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Conformational variety of flexible mono-dentate ligands in coordination compounds; influence of π-involving interactions

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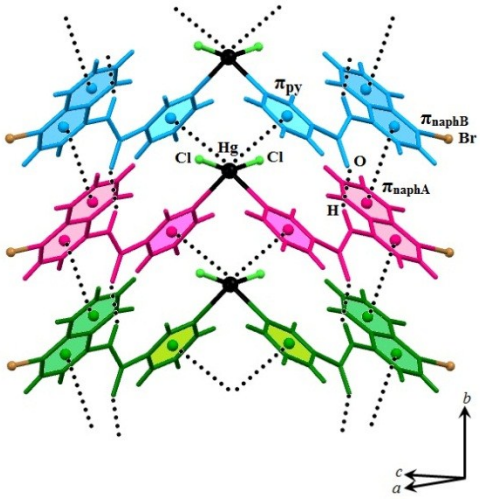
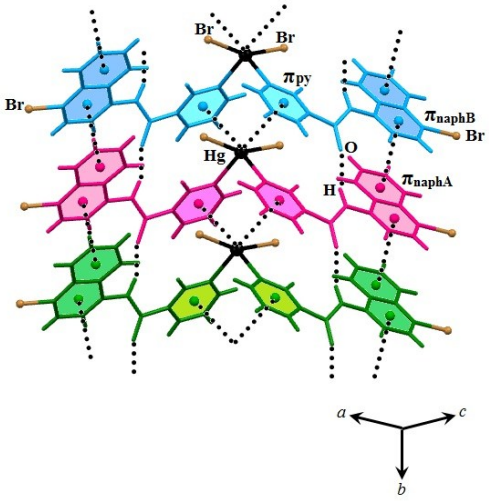
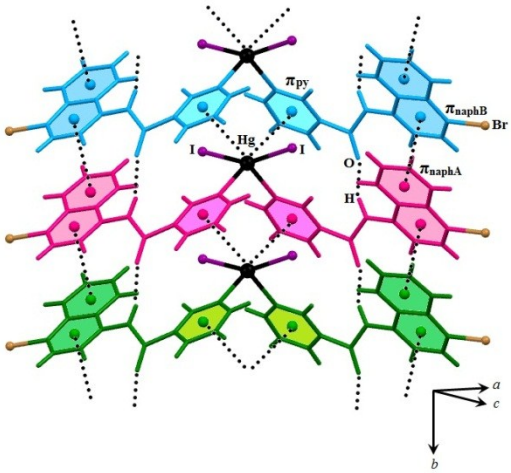


(a)



(b)



(c)

Figure S1. Representation of the 1D linear chain in **2**, (a), **3**, (b) and **4**, (c), through $\pi_{naphtA}\ldots\pi_{naphtB}$, Hg…$\pi_{py}$, and N-H…O interactions.

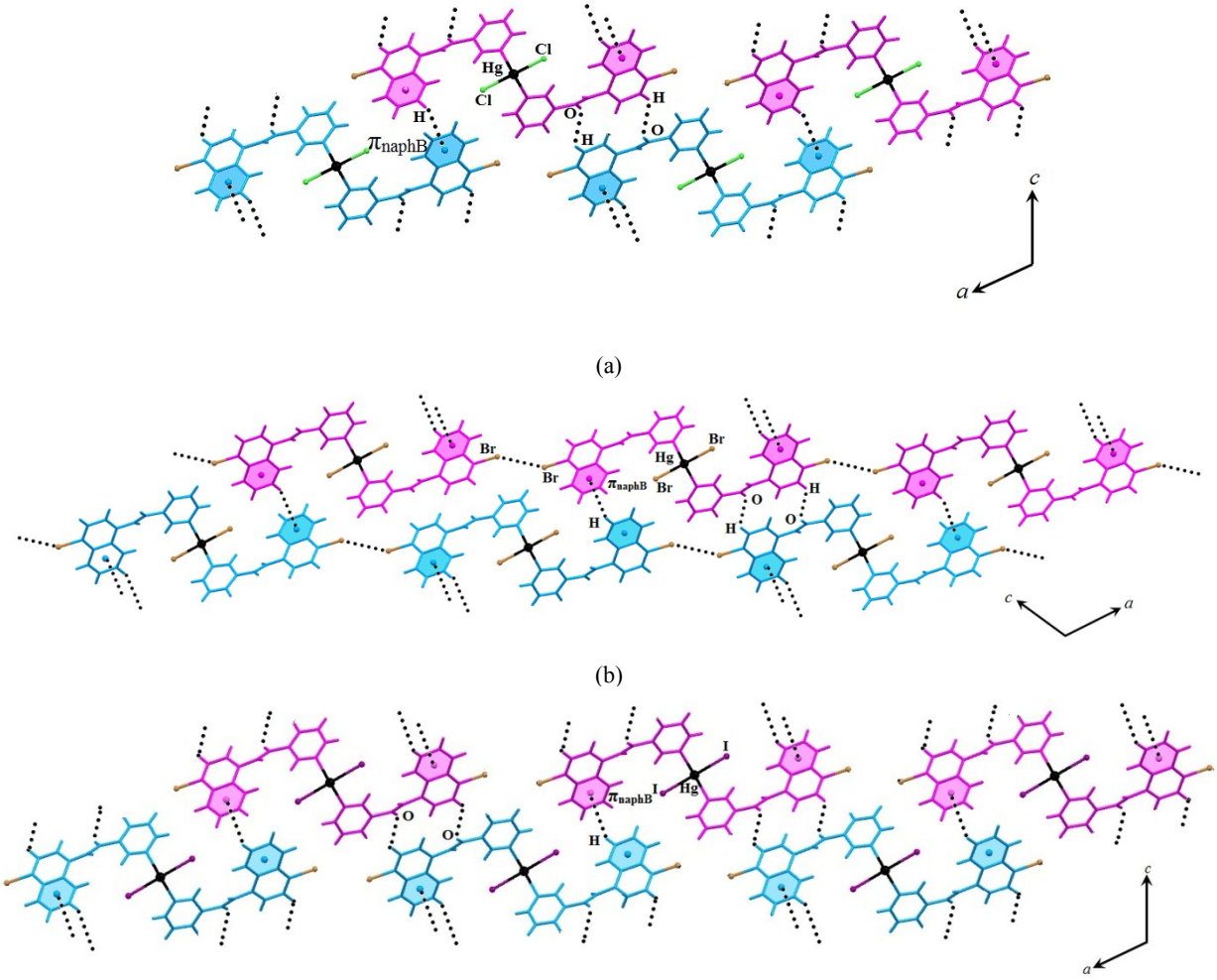


Figure S2. Generation of overall supramolecular packing of complexes **2**, (a), **3**, (b), and **4**, (c) by the cooperation of the C-H… π_{naphtB} interactions and C-H…O hydrogen bonds.

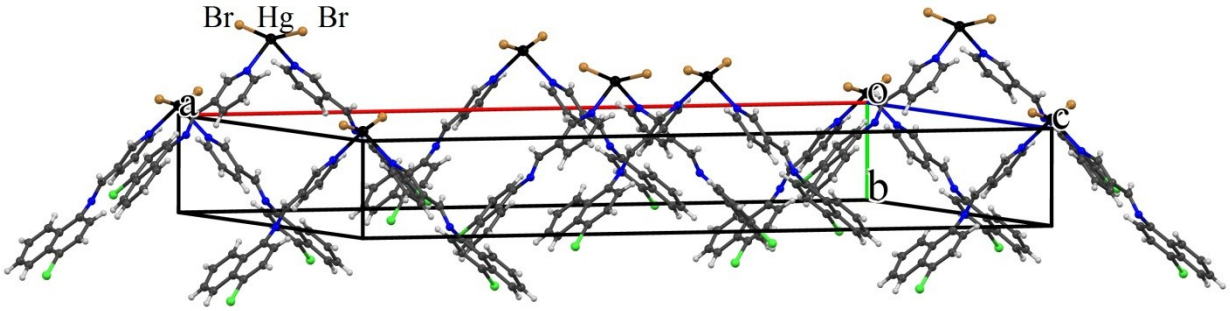


Figure S3. Polar packing in the structure of complex **5**. All molecules have the same orientation along the polar *b*-axis, *e.g.* all Br-Hg-Br moieties are oriented parallel to each other.

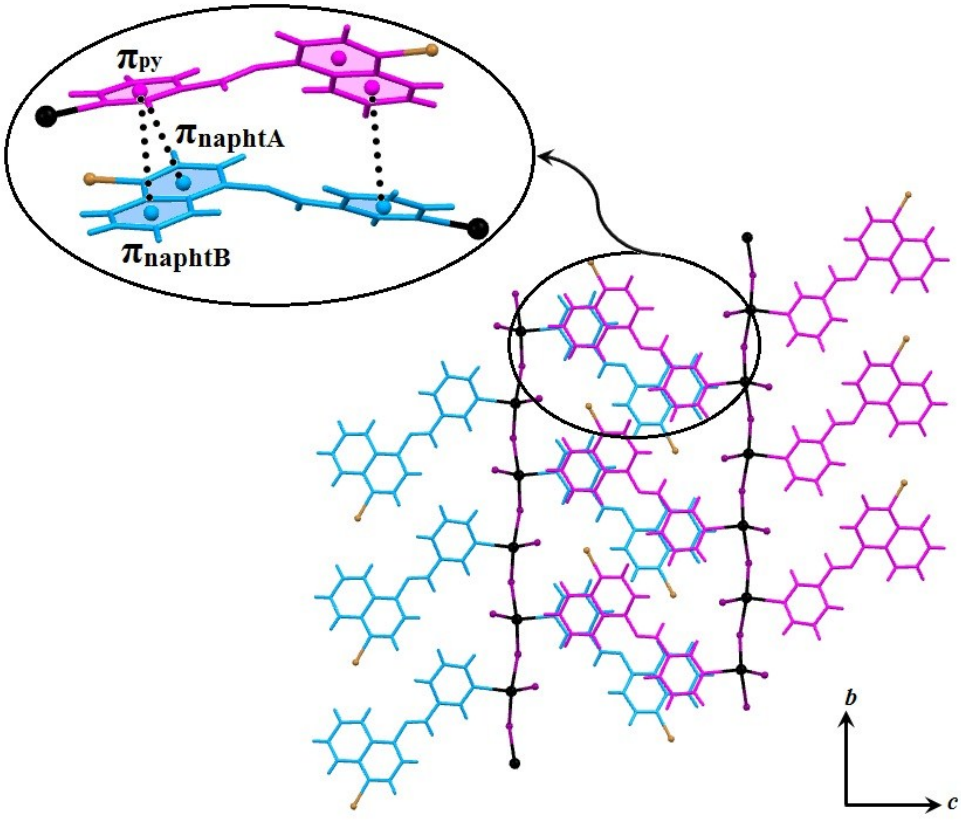
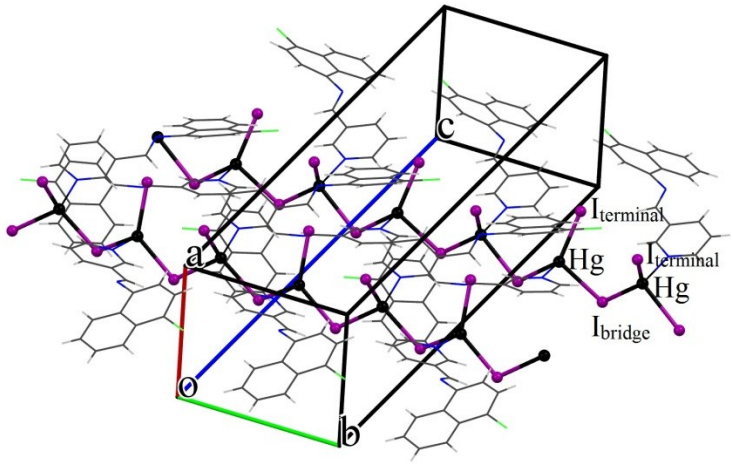
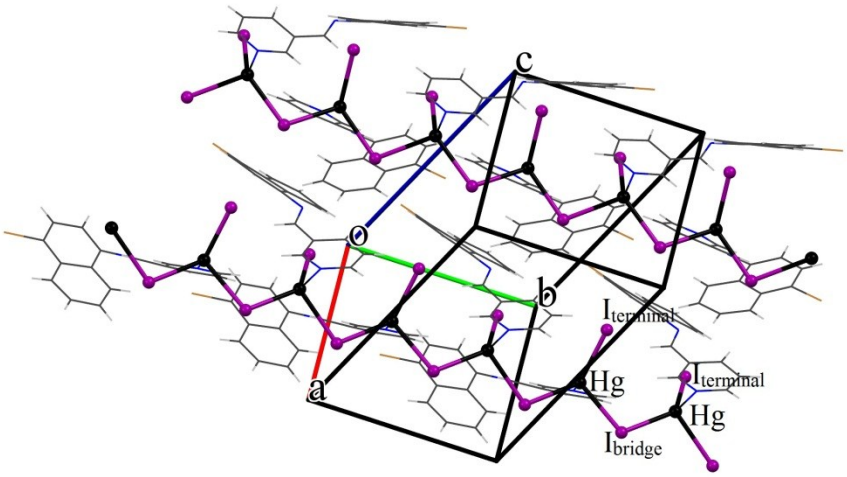


Figure S4. Overall supramolecular structure of **8** from the linkage of neighbouring coordination polymer chains through $\pi_{py}\ldots\pi_{naphtA/B}$ interactions in *a*-direction. Different colours show different adjacent linear chains.



(a)



(b)

Figure S5. Polar packing in the structure of complex **7,** (a) and **8**, (b). The 1D linear chains are oriented in the same direction along the polar *b*-axis and all $I_{terminal}$-Hg-(I_{bridge})-Hg-$I_{terminal}$ moieties are all pointing in the same direction.

Table S1. Selected bond length (Å) and angles (°) around mercury(II) for complexes **1-8**.

		Complex			
		1 (X = Cl)	**2 (X = Cl)**	**3 (X = Br)**	**4 (X = I)**
Bond distance	Hg1-X1	2.351(6)	2.342(6)	2.484(3)	2.649(2)
	Hg1-N1	2.465(13)	2.411(14)	2.449(11)	2.48(2)
Bond angle	X1-Hg1-N1	96.7(4), 98.0(4)^{i}	95.6(4), 99.0(4)^{ii}	98.0(4), 97.3(4)^{iii}	97.5(5), 97.9(5)^{iv}
	X1-Hg1-X1	157.44(17)	157.56(19)	155.14(8)	154.15(8)
	N1-Hg1-N1	98.5(4)	98.3(5)	103.5(4)	106.9(6)
		5 (X=Br)	**6 (X = Br)**	**7 (X = I)**	**8 (X = I)**
Bond distance	Hg1-X1	2.482(3)	2.495(4)	2.650(2)	2.660(2)
	Hg1-X2	-		2.7422(15), 2.8875(15)^{v}	2.7451(19), 2.8975(19)^{vi}
	Hg2-X2	2.477(3)	-	-	-
	Hg1-N1	2.446(19)	2.421(15)	2.38(2)	2.37(2)
	Hg2-N3	2.44(2)	-	-	-
Bond angle	X1-Hg1-X2	-	-	129.60(6), 110.11(5)^{vii}	129.44(6), 109.52(6)^{ix}
	X1-Hg1-X1	154.32(10)^{v}	149.21(7)^{viii}	-	-
	X1-Hg1-N1	101.2(5), 95.9(4)^{v}	90.46(13)	112.9(4)	113.1(4)
	N1-Hg1-N1	96.3(6)^{v}	-	-	-
	X2-Hg1-N1	-	-	98.6(4)	98.0(4)
	X2-Hg1-X2	-		102.49(4)^{vii}	103.49(6)^{ix}
	X2-Hg1-N3	-	97.7(6), 102.9(6)^{viii}	-	-
	N3-Hg1-N3	-	97.3(6)^{viii}	-	-
	X2-Hg2-X2	152.97(10)^{vi}	-	-	-
	X2-Hg2-N3	100.2(5), 97.2(5)^{vi}	-	-	-
	N3-Hg2-N3	99.5(7)	-	-	-

Symmetry codes: (i) 1-x, y, 1.5-z, (ii) -x, y, 1/2-z, (iii) 1-x, y, 1/2-z , (iv) 1-x, y, 1/2-z (v) –x, y, -z, (vi) –x, y, 1-z, (vii) x, -1/2+y, 1/2-z, (viii) 1-x, y, 1/2-z, (ix) x, 1/2+y, -1.5+z

Table S2. Coordination geometry, dimensionality and aromatic interaction parameters (Å and °) for description of π-π interaction in complexes **1**-**8**. Schematic representation of geometrical parameters for definition of π-π stacking between adjacent aromatic rings is shown in Scheme S1. Color of the background behind the interactions is chosen according to Scheme S2 for better clarity.

Complex	Coordination geometry/ dimension	Cg(I)-Cg(J)	Type of π…π stacking	$d_{Cg\text{-}Cg}$[a]	α[b]	β, γ[c]	$d_{plane\text{-}plane}$[d]	d_{offset}[e]
$[HgCl_2(\mathbf{L}^{\mathbf{amide\text{-}Cl}})_2]$, **1**	Seesaw/discrete	Cg(2)-Cg(3)^{i}	$\pi_{naphA}\cdots\pi_{naphB}$	3.669	0.84	14.99, 15.82	3.544, 3.669	0.94, 1.00
		Hg-Cg(1)^{ii}	$Hg\cdots\pi_{py}$	3.675	-	9.92	3.620	0.663
$[HgCl_2(\mathbf{L}^{\mathbf{amide\text{-}Br}})_2]$, **2**	Seesaw/discrete	Cg(2)-Cg(3)^{iii}	$\pi_{naphA}\cdots\pi_{naphB}$	3.687	1.45	15.78, 14.47	3.548, 3.570	1.00, 0.92
		Hg-Cg(1)^{iv}	$Hg\cdots\pi_{py}$	3.643	-	9.31	3.595	0.58
$[HgBr_2(\mathbf{L}^{\mathbf{amide\text{-}Br}})_2]$, **3**	Seesa/discrete	Cg(2)-Cg(3)^{v}	$\pi_{naphA}\cdots\pi_{naphB}$	3.678	0.65	14.61, 14.55	3.559, 3.560	1.23, 0.92
		Hg-Cg(1)^{vi}	$Hg\cdots\pi_{py}$	3.755	-	8.67	3.712	0.56
$[HgI_2(\mathbf{L}^{\mathbf{amide\text{-}Br}})_2]$, **4**	Seesaw/discrete	Cg(2)-Cg(3)^{vii}	$\pi_{naphA}\cdots\pi_{naphB}$	3.668	1.66	14.69, 13.27	3.548, 3.570	0.98
		Hg-Cg(1)^{viii}	$Hg\cdots\pi_{py}$	3.882	-	10.25	3.820	0.69
$[HgBr_2(\mathbf{L}^{\mathbf{imine\text{-}Cl}})_2]$, **5**	Seesaw/discrete	Hg-Cg(1)^{ix}	$Hg\cdots\pi_{py}$	3.764	-	9.80	3.709	0.64
		C_{Imine}-Cg(1)^{x}	$\pi_{Imine}\cdots\pi_{py}$	3.358	-	31.67	3.201	2.95
		Hg-Cg(1)^{xi}	$Hg\cdots\pi_{py}$	3.868	-	11.52	3.790	0.77
$[HgBr_2(\mathbf{L}^{\mathbf{imine\text{-}Br}})_2]$, **6**	Seesaw/discrete	Hg-Cg(1)^{ixv}	$Hg\cdots\pi_{py}$	3.897	-	11.98	3.812	0.80
		C_{Imine}-Cg(1)^{xv}	$\pi_{Imine}\cdots\pi_{py}$	4.177	-	37.60	3.309	2.54
		C_{Imine}-Cg(3)^{xvi}	$\pi_{Imine}\cdots\pi_{naphtB}$	3.553	-	10.89	3.489	0.67
$[HgI_2(\mathbf{L}^{\mathbf{imine\text{-}Cl}})]_n$, **7**	Seesaw/polymer	Cg(1)-Cg(2)^{xii}	$\pi_{py}\cdots\pi_{naphA}$	3.785	10.78	18.80, 27.21	3.583, 3.366	1.21, 1.73
		Cg(1)-Cg(3)^{xii}	$\pi_{py}\cdots\pi_{naphB}$	3.725	5.90	16.14, 10.63	3.578, 3.661	1.03, 0.68
		Cg(3)-Cg(1)^{xiii}	$\pi_{py}\cdots\pi_{naphB}$	3.725	5.90	24.52, 19.92	3.389, 3.502	1.54, 1.26
$[HgI_2(\mathbf{L}^{\mathbf{imine\text{-}Br}})]_n$, **8**	Seesaw/polymer	Cg(1)-Cg(2)^{xvii}	$\pi_{py}\cdots\pi_{naphA}$	3.785	9.62	25.96, 18.32	3.403, 3.593	1.65, 1.19
		Cg(1)-Cg(3)^{xvii}	$\pi_{py}\cdots\pi_{naphB}$	3.760	5.87	11.76, 17.39	3.681, 3.588	0.76, 1.12
		Cg(1)-Cg(3)^{xviii}	$\pi_{py}\cdots\pi_{naphB}$	3.691	5.87	24.48, 19.69	3.359, 3.475	1.52, 1.24

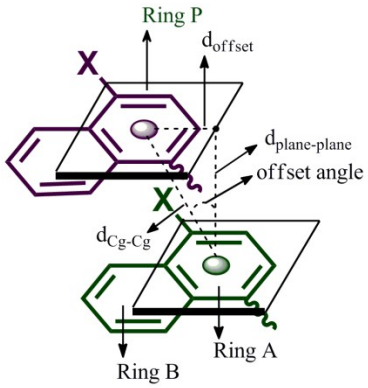
[a] Centroid-centroid distance. [b] Dihedral angle between the ring plane. [c] Offset angles: angle between Cg(I)–Cg(J) vector and normal to plane I, angle between Cg(I)-Cg(J) vector and normal to plane J ($\beta = \gamma$ when $\alpha = 0$). [d] Perpendicular distance of Cg(I) on ring J and perpendicular distance of Cg(J) on ring I. [e] Horizental displacement between Cg(I) and Cg(J), two values if the two rings are not exactly parallel ($\alpha \neq 0$). For **1**-**8**, Cg(1): centroid of C(1)-C(2)-C(3)-N(1)-C(4)-C(5), Cg(2): centroid of C(7)-C(8)-C(9)-C(10)-C(11)-C(16) and Cg(3): centroid of C(11)-C(12)-C(13)-C(14)-C(15)-C(16). Symmetry codes: (i) x, 1+y, z, (ii) x, -1+y, z, (iii) x, -1+y, z, (iv) x, 1+y, z, (v) -x, -1-y, (vi)-z, x, -1+y, z, (vii) 2-x, ½+y, -z, (viii) x, -1+y, z, (ix) x, -1+y, z, (x) x, 1+y, z ,(xi) x, -1+y, z, (xii) -1/2+x, 2-y, 1-z (xiii) 1/2+x, 2-y, 1-z, (ixv) x, -1+y, z, (xv) x, 1+y, z, (xvi) x, -1+y, z, (xvii) 1/2+x, -2-y, -1-z, (xviii) -1/2+x, -2-y, -1-z.

Table S3. Selected hydrogen bonding geometries for compounds **1-6.**

Complex	D-H…A	d(D-H)/Å	d(H**…**A)/Å	d(D…A)/Å	<D-H…A/°	Sym. code
$[HgCl_2(\mathbf{L}^{\mathbf{amide\text{-}Cl}})_2]$, **1**	N2-H2A…O1	0.86	2.100	2.87(1)	148	x, -1+y, z
	C9-H9…O1	0.93	2.740	3.41(2)	130	1-x, 3-y, 2-z
$[HgCl_2(\mathbf{L}^{\mathbf{amide\text{-}Br}})_2]$, **2**	N2-H2A…O1	0.86	2.06	2.86(2)	154	x, 1+y, z
	C9-H9A…O1	0.93	2.870	3.50(3)	126	1/2-x, -1.5-y, 1-z
$[HgBr_2(\mathbf{L}^{\mathbf{amide\text{-}Br}})_2]$, **3**	N2-H2A…O1	0.86	2.090	2.86(2)	148	x, -1+y, z
$[HgI_2(\mathbf{L}^{\mathbf{amide\text{-}Br}})_2]$, **4**	N2-H2A…O1	0.86	2.070	2.85(5)	151	x, -1+y, z
	C9-H9…O1	0.93	2.730	3.41(4)	130	1.5-x, 3.5-y, 1-z
$[HgBr_2(\mathbf{L}^{\mathbf{imine\text{-}Cl}})_2]$, **5**	C2-H2…Br2	0.93	2.900	3.62(2)	135	x, 1+y, -z

Table S4. Selected C-H…π geometries for compound **1-6**.

Complex	C-H…π	H…Cg	Sym. Code
$[HgCl_2(\mathbf{L}^{\mathbf{amide\text{-}Cl}})_2]$, **1**	C14-H14… π_{naphB}	3.182	1/2-x, -1/2+y, 3/2-z
$[HgCl_2(\mathbf{L}^{\mathbf{amide\text{-}Br}})_2]$, **2**	C14-H14… π_{naphB}	3.301	1/2-x,1/2+y, 1/2-z
$[HgBr_2(\mathbf{L}^{\mathbf{amide\text{-}Br}})_2]$, **3**	C14-H14… π_{naphB}	3.347	3/2-x, -1/2+y, 1/2-z
$[HgI_2(\mathbf{L}^{\mathbf{amide\text{-}Br}})_2]$, **4**	C14-H14… π_{naphB}	3.537	3/2-x, -1/2+y, 1/2-z
$[HgBr_2(\mathbf{L}^{\mathbf{imine\text{-}Cl}})_2]$, **5**	C18-H18… π_{naphB}	3.571	-x, -1+y, 1-z
$[HgBr_2(\mathbf{L}^{\mathbf{imine\text{-}Br}})_2]$, **6**	C12-H12… π_{naphB}	3.070	3/2-x, 1/2+y, 3/2-z



Scheme S1. Schematic representation of geometrical parameters for definition of π-π stacking between adjacent aromatic rings.

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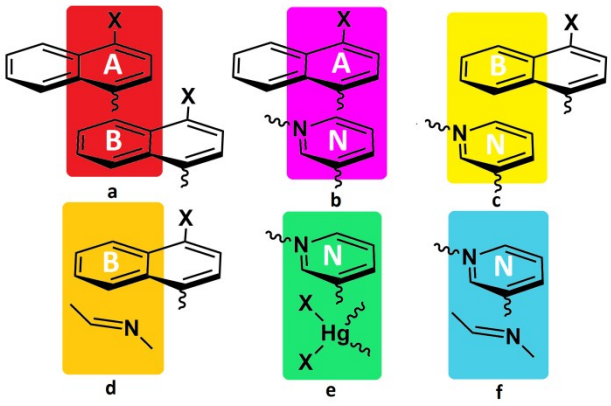

Scheme S2. The various π…π and Hg…π synthons, $\pi_{naphtA}\ldots\pi_{naphtB}$, (a), $\pi_{naphtA}\ldots\pi_{py}$, (b), $\pi_{naphtB}\ldots\pi_{py}$, (c), $\pi_{naphtB}\ldots\pi_{imine}$, (d), Hg…$\pi_{py}$(e), and $\pi_{imine}\ldots\pi_{py}$, (f), in the crystal packing of complexes **1**-**8**.