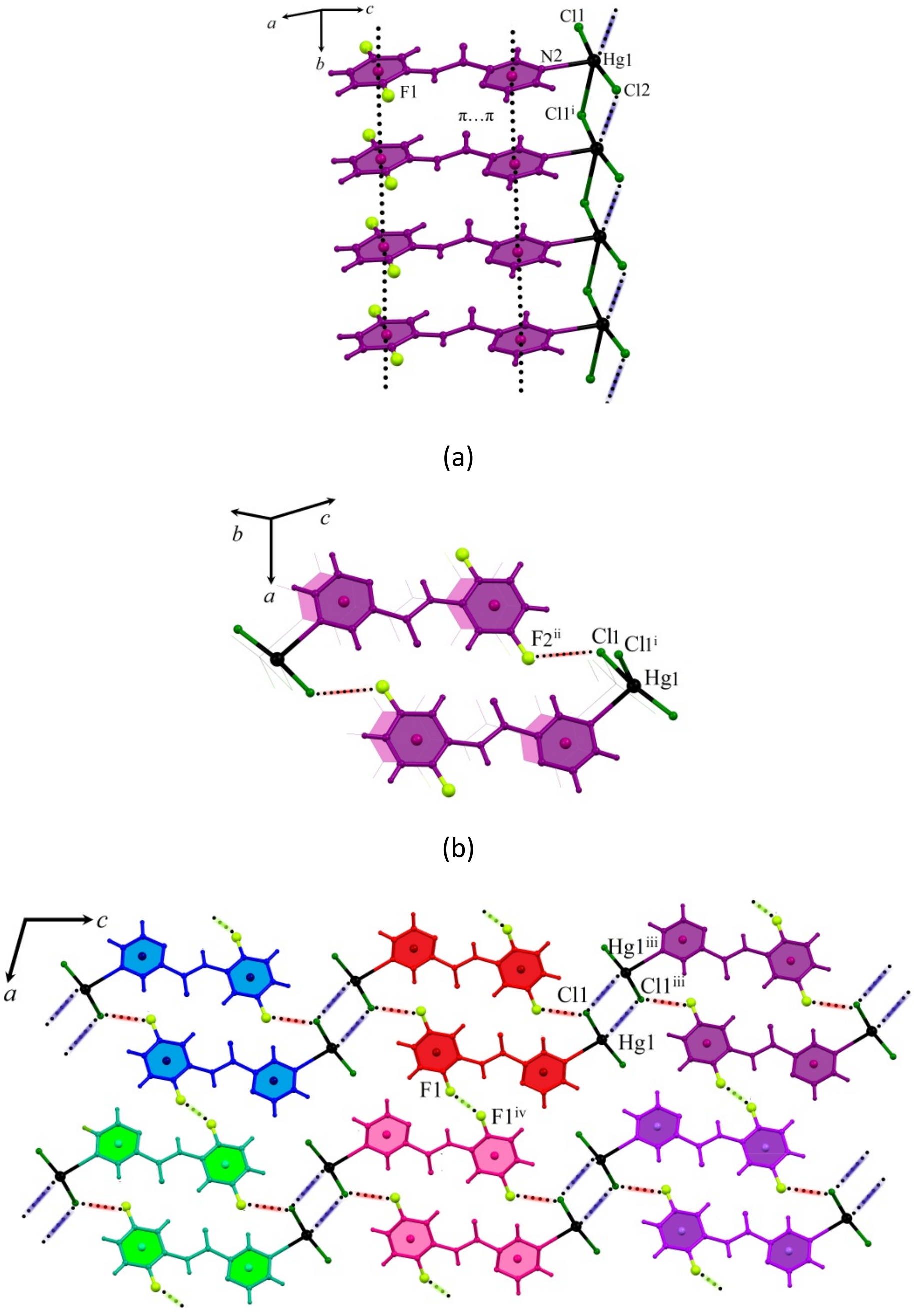


Figure S2. Thermogravimetric analysis of complexes 1-3 with a heating rate of 10 °C/min.

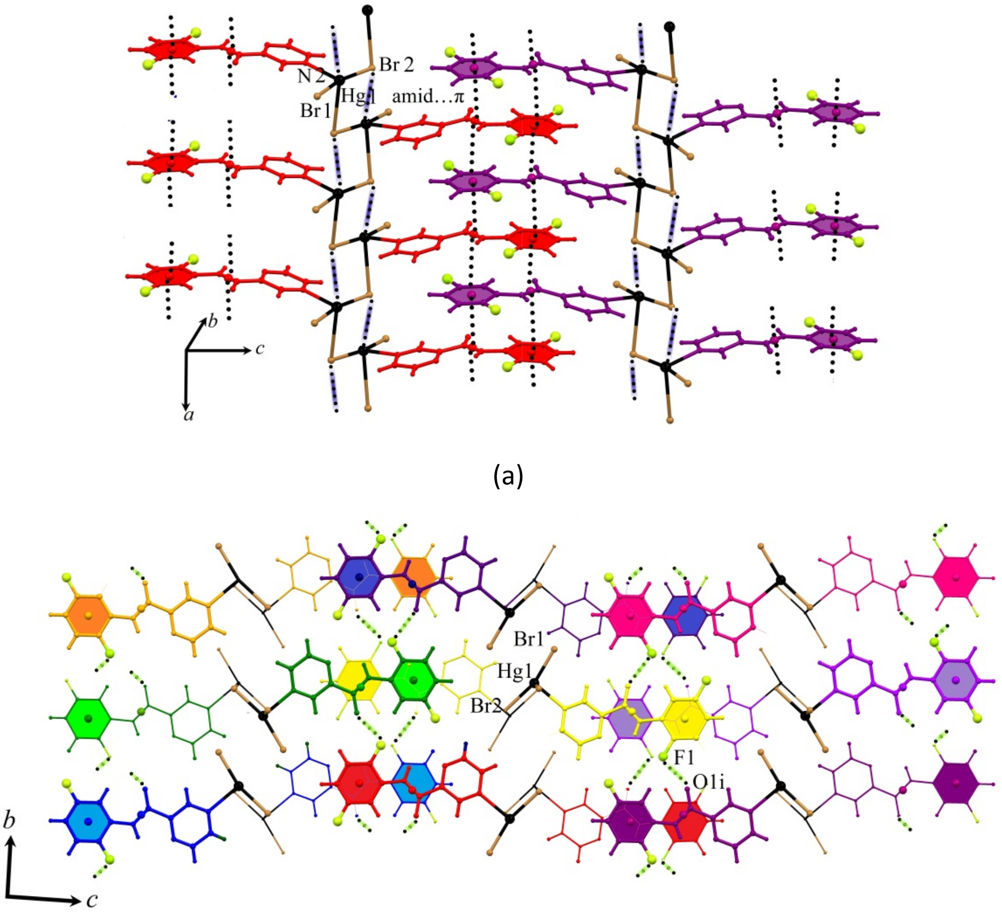


(a)

(b)

(c)

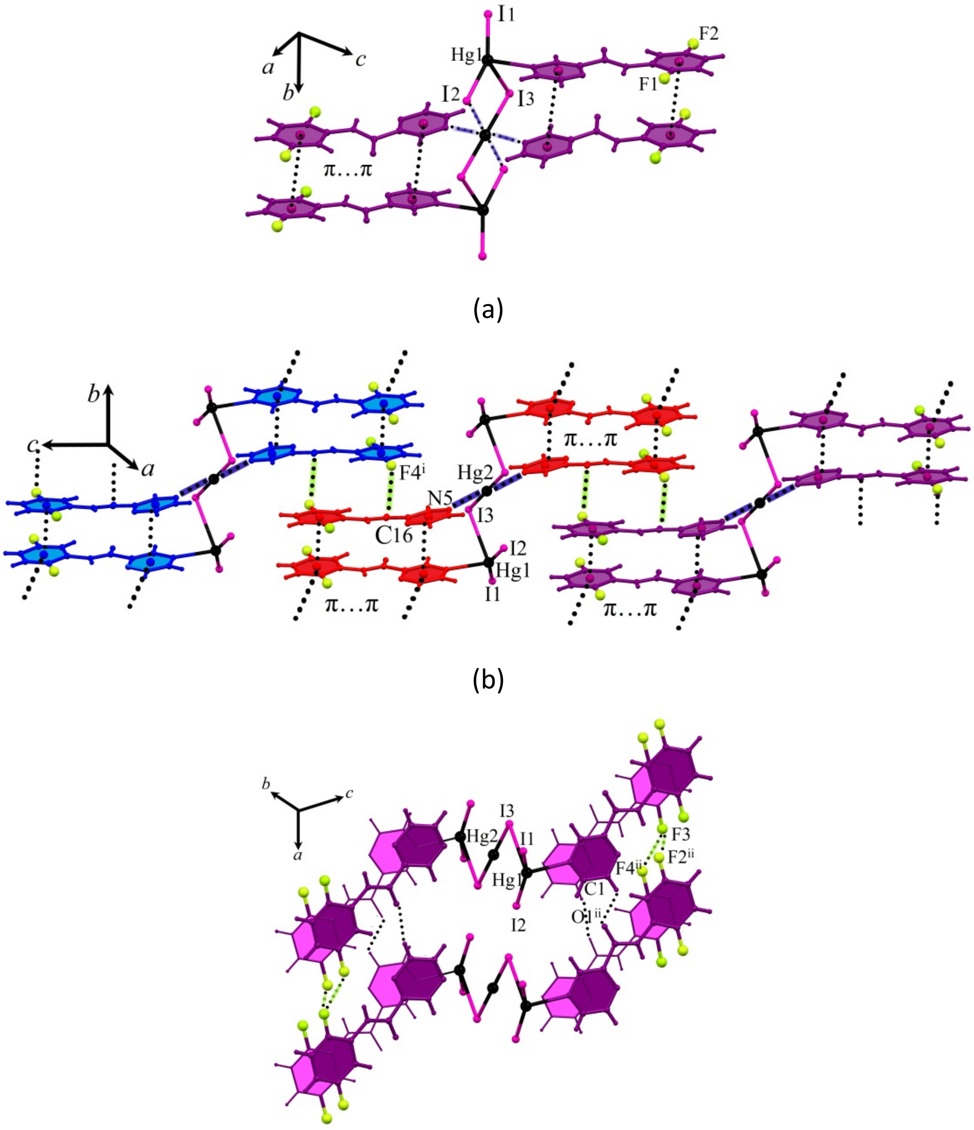
Figure S3. (a) 1D coordination polymeric chain of compound **1** along *b*-axis, Hg…Cl secondary bonding is shown with dark blue dashed-line, (b) double chain of compound **1**, formed *via* C-F…Cl-Hg (c) and Hg…Cl secondary bonding in *ac*-plane and C-F…F-C interactions which hold 2D sheets together. Symmetry codes; (i) x, 1+y, z, (ii) –x, 1-y, -z, (iii) –x, -1/2+y, ½-z, (iv) 1-x, 2-y, -z.



(a)

(b)

Figure S4. (a) Coordination polymer of compound **2** along *a*-axis which accompany with Hg…Br secondary bonding and polymeric chains of compound **2** which are interlocked *via* π_F…amide interaction and (b) C-F…O=C interaction in *bc*-plane. Symmetry codes; (i) -1x, -1/2+y, ½-z.



(a)

(b)

(c)

Figure S5. (a) Representation of three-centered compound **3** with $\pi_F \ldots \pi_F$ and $\pi_{pyz} \ldots \pi_{pyz}$ interactions, Hg…N secondary bonding is marked with dark blue dashed-line, (b) 1D ribbons which are formed through C-F…C=O interaction and $\pi_F \ldots \pi_{pyz}$ interaction that link adjacent ribbon, (d) C-H…O=C and bifurcated F…F interaction that connect 2D sheets. Symmetry codes; (i) -x, -y, 2-z, (ii) 1+x, y, z.

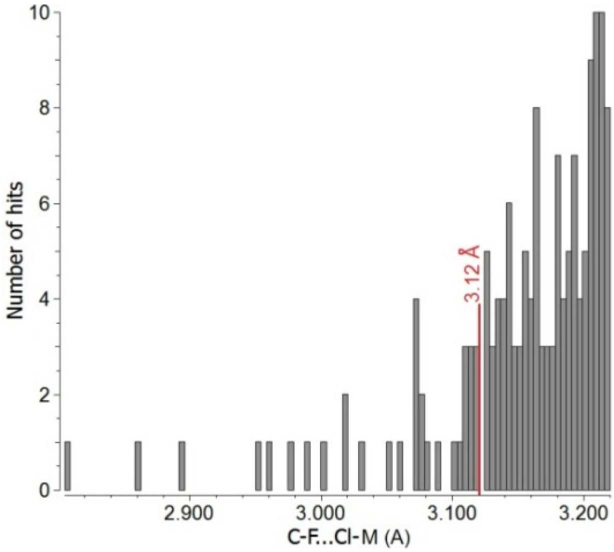


Figure S6. Histogram plot for the C-F…Cl-M (M = any metal) distance from a CSD search. The C-F…Cl-M distance (Å) was defined as contact between C-F and Cl-M fragments without any constrains. The red line shows the C-F…Cl-M equal to 3.12 Å.

Table S1. Crystal data and structural refinement for compounds **1**, **2** and **3**.

	Complex **1**	Complex **2**	Complex **3**
formula	$C_{11}H_7Cl_2F_2HgN_3O$	$C_{11}H_7Br_2F_2HgN_3O$	$C_{44}H_{28}F_8Hg_3I_6N_{12}O_4$
fw	506.69	595.59	2303.95
λ/Å	0.71073	0.71073	0.71073
T/K	298(2)	298(2)	298(2)
crystal.system	Monoclinic	Orthorhombic	Triclinic
space group	$P2_1/c$	*Pbca*	$P\bar{1}$
a/Å	10.988(3)	6.7713(12)	7.8051(9)
b/Å	3.9173(9)	12.7185(15)	13.1360(15)
c/Å	31.538(9)	33.489(4)	14.1342(15)
α/°	90	90	78.497(9)
β/°	99.68(2)	90	85.326(9)
γ/°	90	90	85.781(10)
V/Å^3	1338.2(6)	2884.1(7)	1412.9(3)
D_{calc}/Mg m^{-3}	2.515	2.746	2.708
Z	4	8	1
μ/mm^{-1}	11.921	16.234	11.486
F(000)	936	2160	1038
2θ/°	54.00	54.00	54.00
R(int)	0.0889	0.1020	0.1001
GOOF	0.968	1.032	0.935
$R_1{}^a(I > 2\sigma(I))$	0.0941	0.0928	0.0875
$wR_2{}^b(I > 2\sigma(I))$	0.1497	0.1944	0.1825
CCDC No.	1016889	1016885	1016891

$^aR_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^bwR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma w(F_o^2)2]^{½}$.

Table S2. Selected bond length (Å) and angles (°) around mercury (II) for complexes **1**, **2** and **3**.

		complex		
		1(X=Cl)	**2(X=Br)**	**3(X=I)**
Bond distance	Hg1-X1	2.337(7),3.008(7)^{i}	2.432(2)	2.5954(18)
	Hg1-X2	2.321(7)	2.458(2),3.342(2)^{ii}	2.6143(15)
	Hg1-X3	-	-	3.376(1)
	Hg2-X3	-	-	2.6304(11)
	Hg1-N2	2.532(17)	2.483(18)	2.534(12)
Bond angle	X1-Hg1-X1	93.4(2)^{i}	-	-
	X1-Hg1-X2	91.5(2)^{i}, 170.6(2)	89.6(1)^{ii},163.67(10)	155.83(6)
	X1-Hg1-X3	-	-	97.1(1)
	X2-Hg1-X2	-	91.2(1)^{ii}	-
	X2-Hg1-X3	-	-	95.0(1)
	X1-Hg1-N2	85.1(5), 94.8(5)	99.7(4)	105.1(3)
	X2-Hg1-N2	93.7(5)	96.6(5)	97.0(3)
	X3-Hg1-N2	-	-	84.0(3)
	X3-Hg2-X3	-	-	180.0^{iii}

Symmetry codes: (i) x, 1+y, z, (ii) 1/2+x, 1/2-y, -z, (iii) 1-x, -y, 1-z.

Table S3. Coordination geometry, τ_4 and aromatic interaction parameters (Å and °) for description of π...π interaction in $[HgCl_2L^{2,5\text{-}F}]_n$, **1**, $[HgBr_2L^{2,5\text{-}F}]_n$, **2** and $[Hg_3I_6(L^{2,5\text{-}F})_4]$, **3.**

Complex	Coordination geometry/τ_4	**Cg(I)-Cg(J)**	$d_{Cg\text{-}Cg}$[a]	α[b]	β, γ[c]	$d_{plane\text{-}plane}$[d]	d_{offset}[e]
$[HgCl_2L^{2,5\text{-}F}]_n$, **1**	Seesaw, 0.67	Cg(1)-Cg(1)^{i}	3.917(9)	0	29.18	3.42	1.91
		Cg(2)-Cg(2)^{ii}	3.917(9)	0	27.95	3.46	1.83
$[HgBr_2L^{2,5\text{-}F}]_n$, **2**	Seesaw, 0.69	Cg(2)-C_{amide}	3.328(8)	2.1(5)	4.90, 8.35	3.316(8), 3.293(8)	0.28, 0.48
		Cg(2)-C_{amide}	3.338(9)	2.1(5)	6.60, 8.31	3.316(8), 3.303(7)	0.38, 0.48
		Cg(2)-C_{amide}	3.349(8)	2.1(5)	8.00, 8.42	3.316(8), 3.313(7)	0.47, 0.49
		Cg(2)-C_{amide}	3.480(7)	2.1(5)	8.00, 7.00	3.446(9), 3.454(8)	0.48, 0.42
		Cg(2)-C_{amide}	3.490(10)	2.1(5)	10.00, 6.73	3.446(9), 3.474(7)	0.37, 0.41
$[Hg_3I_6(L^{2,5\text{-}F})_4]$, **3**	Seesaw, 0.70	Cg(1)-Cg(2)^{iii}	3.704(10)	0.2(8)	22.26, 22.43	3.425(7), 3.429(8)	1.41, 1.40
	Pseudo SP, 0	Cg(1)-Cg(3)	3.965(10)	9.8(9)	14.69, 24.37	3.612(7), 3.835(7)	1.63, 1.00
		Cg(2)-Cg(4)	3.789(11)	6.2(9)	21.35, 26.65	3.388(7), 3.529(8)	1.70, 1.37
		Cg(2)-Cg(1)	3.704(10)	0.2(8)	22.43, 22.26	3.429(7), 3.425(7)	1.40, 1.41

[a] Centroid-centroid distance. [b] Dihedral angle between the ring plane. [c] Offset angles: angle between Cg(I)–Cg(J) vector and normal to plane I, angle between Cg(I)-Cg(J) vector and normal to plane J ($\beta = \gamma$ when $\alpha = 0$). [d] Perpendicular distance of Cg(I) on ring J and perpendicular distance of Cg(J) on ring I. [e] Horizental displacement between Cg(I) and Cg(J), two values are presented if two rings are not exactly parallel ($\alpha \neq 0$). Cg(1): centroid of N(1)-C(1)-C(2)-N(2)-C(3)-C(4), Cg(2): centroid of C(6)-C(7)-C(8)-C(9)-C(10)- C(11), Cg(3): centroid of centroid of N(4)-C(12)-C(13)-N(5)-C(14)-C(15), and Cg(4): centroid of C(17)-C(18)-C(19)-C(20)-C(21)-C(38), For **2**, C_{amide}: centroid of O(1)-C(5)-N(3)-H(3A). Symmetry codes: (i) -x, 1-y, -z, (ii) x, 1+y, z, (iii) -x, 1-y, z-2

Table S4. Hg…X parameters (Å and °) for complexes $[HgCl_2L^{2,5-F}]_n$, **1**, $[HgBr_2L^{2,5-F}]_n$, **2** and $[Hg_3I_6(L^{2,5-F})_4]$, **3**.

Compound	Secondary Bonding	Distance (Å)
$[HgCl_2L^{2,5-F}]_n$, **1**	Hg1…Cl2^{i}	3.223(7)
$[HgBr_2L^{2,5-F}]_n$, **2**	Hg1…Br2^{ii}	3.488(2)
$[Hg_3I_6(L^{2,5-F})_4]$, **3**	Hg2…I2	3.572(3)
	Hg2…N5	2.843(5)

Symmetry codes: (i) x, -1+y,z, (ii) -1/2+x, 1/2-y, -z.

Table S5. Hydrogen bonding parameters (Å and °) for complexes $[HgCl_2L^{2,5-F}]_n$, **1** and $[Hg_3I_6(L^{2,5-F})_4]$, **3**.

Compound	**D-H···A**	**d(D-H)**	**d(H···A)**	**d(D···A)**	**<(DHA)**
1	C3-H3...F2^{i}	0.92	2.64	3.53(3)	162
3	C1-H1…O1^{ii}	0.93	2.64	3.33(2)	132
	C12-H12…O2^{ii}	0.93	2.46	3.38(2)	172

Symmetry codes: (i) -x, 2-y, -z, (ii) 1+x, y, z.

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