ELETTRONIC SUPPLEMENTARY INFORMATION

Title: HgBrI: a possible tecton for NLO molecular materials?

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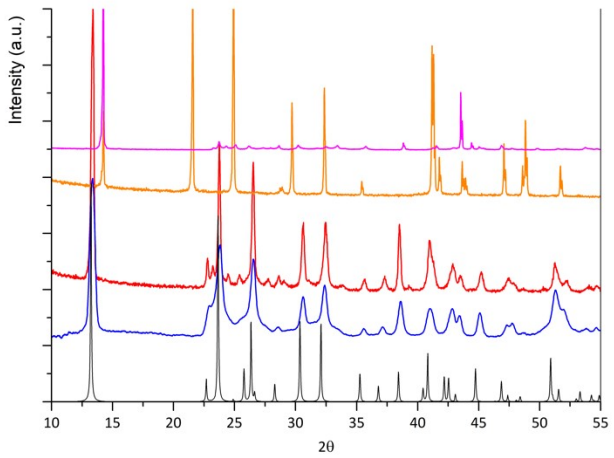

Figure S1. Comparison of experimental (in blue from mechano-chemical synthesis, in red sublimated product) and calculated (in red) PXRD pattern of HgBrI (**1**) and of the starting reagent $HgBr_2$ in pink and HgI_2 (α) in orange.

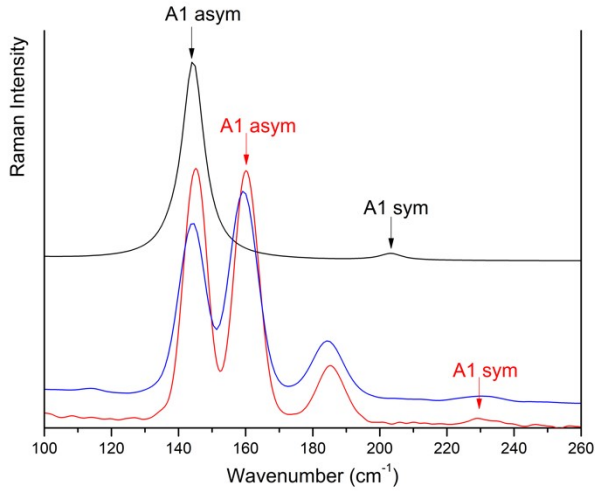

Figure S2. Calculated Raman spectrum of HgBrI (**1**) in black and experimental spectrum of sublimated product (in red) and of product obtained from mechano-chemical synthesis (in blue).

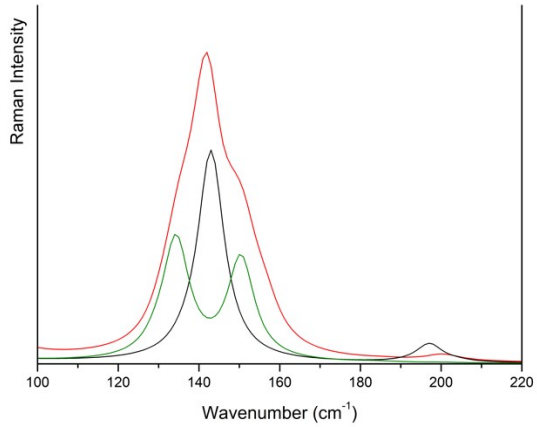

Figure S3. Calculated Raman spectra of HgBrI: in black DFT periodic calculation, in red weighted average of ordinated configurations and in green one of the permutations.

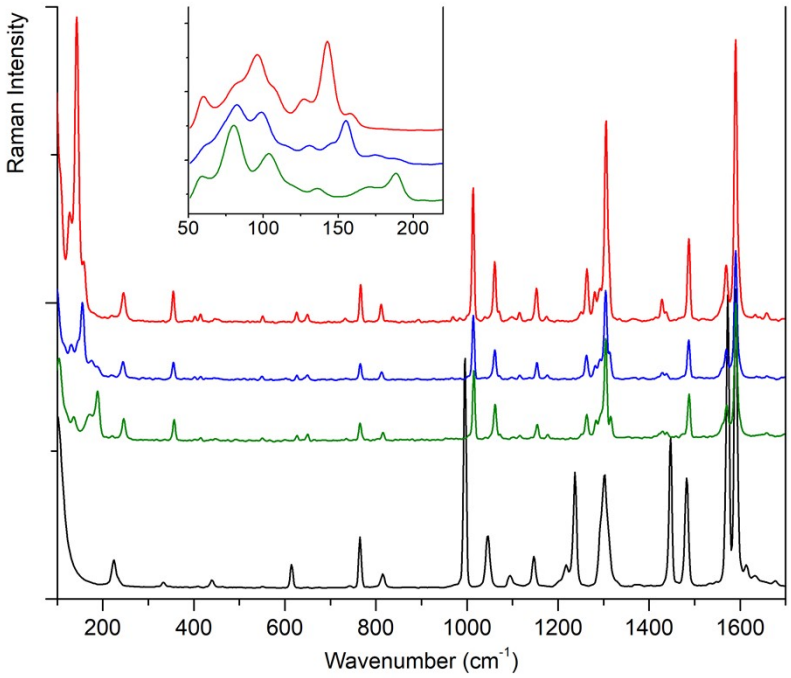

Figure S4. Raman spectra of [Hg(bpy)BrI] (**2**) in blue, [Hg(bpy)Br_2] in green, [Hg(bpy)I_2] in red and bpy ligand in black, in the inset spectral range 50-220 cm^{-1}.

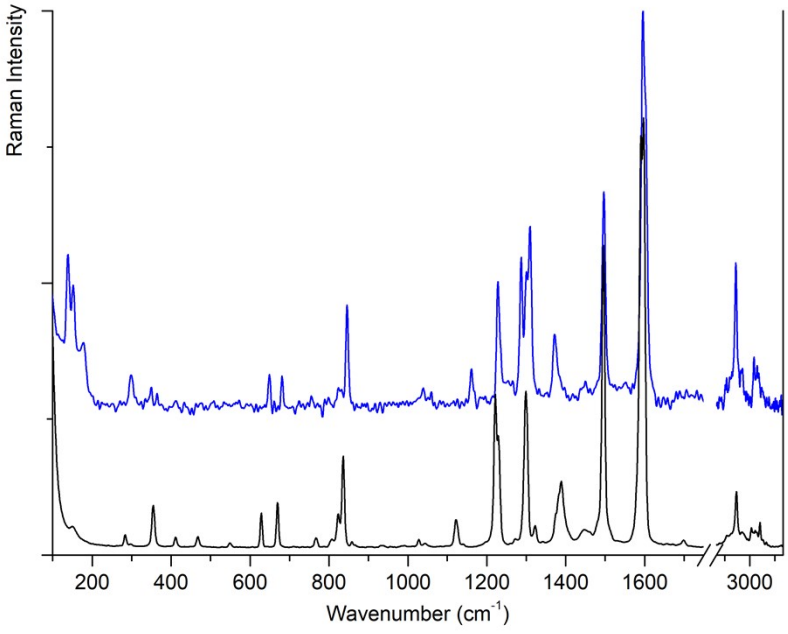

Figure S5. Raman spectra of [Hg(dmbpy)BrI] (**3**) in blue and dmbpy ligand in black.

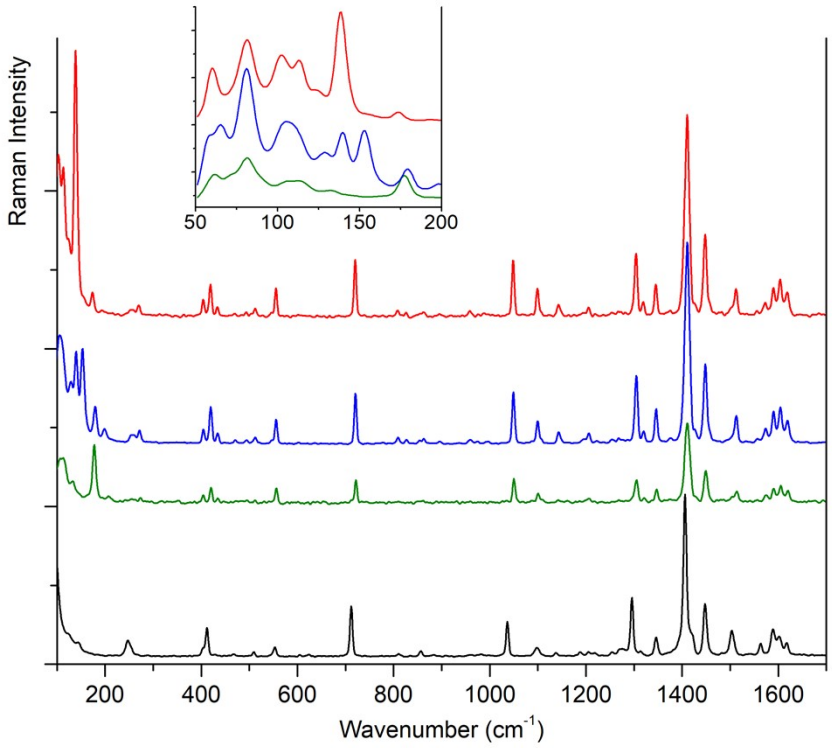

Figure S6. Raman spectra of [Hg(phen)BrI] (**4**) in blue, [Hg(phen)Br_2] (**9**) in green, [Hg(phen)I_2] in red and phen in black, in the inset spectral range 50-200 cm^{-1}.

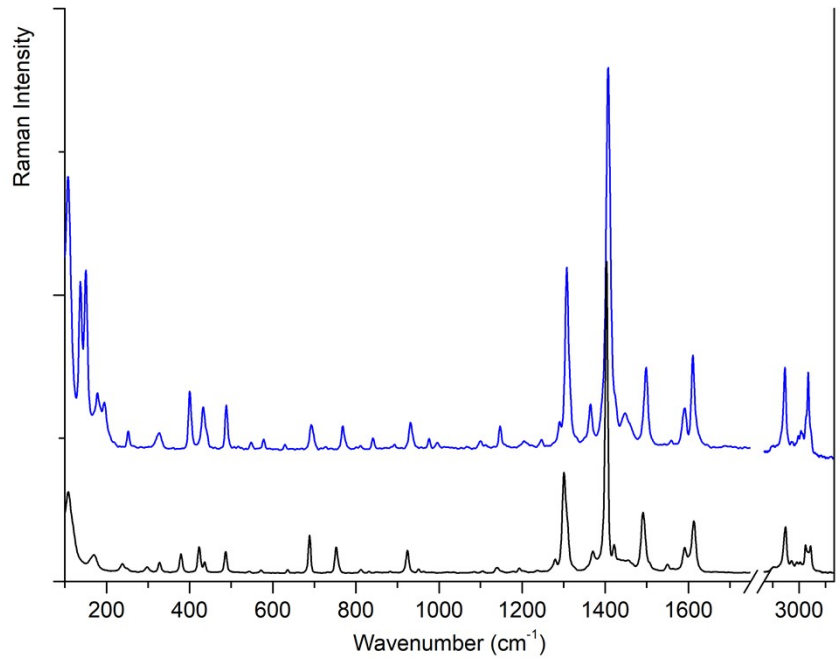

Figure S7. Raman spectra of [Hg(dmphen)BrI] (**5**) in blue and dmphen in black.

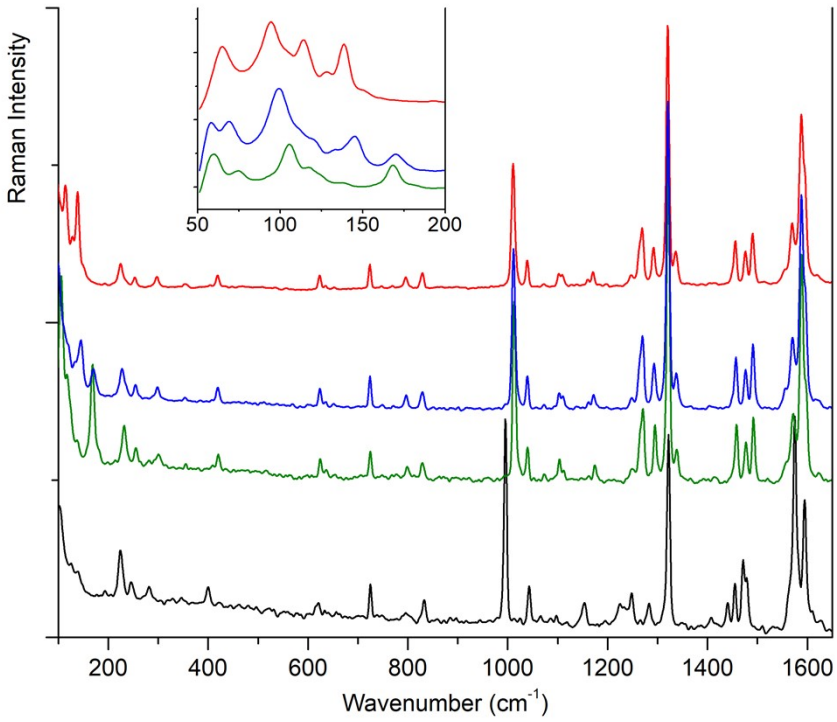

Figure S8. Raman spectra of [Hg(terpy)BrI] (**6**) in blue, [Hg(terpy)Br_2] (**10**) in green, [Hg(phen)I_2] in red and terpy in black, in the inset spectral range 50-200 cm^{-1}.

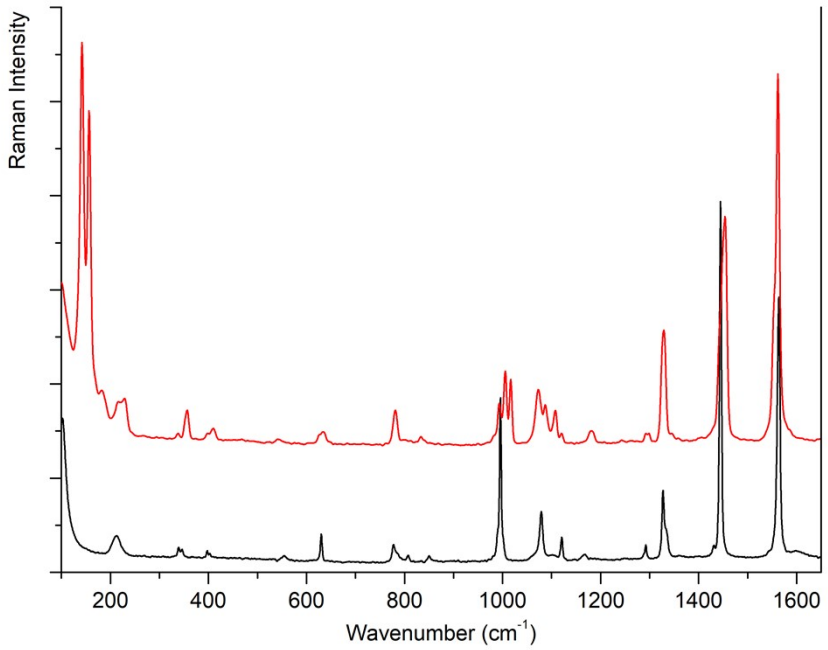

Figure S9. Raman spectra of [Hg(bpym)BrI] (**7**) in red and bpym in black.

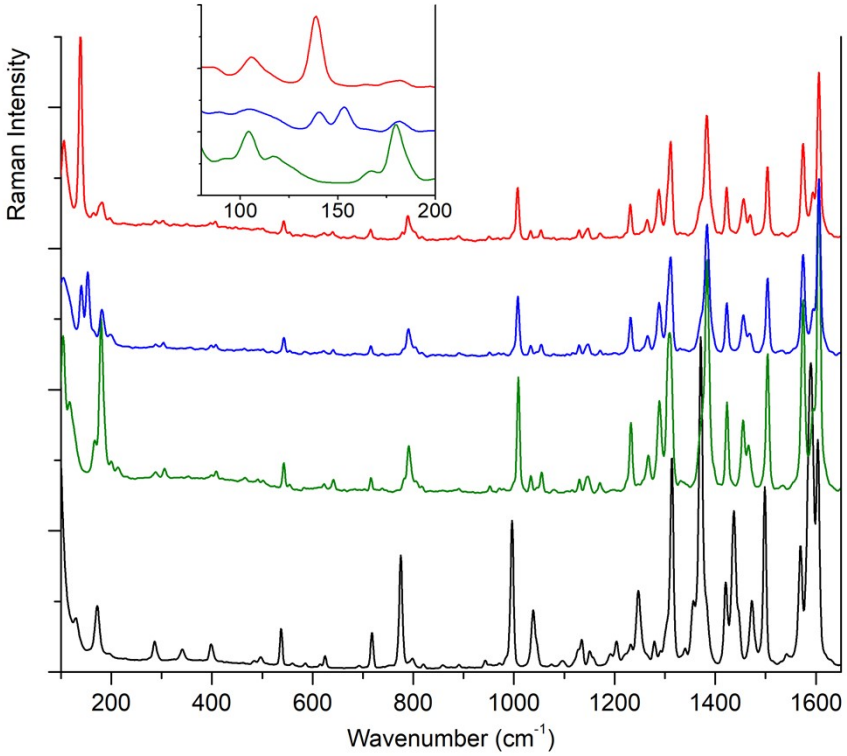

Figure S10. Raman spectra of [Hg(pyNP)BrI] (**8**) in blue, [Hg(pyNP)Br_2] in green, [Hg(pyNP)I_2] in red and pyNP in black, in the inset spectral range 80-200 cm^{-1}.

Table S1. Experimental modes related to Hg coordination in **2**-**10** compared to corresponding ligand.

Ligand (L)		[Hg(L)BrI]	[Hg(L)Br_2]	[Hg(L)Br_2]	Assignment
bpy	1590 vs 1573 vs 1483 m 1447 m	1591 vs 1570 m 1487 m 1430 vw	1591 vs 1570 m 1487 m 1430 vw	1591 vs 1570 m 1487 m 1430 vw	Ring stretching
	1045 w 995 s	1061 m 1014 s	1063 m 1015 s	1061 m 1013 s	Breathing modes
dmbpy	1598 vs 1591 vs 1496 s	1602 sh 1596 vs 1499 s	---	---	Ring stretching
	1035 vw 836 m	1040 vw 846 m	---	---	Breathing modes
phen	1618 w 1602 m 1589 m 1564 w	1620 w 1605 m 1590 m 1574 w	1620 w 1605 m 1590 m 1574 w	1620 w 1605 m 1590 m 1574 w	Ring stretching
	1037 m 712 s	1049 s 720 s	1050 s 720 s	1048 s 720 s	Breathing modes
dmphen	1616 m 1592 w 1550 vw 1491 m	1612 m 1591 w 1560 vw 1499 m	---	---	Ring stretching
	963 vw 951 w 924 m 753 m	997 vw 976 w 932 m 768 m	---	---	Breathing modes
terpy	1595 s 1575 vs 1479 m 1471 m	1596 sh 1588 s 1570 m 1490 m 1476 m	1596 sh 1588 s 1572 m 1490 m 1476 m	1596 sh 1588 s 1570 m 1490 m 1476 m	Ring stretching
	1045 m 995 vs	1039 w 1012 s	1039 w 1013 s	1039 w 1011 s	Breathing modes
pyNP	1604 s 1590 vs 1569 m 1540 vw	1608 vs 1596 w 1575 m 1532 vw	1606 vs 1595 vw 1575 s 1535 vw	1606 vs 1595 w 1575 m 1533 vw	Ring stretching
	1075 vw 1047 sh 1038 w 997 m 775 m	1053 vw 1034 w 1008 m 1000 sh 791 w 781 sh	1056 w 1034 w 1009 m 1007 sh 792 w 783 sh	1054 vw 1032 vw 1008 m 998 sh 790 w 778 vw	Breathing modes
bpym	1564 s 1445 vs	1562 vs 1555 sh 1454 s 1443 sh	---	----	Ring stretching
	1120 vw 1080 w 995 m	1009 w 1089 m 1073 m 1017 m 1006 m 993 w	---	----	Breathing modes

s = strong, m = medium, w = weak, sh=shoulder, v=very

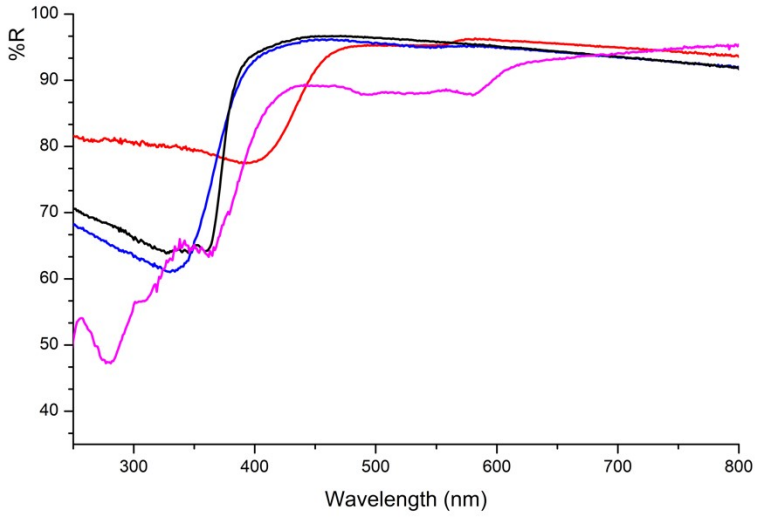

Figure S11. Reflectance spectra of HgBrI (**1**) in red, [Hg(bpy)BrI] (**2**) in blue, [Hg(phen)BrI] (**4**) in black and [Hg(pyNP)BrI] (**8**) in pink.

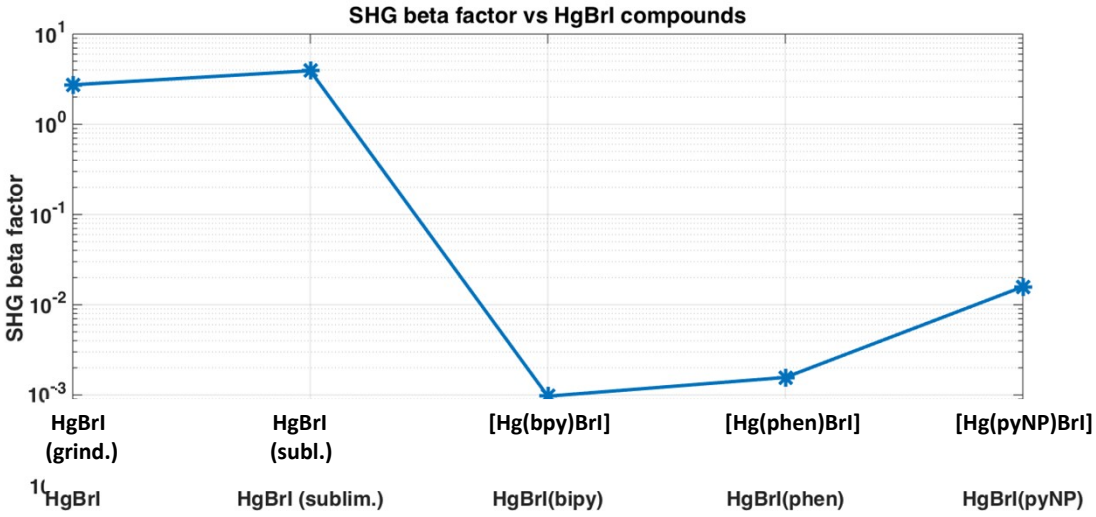

Figure S12. SHG β factor of HgBrI (**1**) (powder from mechano-chemical synthesis and sublimated product), [Hg(bpy)BrI] (**2**), [Hg(phen)BrI] (**4**) and [Hg(pyNP)BrI] (**8**).

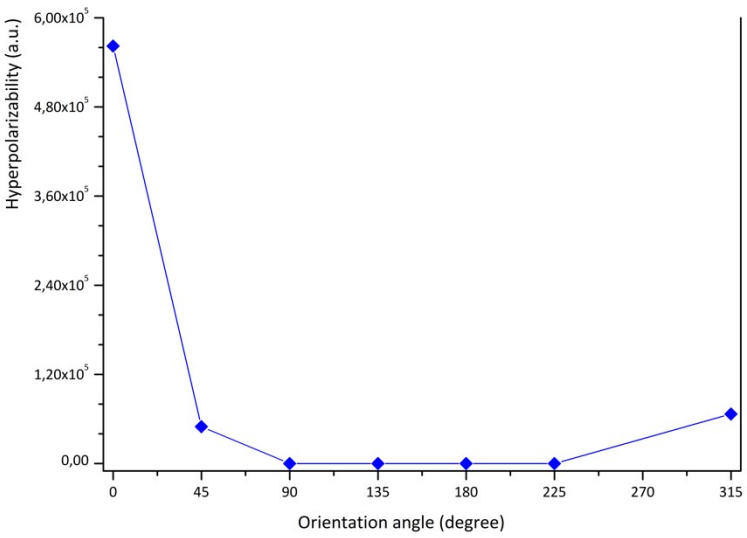

Figure S13. Intensity of SHG emission of a single crystal of [Hg(bpy)BrI] (**2**) oriented along seven angles.

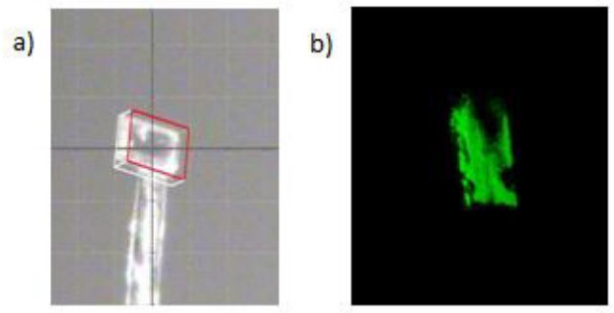

Image S1. (a) Photo of the indexed crystal of [Hg(bpy)BrI] (**2**) and (b) SHG Microscopy image of the same crystal along the angle of maximum emission.

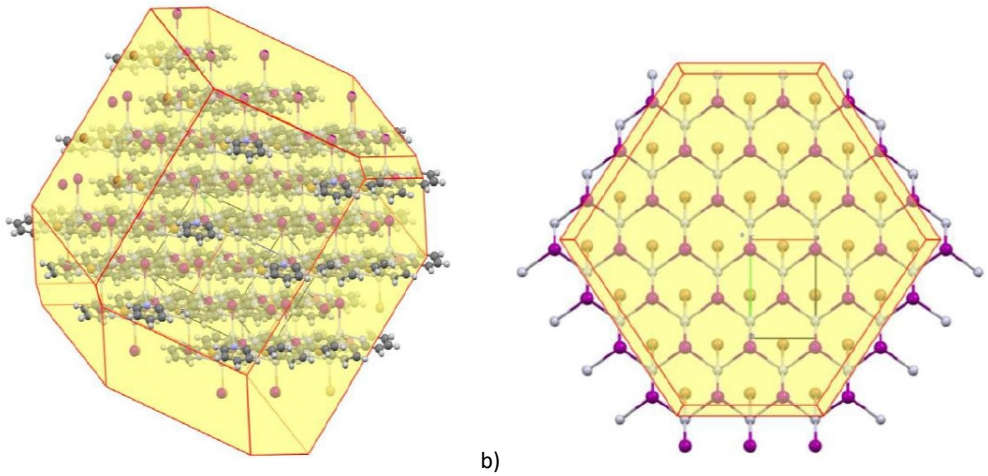

Figure S14. Crystal morphology of (a) indexed single crystal of [Hg(bpy)BrI] (**2**) along crystal face (010) and (b) HgBrI (**1**) along *z* axis. (Violet: iodine; grey: mercury; brown: bromide; grey: carbon; blue: nitrogen; white: hydrogen – ORTEP plot 50%).

Table S2. Calculated tensor components (a.u.) of the centrosymmetric (CS) and noncentrosymmetric (NCS) permutations of [Hg(bpy)BrI] (**2**).

	Permutation 1 (CS)		Permutation 2 (NCS)		Permutation 3 (NCS)		Permutation 4 (CS)	
Component	**B**	**χ^2**	**B**	**χ^2**	**β**	**χ^2**	**β**	**χ^2**
xxx	-4.9618	-0.0078	-111.6000	-0.1754	112.7800	0.1772	-0.1668	-0.0003
xxy	0.4850	0.0008	-13.9800	-0.0220	12.3410	0.0194	-0.3270	-0.0005
xxz	0.1661	0.0003	173.2700	0.2723	-175.8500	-0.2763	0.0930	0.0001
xyy	0.7856	0.0012	-220.2200	-0.3460	219.6400	0.3451	0.4467	0.0007
xyz	-0.1053	-0.0002	-165.6000	-0.2602	167.6000	0.2634	-0.0931	-0.0001
xzz	0.2484	0.0004	-97.9910	-0.1540	98.1600	0.1542	0.1866	0.0003
yyy	1.5703	0.0025	191.6500	0.3011	-193.8400	-0.3046	-0.5512	-0.0009
yyz	0.0467	0.0001	-64.4670	-0.1013	67.6840	0.1064	0.0890	0.0001
yzz	0.0745	0.0001	-398.4500	-0.6261	399.8500	0.6283	-0.4368	-0.0007
zzz	-0.3813	-0.0006	-23.5280	-0.0370	27.6180	0.0434	1.4800	0.0023

Table S3. Calculated tensor components (a.u.) of HgBrI (**1**).

Component	**B**	**χ^2**
xxx	0.0000	0.0000
xxy	0.0000	0.0000
xxz	-1196.7000	-4.9925
xyy	0.0000	0.0000
xyz	0.0000	0.0000
xzz	0.0000	0.0000
yyy	0.0000	0.0000
yyz	531.1100	2.2157
yzz	0.0000	0.0000
zzz	1592.4000	6.6434

2. DETAILS OF EXPERIMENTAL PROCEDURE

Single crystal data of compound **1**-**10** have been collected on a Gemini R Ultra diffractometer equipped with a nitrogen Oxford Diffraction CryojetHT device (Agilent Technologies UK Ltd., Oxford, U.K.) using graphite-monochromatic Mo(Kα) radiation (λ=0.71073 Å) with the ω-scan method. CrysAlisPro software (CrysAlis PRO 1.171.38.46 (Rigaku OD, 2015) has been used for retrieving cell parameters, for performing data reduction and for absorption correction (with multi-scan technique). All structures were solved by direct methods using ShelXS-14 [1] and refined with full-matrix least-squares on F^2 using the SHELXL-14 [2] in Olex^2 program [3]. All non-hydrogen atoms have been anisotropically refined. Hydrogen atoms have been calculated and riding on the corresponding atom. For measurement at low temperature of **1** and **2**, crystal was cooled through a nitrogen flux from room to 200 K in about 30 minutes and temperature was kept at 200 K during data collection. Structures images have been obtained using Mercury software [4]. Crystal data and refinement, selected bonds lengths and angles amplitudes and asymmetric units of compounds are reported in Crystallographic Tables. The crystallographic data for **1**-**10** have been deposited within the Cambridge Crystallographic Data Centre as supplementary publications under the CCDC numbers 2086278-2086292. This information can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cifcodeCCDC.

Powder data have been collected using a X'Pert powder diffractometer operating in a Bragg–Brentano geometry, equipped with a graphite crystal monochromator and using Cu(Kα1) radiation (λ=1.5406 Å). The elemental analyses (C, H, N and S) were carried out using a Thermo FlashEA 1112 CHNS-O analyser. Uv-Vis reflectance spectra were recorded on samples (diluted in Aerosil Ox 50) with a Cary 5000 UV-Vis spectrophotometer.

FT-Raman spectra were obtained with a Bruker Vertex 70 spectrometer, equipped with the RAMII accessory, by exciting with a 1064 nm laser, with a resolution of 4 cm^{-1}. Attenuated Total Reflectance (ATR) and Far Infrared Spectroscopy (FIR) spectra were recorded in the 4000–0 cm^{-1} range using a Bruker Vertex 70 spectrophotometer, equipped with a Harrick MVP2 ATR cell and DTGS detectors (either with Si or KBr beamsplitters). The adopted resolution was equal to 4 cm^{-1} in all cases.

SHG emission was measured using two different methods: one using a NLO Multimodal microscope to get the SHG signal from a single crystal of [Hg(bpy)BrI] (**2**) at different excitation angles, and the second using a specific excitation geometry over a sample of powder of HgBrI, [Hg(bpy)BrI] (**2**), [Hg(phen)BrI] (**4**) and [Hg(pyNP)BrI] (**8**). In both measurements, the samples were excited using a pulsed source of about 5 ps pulse length and a wavelength of 1064 nm, generated by a master laser (picoTrain, HighQLaser). For such regards the SHG measurement of powder samples in the optical geometry adopted the excitation beam was deflected by a deformable mirror (Thorlabs DMH40-P01) and focused using a plano-convex lens with 25 mm of focal length on the powder sample. The powder was placed on a holder oriented at 45 degrees with respect to propagation direction of the excitation beam. The SHG signal was then acquired at 90 degrees with respect to the excitation beam propagation axis. The SHG signal was spectrally filtered and focused on a PMT using another plano-convex lens with 25 mm of focal length. For each sample the excitation beam was scanned with 360 angle points on an ideally circular closed line using the deformable mirror, and for each point the excitation power was changed cyclically 8 times. For each point the SHG intensity together with a portion of the excitation power were measured in two separate channels over 36500 times using a data acquisition card at a sample rate of 1 kS/s. For each position was then extracted the fitting parameter related to the following quadratic function that should represent the hyperpolarizability behaviour of the sample:

$$y = ax^2 + b$$

The parameters *a* and *b* were computed for all the positions, and the maximum value of *a* over the collected position was selected in order to take into account the maximum statistical potential of the related powder SHG emissions, since this is strongly related to the excitation angle with respect to the crystal's orientation in the powder.

In order to get SHG signal from a single crystal at different excitation angles, a single crystal of the compound was mounted in special sample holders and imaged using SHG microscopy technique. The excitation source was focused on the sample using a lens, and the emitted signal was collected by a PMT in the forward direction using a 4x lens, optically filtered allowing only a suitable transmission window peaked at 532 nm. Using an excitation lens with a numerical aperture of 0.75, the excitation wave vectors could have multiple angles easing the phase matching condition. In order to extract the emission ratios, the crystal was imaged in 3D several times at different excitation intensities. The single crystal was image-oriented in seven orthogonal angles with respect to the sample holder axis. The beam was transmitted through a polarizer beamsplitter, allowing only horizontal linear polarization exciting the sample. A very small part of the excitation signal was split with a broadband beamsplitter window and sent to a powermeter (PM30, Thorlabs with sensor S120B, Thorlabs). The analogue output of the powermeter was measured simultaneously with the second harmonic signal generated by the samples. Samples were 3D imaged in each orthogonal angle collecting about 15 Z slice images, setting the Z pitch between images in a way to acquire the whole sample. Using ImageJ software [5], a specific plug-in was developed to extract the average SHG signal from each slice of the 3D images. Before running the plug-in over the set of the collected 3D images, an overall max intensity Z projection was performed, and the region outside the compound shape was cleared and it was manually

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[3] Dolomanov, O.V.; Bourhis, L. J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H. OLEX2: A Complete Structure Solution, Refinement And Analysis Program. *J. Appl. Crystallogr.* **2009**, *42*, 339–341.
[4] (a) Macrae, C.F.; Bruno, I.J.; Chisholm, J.A.; Edgington, P.R.; McCabe, P.; Pidcock, E.; Rodriguez-Monge, L.; Taylor, R.; van de Streek, J.; Wood, P.A.; *J. Appl. Cryst.* **2008**, *41*, 466–470; (b) Macrae, C.F.; Edgington, P.R., McCabe, P.; Pidcock, E.; Shields, G.P.; Taylor, R.; Towler, M.; van de Streek, J. *J. Appl. Cryst.* **2006**, *39*, 453–457; (c) Bruno, I.J.; Cole, J.C.; Edgington, P.R.; Kessler, M.K.; Macrae, C.F.; McCabe, P.; Pearson, J.; Taylor, R. *Acta Cryst.* **2002**, *B58*, 389–397; (d) Taylor, R.; Macrae, C.F.; *Acta Cryst.* **2001**, B57, 815–827.
[5] Rasband, W.S. Image J (1997–2014) US National Institutes of Health, Bethesda, Maryland, USA. http://imagej.nih.gov/ij/

chosen a threshold value to discriminate the foreground object from the background. The plug-in was then launched using as input parameters the chosen threshold value and the size in pixel units of the smaller objects recognizable as foreground to filter false objects due to noise out from computation of the intensity average. At the end of the plug-in, a result table was computed containing all the average intensities per slice images and the overall 3D image average intensities. Since the second harmonic signals measured in function of the excitation power must have a quadratic dependence, the plugin also processes the average intensities per excitation power and extracts the fitting parameter related to the following quadratic function that should represent the hyperpolarizability behaviour of the sample:

$$y = ax^2 + b$$

The parameters *a* and *b* were computed for all the orientation angles, and an average value of *a* was extracted in order to take into account an average behaviour of the crystal's emissions.

Periodic simulations on the experimental cells were carried out with the CRYSTAL17 code. All the calculations were performed with the B3LYP-D*0, which is the B3LYP functional [6] plus the a posteriori correction term (D*0) to account for dispersive interactions (partly missed in pure DFT). The D*0 is a modification of the D* scheme [7], which, in turn, recalls the original Grimme D2 correction [8] optimized for solid systems (the van der Walls atomic radii (R0) coefficients are scaled by 1.3 for hydrogen and 1.05 for all the other atoms). The further modification of the D*0 means that C6 coefficients on positively charged metals are set to 0 (i.e. no dispersion on Hg atoms). This approach was already tested, providing good results, especially on alkali and alkaline-earth metals [9], but it is successfully translated also to transition metals. The basis set chosen is the Ahlrichs TZVP, modified for solid systems [10] on all the atoms but mercury, for which a HayWadt-64-4(31d) was used [11]. The tolerance on energy for the convergence of the self-consistent field (SCF) iterative procedure was set to the default (i.e. 10^{-7} Hartree on geometry optimization and 10^{-11} Hartree on frequency calculations). Tolerances in the integral calculation were set to 10^{-9} Hartree for Coulomb overlap, Coulomb penetration, exchange overlap and exchange pseudo-overlap in the direct space and to 10^{-30} Hartree for the exchange pseuso-overlap in the reciprocal space. The Pack-Monkhorst/Gilat shrinking factors for the reciprocal space on pure HgBrI phase were set to 8, while for the larger cell of [Hg(bpy)BrI] (**2**) they were set to 2. The tolerance on gradients and displacements were tightened to 0.0001 au and 0.0004 bohr, respectively. Vibrational frequencies were computed at the Γ point by numerical differentiation of analytical first derivatives (3 displacements for each atom of the unit cell, one for each cartesian direction). [12] In few cases, where small (less than 10 cm^{-1}) imaginary frequencies appear, we relied on the central difference formula, i.e. 6 displacements for each atom of the unit cell, two for each cartesian direction (so reducing spurious numerical errors). IR and Raman intensities were evaluated through the Couple-Perturbed Hartree-Fock (CPHF) method [13] to simulate IR and Raman spectra of the compounds studied. Raman intensities were corrected for the experimental parameters at which spectra were recorded, by including the working temperature and laser wavelength in the calculation.

Because of the uncertainty of the Br and I positions in the structure of **1**, all the possible permutations on the crystallographic cell of Br and I were optimized. In the specific, as the crystallographic cell consists of 4 HgBrI formula units, the number of possible permutations are: $\frac{8!}{4! * 4!} = 70$. Among the isomers generated, 24 out of 70 present one or more imaginary frequencies (even when removing symmetry constraints and using the central difference formula) and, accordingly, they were not used for further analysis. Moreover, some of the remaining structures collapsed on the same local minimum during the optimization procedure. After the cleaning process of all the unstable and repetitive isomers, 25 structures were used to build up the final spectrum. Therefore, all the Raman spectra were merged together, rescaling the intensities by the proper Boltzmann factor, calculated from the corresponding enthalpies of each configuration (with respect to the most stable isomer). Similarly, also for structure of [Hg(bpy)BrI] (**2**) the effect of the substitutional disorder was taken into account, obtaining 4 possible permutations of the Br and I positions.

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3. CRYSTALLOGRAPHIC TABLES

Table S4. Crystal data and structure refinement for HgBrI (**1**) at 299 K (a) and at 200 K (b).

	(a)	(b)
Empirical formula	BrHgI	BrHgI
Formula weight	407.40	407.40
Temperature/K	299.0	200.00(10)
Crystal system	Orthorhombic	Orthorhombic
Space group	$Cmc2_1$	$Cmc2_1$
a/Å	4.6816(11)	4.6018(10)
b/Å	7.1488(15)	6.8966(12)
c/Å	13.371(3)	12.648(3)
α/°	90	90
β/°	90	90
γ/°	90	90
Volume/Å^3	447.48(17)	401.40(15)
Z	4	4
ρ_{calc} /g·cm^{-3}	6.047	6.741
μ/mm^{-1}	49.995	55.735
F(000)	672.0	672.0
Crystal size/mm^3	0.35 × 0.33 × 0.22	0.25 × 0.22 × 0.15
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	9.146 to 58.454	9.67 to 52.73
Index ranges	-6 ≤ h ≤ 4, -7 ≤ k ≤ 9, -13 ≤ l ≤ 17	-5 ≤ h ≤ 5, -6 ≤ k ≤ 8, -15 ≤ l ≤ 15
Reflections collected	876	1784
Independent reflections	467 [R_{int} =0.0347, R_{sigma} =0.0434]	457 [R_{int}= 0.0883, R_{sigma}= 0.0666]
Data/restraints/parameters	467/1/20	457/37/20
Goodness-of-fit on F^2	1.097	1.109
Final R indexes [I>=2σ (I)]	R_1= 0.0432, wR_2= 0.1003	R_1= 0.0649, wR_2= 0.1690
Final R indexes [all data]	R_1= 0.0523, wR_2= 0.1116	R_1= 0.0725, wR_2= 0.1754
Largest diff. peak/hole / e Å^{-3}	1.28/-1.96	3.94/-2.89
Flack parameter	0.01(2)	0.06(4)

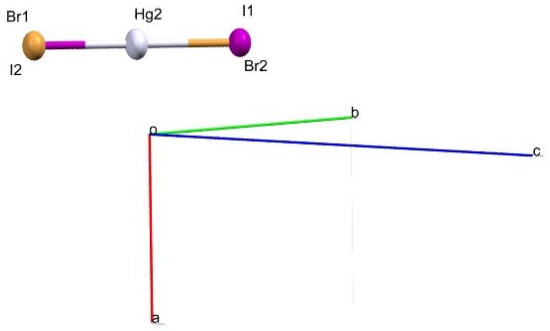

Figure S15. ORTEP plot of the asymmetric unit for HgBrI (**1**) (*a* axis =red, *b* axis=green, *c* axis= blue).

Table S5. Bond Lengths for HgBrI (1) at 299 K (a) and at 200 K (b).

	Atom	Atom	Length/Å	Atom	Atom	Length/Å
a)	Hg1	Br2	2.569(3)	Hg1	Br1	2.542(4)
	Hg1	I2	2.542(4)	Hg1	I1	2.569(3)
b)	Hg1	I1A^1	3.263(5)	Hg1	Br1A	2.478(6)
	Hg1	I1A^2	3.263(5)	Hg1	Br2A	2.477(6)
	Hg1	I1A	2.477(6)	Hg1	I2A	2.478(6)
	^{1} = 1/2+X,-1/2+Y,+Z; ^{2} = -1/2+X,-1/2+Y,+Z					

Table S6. Bond Angles for HgBrI (**1**) at 299 K (a) and at 200 K (b).

	Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
a)	I2	Hg1	Br2	179.27(17)	Br1	Hg1	I1	179.27(17)
b)	I1A[1]	Hg1	I1A[2]	89.70(17)	Br2A	Hg1	I1A	0.0
	I1A	Hg1	I1A[1]	91.44(16)	Br2A	Hg1	Br1A	179.8(3)
	I1A	Hg1	I1A[2]	91.44(16)	Br2A	Hg1	I2A	179.8(3)
	I1A	Hg1	Br1A	179.8(3)	I2A	Hg1	I1A[2]	88.39(14)
	I1A	Hg1	I2A	179.8(3)	I2A	Hg1	I1A[1]	88.39(14)
	Br1A	Hg1	I1A[2]	88.39(14)	I2A	Hg1	Br1A	0.0
	Br1A	Hg1	I1A[1]	88.39(14)	Hg1[3]	I1A	Hg1[4]	89.69(17)
	Br2A	Hg1	I1A[1]	91.44(16)	Hg1	I1A	Hg1[3]	91.44(16)
	Br2A	Hg1	I1A[2]	91.44(16)	Hg1	I1A	Hg1[4]	91.44(16)
	[1] = -1/2+X,-1/2+Y,+Z; [2] = 1/2+X,-1/2+Y,+Z; [3] = 1/2+X,1/2+Y,+Z; [4] = -1/2+X,1/2+Y,+Z							

Table S7. Atomic Occupancy for HgBrI (**1**) at 299 K.

Atom	*Occupancy*	Atom	*Occupancy*
Br1	0.5	Br2	0.5
I1	0.5	I2	0.5

Table S8. Comparison of the results of centrosymmetric and noncentrosymmetric refinements for [Hg(bpy)BrI] (**2**) obtained from measurements at 299 K (a) and 200 K (b) on the same crystal.

(a)	**Empirical formula**	$C_{10}H_8BrHgIN_2$	$C_{10}H_8BrHgIN_2$
	Formula weight	563.58	563.58
	Temperature/K	299	299
	Crystal system	Triclinic	Triclinic
	Space group	*P*-1	*P*1
	a/Å	8.6933(5)	8.6933(5)
	b/Å	9.1875(7)	9.1875(7)
	c/Å	9.4039(8)	9.4039(8)
	α/°	118.877(8)	118.877(8)
	β/°	102.032(6)	102.032(6)
	γ/°	96.897(5)	96.897(5)
	Volume/Å³	621.51(9)	621.51(9)
	Z	2	2
	ρ_{calc}/g cm³	3.012	3.012
	μ/mm⁻¹	18.049	18.049
	F(000)	500.0	500.0
	Crystal size/mm³	0.15 × 0.11 × 0.09	0.15 × 0.11 × 0.09
	Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
	2Θ range for data collection/°	6.942 to 61.014	6.942 to 61.014
	Index ranges	-12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -13 ≤ l ≤ 13	-12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -13 ≤ l ≤ 13
	Reflections collected	17090	17090
	Independent reflections	3784 [R_{int}= 0.0787, R_{sigma}= 0.0664]	7555 [R_{int}= 0.0665, R_{sigma}= 0.0990]
	Data/restraints/parameters	3784/0/155	7555/195/290
	Goodness-of-fit on F²	1.011	0.987
	Final R indexes [I>=2σ (I)]	R_1= 0.0436, wR_2= 0.0731	R_1= 0.0521, wR_2= 0.0748
	Final R indexes [all data]	R_1= 0.0944, wR_2= 0.0889	R_1= 0.1215, wR_2= 0.0978
	Largest diff. peak/hole / e Å⁻³	1.07/-1.18	1.04/-1.15
(b)	**Empirical formula**	$C_{10}H_8BrHgIN_2$	$C_{10}H_8BrHgIN_2$
	Formula weight	563.58	563. 58
	Temperature/K	200.00(10)	200.00(10)
	Crystal system	Triclinic	Triclinic
	Space group	*P*-1	*P*1
	a/Å	8.6535(7)	8.6535(7)
	b/Å	9.1595(11)	9.1595(11)
	c/Å	9.3691(11)	9.3691(11)
	α/°	119.058(12)	119.058(12)
	β/°	102.403(8)	102.403(8)
	γ/°	96.859(8)	96.859(8)
	Volume/Å³	611.83(13)	611.83(13)

	Z	2	2
	ρ_{calc}/g cm^3	3.059	3.059
	μ/mm^{-1}	18.335	18.335
	F(000)	500.0	500.0
	Crystal size/mm^3	0.15 × 0.12 × 0.09	0.15 × 0.12 × 0.09
	Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
	2Θ range for data collection/°	6.96 to 61.012	6.96 to 61.012
	Index ranges	-10 ≤ h ≤ 12, -13 ≤ k ≤ 13, -13 ≤ l ≤ 13	-10 ≤ h ≤ 12, -13 ≤ k ≤ 13, -13 ≤ l ≤ 13
	Reflections collected	10789	10789
	Independent reflections	3725 [R_{int}= 0.0744, R_{sigma}= 0.0876]	5843 [R_{int}= 0.0637, R_{sigma}= 0.1012]
	Data/restraints/parameters	3725/206/154	5843/201/299
	Goodness-of-fit on F^2	1.034	1.024
	Final R indexes [I>=2σ (I)]	R_1= 0.0498, wR_2= 0.0870	R_1= 0.0550, wR_2= 0.1210
	Final R indexes [all data]	R_1= 0.0827, wR_2= 0.1023	R_1= 0.0927, wR_2= 0.1465
	Largest diff. peak/hole / e Å^{-3}	1.44/-1.86	1.48/-2.21

Table S9. Crystal data and structure refinement for [Hg(bpy)BrI] (**2**) in the noncentrosymmetric refinement.

Empirical formula	$C_{10}H_8BrHgIN_2$
Formula weight	563.58
Temperature/K	298.00
Crystal system	Triclinic
Space group	*P*1
a/Å	8.6880(4)
b/Å	9.1908(5)
c/Å	9.3998(6)
α/°	118.781(6)
β/°	102.005(5)
γ/°	96.962(4)
Volume/Å^3	621.64(7)
Z	2
ρ_{calc}/g·cm^{-3}	3.011
μ/mm^{-1}	18.045
F(000)	500.0
Crystal size/mm^3	0.12 × 0.1 × 0.08
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.948 to 52.726
Index ranges	-10 ≤ h ≤ 10, -11 ≤ k ≤ 11, -11 ≤ l ≤ 11
Reflections collected	9237
Independent reflections	5026 [R_{int} = 0.0379, R_{sigma} = 0.0634]
Data/restraints/parameters	5026/147/271
Goodness-of-fit on F^2	1.051
Final R indexes [I>=2σ (I)]	R_1 = 0.0551, wR_2 = 0.1374
Final R indexes [all data]	R_1 = 0.0826, wR_2 = 0.1596
Largest diff. peak/hole / e Å^{-3}	1.80/-2.13
Flack parameter	0.44(3)

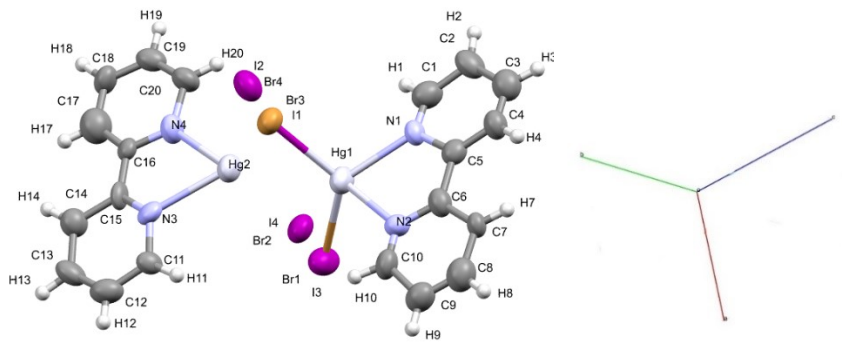

Figure S16. ORTEP plot of the asymmetric unit for [Hg(bpy)BrI] (**2**) (*a* axis =red, *b* axis=green, *c* axis= blue).

Table S10. Bond Lengths for [Hg(bpy)BrI] (**2**).

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Hg1	I1	2.622(4)		C17	C18	1.40(7)
Hg1	Br1	2.575(4)		C16	C15	1.40(5)
Hg1	N1	2.32(3)		C5	C4	1.35(6)
Hg1	N2	2.45(3)		C5	N1	1.44(5)
Hg1	I3	2.575(4)		C5	C6	1.56(6)
Hg1	Br3	2.622(4)		C15	C14	1.42(6)
Hg2	Br4	2.614(4)		C1	C2	1.42(7)
Hg2	Br2	2.623(4)		C1	N1	1.22(6)
Hg2	N3	2.43(4)		C11	C12	1.37(7)
Hg2	N4	2.36(4)		C2	C3	1.46(6)
Hg2	I4	2.623(4)		C13	C14	1.48(6)
Hg2	I2	2.614(4)		C13	C12	1.34(6)
N3	C15	1.26(5)		C4	C3	1.23(6)
N3	C11	1.44(5)		N2	C10	1.16(5)
N4	C20	1.50(5)		N2	C6	1.32(5)
N4	C16	1.34(5)		C10	C9	1.54(6)
C19	C20	1.33(6)		C7	C6	1.40(6)
C19	C18	1.36(6)		C7	C8	1.46(7)
C17	C16	1.32(7)		C9	C8	1.26(7)

Table S11. Bond Angles for [Hg(bpy)BrI] (**2**).

Atom	Atom	Atom	Angle/˚		Atom	Atom	Atom	Angle/˚
Br1	Hg1	I1	122.39(14)		C16	N4	C20	118(3)
Br1	Hg1	Br3	122.39(14)		C20	C19	C18	125(4)
N1	Hg1	I1	103.8(8)		C16	C17	C18	125(5)
N1	Hg1	Br1	132.4(8)		C19	C20	N4	117(4)
N1	Hg1	N2	71.9(11)		N4	C16	C15	113(3)
N1	Hg1	I3	132.4(8)		C17	C16	N4	120(4)
N1	Hg1	Br3	103.8(8)		C17	C16	C15	127(4)
N2	Hg1	I1	121.4(8)		C4	C5	N1	122(4)
N2	Hg1	Br1	91.4(8)		C4	C5	C6	125(4)
N2	Hg1	I3	91.4(8)		N1	C5	C6	113(3)
N2	Hg1	Br3	121.4(8)		N3	C15	C16	122(3)
I3	Hg1	I1	122.39(14)		N3	C15	C14	117(4)
I3	Hg1	Br1	0.0		C16	C15	C14	120(4)
I3	Hg1	Br3	122.39(14)		C19	C18	C17	115(4)
Br3	Hg1	I1	0.0		N1	C1	C2	128(5)
Br4	Hg2	Br2	122.96(13)		C12	C11	N3	117(4)
Br4	Hg2	I4	122.96(13)		C1	C2	C3	114(4)
Br2	Hg2	I4	0.0		C12	C13	C14	122(4)
N3	Hg2	Br4	129.2(7)		C3	C4	C5	124(5)
N3	Hg2	Br2	106.8(7)		C4	C3	C2	117(5)
N3	Hg2	I4	106.8(7)		C15	C14	C13	117(4)
N3	Hg2	I2	129.2(7)		C5	N1	Hg1	119(2)
N4	Hg2	Br4	93.8(9)		C1	N1	Hg1	128(3)
N4	Hg2	Br2	121.8(9)		C1	N1	C5	112(4)
N4	Hg2	N3	65.7(11)		C10	N2	Hg1	122(3)
N4	Hg2	I4	121.8(9)		C10	N2	C6	122(4)
N4	Hg2	I2	93.8(9)		C6	N2	Hg1	115(3)
I2	Hg2	Br4	0.0		N2	C10	C9	126(4)
I2	Hg2	Br2	122.96(13)		C6	C7	C8	113(4)
I2	Hg2	I4	122.96(13)		N2	C6	C5	120(4)
C15	N3	Hg2	117(3)		N2	C6	C7	122(4)
C15	N3	C11	126(4)		C7	C6	C5	118(4)
C11	N3	Hg2	114(2)		C8	C9	C10	111(5)
C20	N4	Hg2	120(3)		C9	C8	C7	127(5)
C16	N4	Hg2	122(3)		C13	C12	C11	119(4)

Table S12. Atomic Occupancy for [Hg(bpy)BrI] (**2**).

Atom	*Occupancy*	Atom	*Occupancy*
I2	0.472(11)	Br4	0.528(11)
I4	0.517(9)	Br2	0.483(9)

Table S13. Crystal data and structure refinement for [Hg(dmbpy)BrI] (**3**).

Identification code	HgBrI(dmbipy)
Empirical formula	C12H12BrHgIN2
Formula weight	591.64
Temperature/K	297.00
Crystal system	orthorhombic
Space group	*Pbca*
a/Å	14.9218(16)
b/Å	13.996(2)
c/Å	15.1066(17)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3155.0(7)
Z	8
ρcalc/g cm^{-3}	2.491
μ/mm^{-1}	14.229
F(000)	2128.0
Crystal size/mm^3	0.13 × 0.1 × 0.08
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.71 to 52.744
Index ranges	-18 ≤ h ≤ 18, -17 ≤ k ≤ 17, -18 ≤ l ≤ 15
Reflections collected	25849
Independent reflections	3224 [Rint = 0.0885, Rsigma = 0.0529]
Data/restraints/parameters	3224/0/156
Goodness-of-fit on F^2	1.038
Final R indexes [I>=2σ (I)]	R1 = 0.0565, wR2 = 0.1501
Final R indexes [all data]	R1 = 0.1065, wR2 = 0.1822
Largest diff. peak/hole / e Å^{-3}	1.90/-1.71

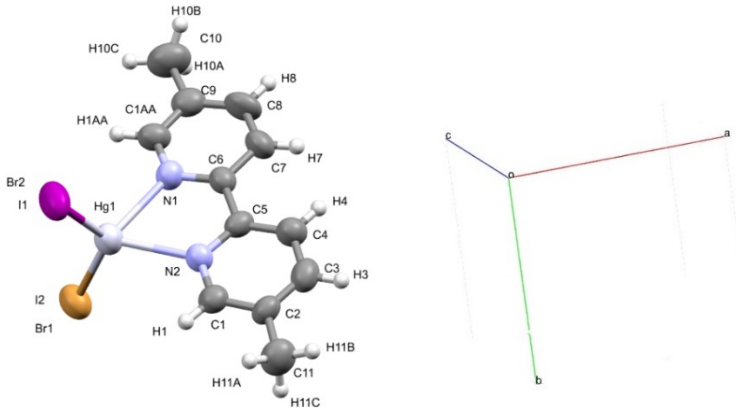

Figure S17. ORTEP plot of the asymmetric unit for [HgBrI(dmbipy)] (**3**) (*a* axis =red, *b* axis=green, *c* axis= blue).

Table S14. Bond Lengths for [Hg(dmbpy)BrI] (**3**).

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Hg1	Br1	2.6504(14)		C6	C7	1.396(19)
Hg1	I1	2.6476(14)		C5	C4	1.357(19)
Hg1	N1	2.377(11)		C1AA	C9	1.36(2)
Hg1	N2	2.387(10)		C1	C2	1.381(18)
Hg1	I2	2.6504(14)		C9	C8	1.38(2)
Hg1	Br2	2.6476(14)		C9	C10	1.49(2)
N1	C6	1.338(16)		C7	C8	1.36(2)

Atom	Atom	Length/Å		Atom	Atom	Length/Å
N1	C1AA	1.333(16)		C4	C3	1.39(2)
N2	C5	1.348(16)		C11	C2	1.49(2)
N2	C1	1.346(16)		C2	C3	1.36(2)

Table S15. Bond Angles for [Hg(dmbpy)BrI] (**3**).

Atom	Atom	Atom	Angle/˚		Atom	Atom	Atom	Angle/˚
Br1	Hg1	I2	0.0		C1	N2	C5	118.2(11)
I1	Hg1	Br1	130.17(5)		N1	C6	C5	118.2(11)
I1	Hg1	I2	130.17(5)		N1	C6	C7	118.8(13)
N1	Hg1	Br1	105.6(3)		C7	C6	C5	123.0(12)
N1	Hg1	I1	114.1(3)		N2	C5	C6	117.0(11)
N1	Hg1	N2	70.5(4)		N2	C5	C4	120.8(12)
N1	Hg1	I2	105.6(3)		C4	C5	C6	122.1(13)
N1	Hg1	Br2	114.1(3)		N1	C1AA	C9	125.0(15)
N2	Hg1	Br1	114.0(3)		N2	C1	C2	124.0(13)
N2	Hg1	I1	106.9(2)		C1AA	C9	C8	115.8(14)
N2	Hg1	I2	114.0(3)		C1AA	C9	C10	122.8(16)
N2	Hg1	Br2	106.9(2)		C8	C9	C10	121.2(15)
Br2	Hg1	Br1	130.17(5)		C8	C7	C6	120.4(14)
Br2	Hg1	I1	0.0		C5	C4	C3	119.9(14)
Br2	Hg1	I2	130.17(5)		C7	C8	C9	120.5(14)

Table S16. Atomic Occupancy for [Hg(dmbpy)BrI] (**3**).

Atom	*Occupancy*	Atom	*Occupancy*
Br2	0.50	I1	0.50
I2	0.50	Br1	0.50

Table S17. Crystal data and structure refinement for [Hg(phen)BrI] (**4**).

Identification code	HgBrI(phen)
Empirical formula	C12H8BrHgIN2
Formula weight	587.60
Temperature/K	298.00
Crystal system	Triclinic
Space group	*P*-1
a/Å	7.8750(3)
b/Å	9.3730(4)
c/Å	9.8830(4)
α/°	91.545(3)
β/°	111.574(4)
γ/°	101.420(3)
Volume/Å^3	660.96(5)
Z	2
ρcalcg/cm3	2.952
μ/mm^{-1}	16.979
F(000)	524.0
Crystal size/mm^3	0.13 × 0.1 × 0.08
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.644 to 58.776
Index ranges	-10 ≤ h ≤ 10, -12 ≤ k ≤ 12, -13 ≤ l ≤ 12
Reflections collected	13761
Independent reflections	3276 [Rint = 0.1133, Rsigma = 0.0858]
Data/restraints/parameters	3276/0/154
Goodness-of-fit on F^2	0.875
Final R indexes [I>=2σ (I)]	R1 = 0.0411, wR2 = 0.0852
Final R indexes [all data]	R1 = 0.0745, wR2 = 0.0924
Largest diff. peak/hole / e Å^{-3}	1.39/-1.69

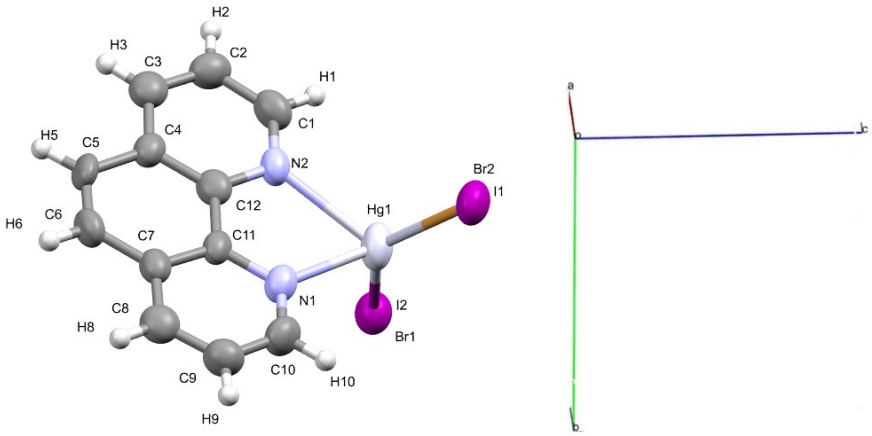

Figure S18. ORTEP plot of the asymmetric unit for [Hg(phen)BrI] (**4**) (*a* axis =red, *b* axis=green, *c* axis= blue).

Table S18. Atomic Occupancy for [Hg(phen)BrI] (**4**).

Atom	*Occupancy*		Atom	*Occupancy*
I1	0.496(8)		I1A	0.504(8)
Br1A	0.504(8)		Br1	0.496(8)

Table S19. Bond Lengths for [Hg(phen)BrI] (**4**).

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Hg1	I2	2.5952(6)		N1	C10	1.304(9)
Hg1	I1	2.5832(7)		C11	C7	1.406(10)
Hg1	N2	2.425(6)		C1	C2	1.396(11)
Hg1	N1	2.405(6)		C4	C3	1.416(10)
Hg1	Br1	2.5952(6)		C4	C5	1.445(10)
Hg1	Br2	2.5832(7)		C7	C6	1.431(10)
N2	C12	1.365(9)		C7	C8	1.420(10)
N2	C1	1.323(9)		C2	C3	1.351(12)
C12	C11	1.430(9)		C5	C6	1.393(10)
C12	C4	1.405(10)		C10	C9	1.398(11)
N1	C11	1.376(8)		C9	C8	1.356(11)

Table S20. Bond Angles for [Hg(phen)BrI] (**4**).

Atom	Atom	Atom	Angle/˚		Atom	Atom	Atom	Angle/˚
I2	Hg1	Br1	0.0		C11	N1	Hg1	116.0(4)
I1	Hg1	I2	137.38(2)		C10	N1	Hg1	126.8(5)
I1	Hg1	Br1	137.38(2)		C10	N1	C11	117.2(6)
N2	Hg1	I2	101.00(12)		N1	C11	C12	119.0(6)
N2	Hg1	I1	114.25(12)		N1	C11	C7	122.2(6)
N2	Hg1	Br1	101.00(12)		C7	C11	C12	118.8(6)
N2	Hg1	Br2	114.25(12)		N2	C1	C2	122.5(7)
N1	Hg1	I2	111.83(12)		C12	C4	C3	118.8(7)
N1	Hg1	I1	102.68(13)		C12	C4	C5	120.8(6)
N1	Hg1	N2	69.64(19)		C3	C4	C5	120.4(7)
N1	Hg1	Br1	111.83(12)		C11	C7	C6	121.1(7)
N1	Hg1	Br2	102.68(13)		C11	C7	C8	118.3(7)
Br2	Hg1	I2	137.38(2)		C8	C7	C6	120.6(7)
Br2	Hg1	I1	0.0		C3	C2	C1	120.4(7)
Br2	Hg1	Br1	137.38(2)		C2	C3	C4	118.3(7)
C12	N2	Hg1	115.6(4)		C6	C5	C4	118.7(6)
C1	N2	Hg1	125.0(5)		N1	C10	C9	124.3(7)
C1	N2	C12	119.0(6)		C5	C6	C7	120.4(7)
N2	C12	C11	119.0(6)		C8	C9	C10	120.0(7)
N2	C12	C4	120.9(6)		C9	C8	C7	117.9(8)
C4	C12	C11	120.1(6)					

Table S21. Crystal data and structure refinement for [Hg(dmphen)BrI] (**5**).

Identification code	HgBrI(neo)
Empirical formula	C14H12BrHgIN2
Formula weight	615.66
Temperature/K	298.00
Crystal system	monoclinic
Space group	I2/a
a/Å	9.7192(10)
b/Å	11.4387(11)
c/Å	14.6753(18)
α/°	90
β/°	102.712(11)
γ/°	90
Volume/Å^3	1591.5(3)
Z	4
ρcalc/g cm^{-3}	2.569
μ/mm^{-1}	14.109
F(000)	1112.0
Crystal size/mm^3	0.13 × 0.11 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	7.124 to 52.732
Index ranges	-12 ≤ h ≤ 9, -14 ≤ k ≤ 10, -18 ≤ l ≤ 18
Reflections collected	4047
Independent reflections	1623 [Rint = 0.0486, Rsigma = 0.0629]
Data/restraints/parameters	1623/0/88
Goodness-of-fit on F^2	1.021
Final R indexes [I>=2σ (I)]	R1 = 0.0431, wR2 = 0.0807
Final R indexes [all data]	R1 = 0.0754, wR2 = 0.0964
Largest diff. peak/hole / e Å^{-3}	1.06/-0.87

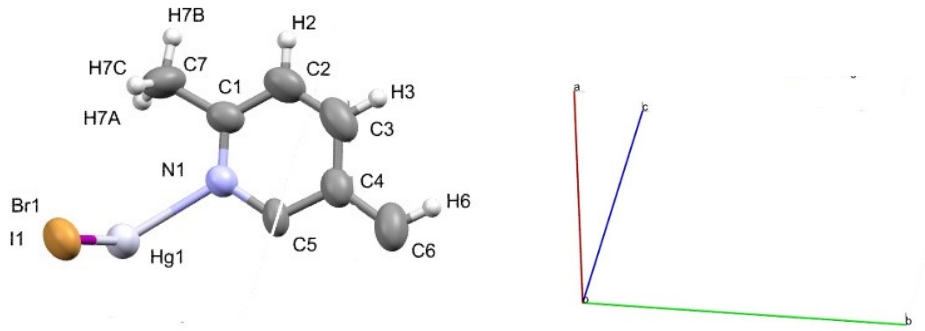

Figure S19. ORTEP plot of the asymmetric unit for [Hg(dmphen)BrI] (**5**) (*a* axis =red, *b* axis=green, *c* axis= blue).

Table S22. Atomic Occupancy for [Hg(dmphen)BrI] (**5**).

Atom	***Occupancy***
I1	0.50
Br1	0.50

Table S23. Bond Lengths for [Hg(dmphen)BrI] (**5**).

Atom	**Atom**	**Length/Å**		**Atom**	**Atom**	**Length/Å**
Hg1	I1	2.6033(9)		C1	C7	1.507(14)
Hg1	N1^1	2.408(7)		C5	C5^1	1.404(17)
Hg1	N1	2.408(7)		C5	C4	1.419(12)
Hg1	Br1	2.6033(9)		C2	C3	1.352(14)
Hg1	Br1^1	2.6034(9)		C3	C4	1.410(14)
N1	C1	1.325(11)		C4	C6	1.408(13)
N1	C5	1.371(10)		C6	C6^1	1.34(2)
C1	C2	1.407(14)				
^{1}= 3/2-X,+Y,1-Z						

Table S24. Bond Angles for [Hg(dmphen)BrI] (**5**).

Atom	Atom	Atom	Angle/˚		Atom	Atom	Atom	Angle/˚
I1	Hg1	Br1[1]	136.57(5)		N1	C1	C2	121.5(9)
I1	Hg1	Br1	0.0		N1	C1	C7	116.5(8)
N1[1]	Hg1	I1	104.57(17)		C2	C1	C7	122.0(9)
N1	Hg1	I1	110.74(16)		N1	C5	C5[1]	119.8(5)
N1	Hg1	N1[1]	70.1(3)		N1	C5	C4	120.4(8)
N11	Hg1	Br1	104.57(17)		C5[1]	C5	C4	119.8(5)
N1	Hg1	Br1[1]	104.57(17)		C3	C2	C1	119.0(10)
N11	Hg1	Br1[1]	110.75(16)		C2	C3	C4	121.3(9)
N1	Hg1	Br1	110.74(16)		C3	C4	C5	117.0(9)
Br1	Hg1	Br1[1]	136.57(5)		C6	C4	C5	118.5(9)
C1	N1	Hg1	124.1(6)		C6	C4	C3	124.5(9)
C1	N1	C5	120.8(7)		C6[1]	C6	C4	121.7(6)
C5	N1	Hg1	115.1(5)					
[1]= 3/2-X,+Y,1-Z								

Table S25. Crystal data and structure refinement for [Hg(terpy)BrI] (**6**).

Identification code	HgBrI(terpy)
Empirical formula	C15H11BrHgIN3
Formula weight	640.67
Temperature/K	298.00
Crystal system	monoclinic
Space group	I2/a
a/Å	14.2230(7)
b/Å	9.7175(3)
c/Å	11.9627(5)
α/°	90
β/°	95.902(4)
γ/°	90
Volume/Å^3	1644.61(12)
Z	4
ρcalc/g cm^{-3}	2.587
μ/mm^{-1}	13.661
F(000)	1160.0
Crystal size/mm^3	0.12 × 0.11 × 0.08
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.848 to 52.744
Index ranges	-17 ≤ h ≤ 17, -12 ≤ k ≤ 12, -14 ≤ l ≤ 13
Reflections collected	7813
Independent reflections	1684 [Rint = 0.0403, Rsigma = 0.0277]
Data/restraints/parameters	1684/0/97
Goodness-of-fit on F^2	1.050
Final R indexes [I>=2σ (I)]	R1 = 0.0303, wR2 = 0.0692
Final R indexes [all data]	R1 = 0.0365, wR2 = 0.0725
Largest diff. peak/hole / e Å^{-3}	1.16/-0.75

Table S26. Atomic Occupancy for [Hg(terpy)BrI] (**6**).

Atom	*Occupancy*
I2	0.50
Br1	0.50

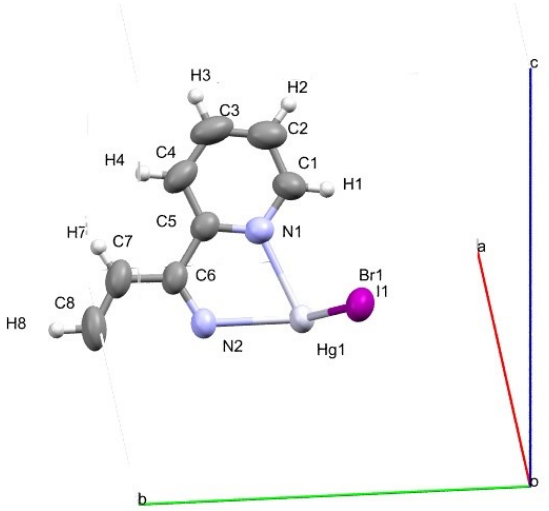

Figure S20. ORTEP plot of the asymmetric unit for [Hg(terpy)BrI] (**6**) (*a* axis =red, *b* axis=green, *c* axis= blue).

Table S27. Bond Lengths for [Hg(terpy)BrI] (**6**).

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Hg1	I1[1]	2.6583(6)		N2	C6[1]	1.331(7)
Hg1	I1	2.6583(6)		C5	C6	1.485(9)
Hg1	N1	2.430(5)		C5	C4	1.380(8)
Hg1	N1[1]	2.430(5)		C6	C7	1.391(8)
Hg1	N2	2.439(7)		C2	C1	1.373(11)
Hg1	Br1	2.6583(6)		C2	C3	1.370(12)
N1	C5	1.349(8)		C4	C3	1.384(11)
N1	C1	1.340(9)		C7	C8	1.376(9)
N2	C6	1.331(7)				
[1]= 3/2-X,+Y,-Z						

Table S28. Bond Angles for [Hg(terpy)BrI] (**6**).

Atom	Atom	Atom	Angle/˚		Atom	Atom	Atom	Angle/˚
I1	Hg1	I1[1]	122.60(3)		C1	N1	C5	120.3(6)
I1	Hg1	Br1	0.0		C6[1]	N2	Hg1	119.5(4)
N1[1]	Hg1	I1	101.87(12)		C6	N2	Hg1	119.5(4)
N1	Hg1	I1[1]	101.87(12)		C6	N2	C6[1]	121.0(8)
N1[1]	Hg1	I1[1]	99.44(12)		N1	C5	C6	116.8(5)
N1	Hg1	I1	99.43(12)		N1	C5	C4	119.7(6)
N1	Hg1	N1[1]	134.7(3)		C4	C5	C6	123.5(6)
N1	Hg1	N2	67.37(13)		N2	C6	C5	117.1(5)
N1[1]	Hg1	N2	67.36(13)		N2	C6	C7	121.1(7)
N1	Hg1	Br1	99.43(12)		C7	C6	C5	121.8(6)
N1[1]	Hg1	Br1	101.87(12)		C3	C2	C1	118.3(8)
N2	Hg1	I1[1]	118.699(14)		N1	C1	C2	122.1(7)
N2	Hg1	I1	118.699(14)		C5	C4	C3	119.8(7)
N2	Hg1	Br1	118.699(14)		C8	C7	C6	117.8(8)
Br1	Hg1	I1[1]	122.60(3)		C7[1]	C8	C7	121.2(10)
C5	N1	Hg1	119.3(4)		C2	C3	C4	119.8(7)
C1	N1	Hg1	120.4(5)					
[1]=3/2-X,+Y,-Z								

Table S29. Crystal data and structure refinement for $[Hg_2(bpym)Br_2I_2]$ (**7**).

Identification code	(HgBrI)2(bpym)
Empirical formula	C8H6Br2Hg2I2N4
Formula weight	972.97
Temperature/K	298.00
Crystal system	monoclinic

Space group	P21/c
a/Å	7.4986(9)
b/Å	13.7515(12)
c/Å	8.5348(8)
α/°	90
β/°	93.782(10)
γ/°	90
Volume/Å^3	878.17(15)
Z	2
ρcalc/g cm^{-3}	3.680
μ/mm^{-1}	25.515
F(000)	836.0
Crystal size/mm^3	0.11 × 0.08 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	7.61 to 52.74
Index ranges	-9 ≤ h ≤ 9, -17 ≤ k ≤ 17, -9 ≤ l ≤ 10
Reflections collected	5983
Independent reflections	1795 [Rint = 0.0520, Rsigma = 0.0522]
Data/restraints/parameters	1795/0/82
Goodness-of-fit on F^2	1.066
Final R indexes [I>=2σ (I)]	R1 = 0.0599, wR2 = 0.1667
Final R indexes [all data]	R1 = 0.0932, wR2 = 0.2066
Largest diff. peak/hole / e Å^{-3}	2.67/-1.64

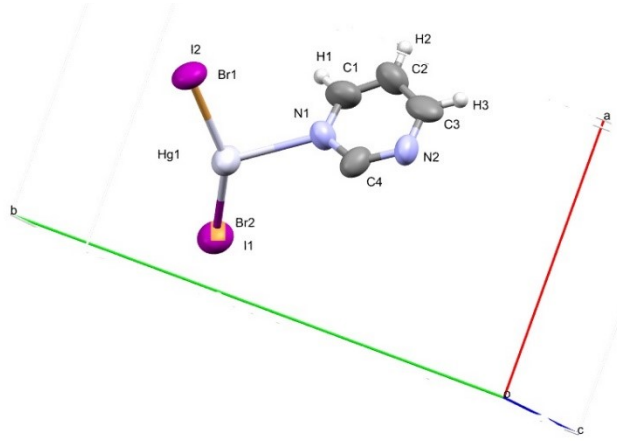

Figure S21. ORTEP plot of the asymmetric unit for [Hg(bpym)BrI]$_2$ (**7**).

Table S30. Atomic Occupancy for [Hg_2(bpym)Br_2I_2] (**7**).

Atom	*Occupancy*		Atom	*Occupancy*
I1	0.50		Br2	0.50
I2	0.50		Br1	0.50

Table S31. Bond Lengths for [Hg_2(bpym)Br_2I_2] (**7**).

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Hg1	Br1	2.6100(15)		N1	C4	1.36(2)
Hg1	I1	2.5449(18)		C1	C2	1.31(3)
Hg1	N1	2.537(13)		N2	C4	1.33(2)
Hg1	N2^1	2.595(14)		N2	C3	1.33(3)
Hg1	I2	2.6100(15)		C4	C4^1	1.49(4)
Hg1	Br2	2.5449(18)		C3	C2	1.40(3)
N1	C1	1.32(2)				
^{1} = 1-X,1-Y,1-Z						

Table S32. Bond Angles for $[Hg_2(bpym)Br_2I_2]$ (**7**).

Atom	Atom	Atom	Angle/˚		Atom	Atom	Atom	Angle/˚
I1	Hg1	Br1	150.24(6)		Br2	Hg1	I2	150.24(6)
I1	Hg1	N2[1]	90.0(3)		C1	N1	Hg1	123.7(13)
I1	Hg1	I2	150.24(6)		C1	N1	C4	116.8(16)
N1	Hg1	Br1	96.6(3)		C4	N1	Hg1	119.4(12)
N1	Hg1	I1	109.5(3)		C2	C1	N1	125(2)
N1	Hg1	N2[1]	65.6(5)		C4	N2	Hg1[1]	117.4(12)
N1	Hg1	I2	96.6(3)		C3	N2	Hg1[1]	124.9(13)
N1	Hg1	Br2	109.5(3)		C3	N2	C4	117.7(16)
N2[1]	Hg1	Br1	114.4(3)		N1	C4	C4[1]	117.6(19)
N2[1]	Hg1	I2	114.4(3)		N2	C4	N1	122.5(17)
I2	Hg1	Br1	0.0		N2	C4	C4[1]	119.9(17)
Br2	Hg1	Br1	150.24(6)		N2	C3	C2	122(2)
Br2	Hg1	I1	0.0		C1	C2	C3	115(2)
Br2	Hg1	N2[1]	90.0(3)					
[1] = 1-X,1-Y,1-Z								

Table S33. Crystal data and structure refinement for [Hg(pyNP)BrI] (**8**).

Identification code	HgBrI(pyNP)(centro)
Empirical formula	C13H9BrHgIN3
Formula weight	614.63
Temperature/K	298.00
Crystal system	Triclinic
Space group	*P*-1
a/Å	7.88287(18)
b/Å	8.4128(2)
c/Å	12.8356(4)
α/°	76.521(2)
β/°	88.160(2)
γ/°	64.590(2)
Volume/Å^3	745.46(4)
Z	2
ρcalc/g cm^{-3}	2.738
μ/mm^{-1}	15.063
F(000)	552.0
Crystal size/mm^3	0.15 × 0.12 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.388 to 52.742
Index ranges	-9 ≤ h ≤ 9, -10 ≤ k ≤ 10, -16 ≤ l ≤ 16
Reflections collected	29565
Independent reflections	3028 [Rint = 0.0583, Rsigma = 0.0254]
Data/restraints/parameters	3028/0/172
Goodness-of-fit on F^2	1.041
Final R indexes [I>=2σ (I)]	R1 = 0.0322, wR2 = 0.0756
Final R indexes [all data]	R1 = 0.0421, wR2 = 0.0807
Largest diff. peak/hole / e Å^{-3}	0.87/-0.99

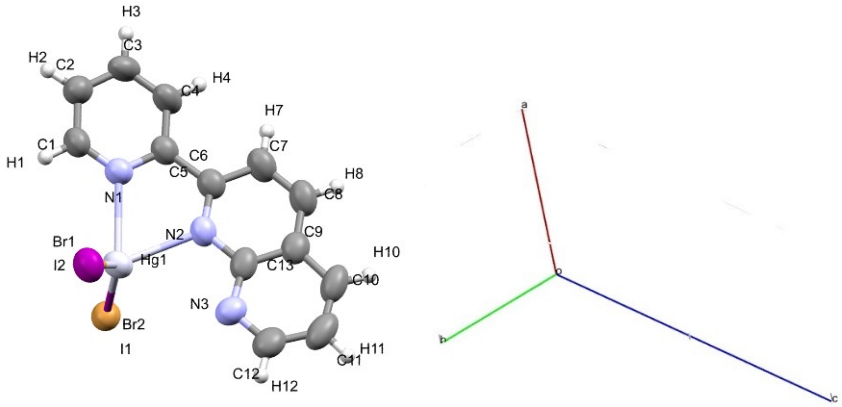

Figure C22. ORTEP plot of the asymmetric unit for [Hg(pyNP)BrI] (**8**) *a* axis =red, *b* axis=green, *c* axis= blue.

Table S34. Atomic Occupancy for [Hg(pyNP)BrI] (**8**).

Atom	*Occupancy*		Atom	*Occupancy*
I2	0.577(9)		Br2	0.599(9)
I1	0.401(9)		Br1	0.423(9)

Table S35. Bond Lengths for [Hg(pyNP)BrI] (**8**).

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Hg1	I1	2.5978(6)		C6	C5	1.494(10)
Hg1	I2	2.5743(6)		C6	C7	1.417(10)
Hg1	N2	2.377(5)		C5	C4	1.376(10)
Hg1	N1	2.447(5)		C9	C13	1.417(10)
Hg1	Br1	2.5743(6)		C9	C8	1.389(11)
Hg1	Br2	2.5978(6)		C9	C10	1.396(11)
N2	C6	1.319(8)		C1	C2	1.387(10)
N2	C13	1.361(9)		C8	C7	1.380(11)
N1	C5	1.345(8)		C3	C2	1.357(11)
N1	C1	1.322(9)		C3	C4	1.365(11)
N3	C13	1.349(9)		C12	C11	1.410(12)
N3	C12	1.301(10)		C10	C11	1.357(13)

Table S36. Bond Angles for [Hg(pyNP)BrI] (**8**).

Atom	Atom	Atom	Angle/˚		Atom	Atom	Atom	Angle/˚
I2	Hg1	I1	140.79(2)		N2	C6	C5	116.6(6)
I2	Hg1	Br2	140.79(2)		N2	C6	C7	121.7(7)
N2	Hg1	I1	102.87(12)		C7	C6	C5	121.6(6)
N2	Hg1	I2	110.98(12)		N1	C5	C6	116.5(6)
N2	Hg1	N1	67.68(19)		N1	C5	C4	120.1(7)
N2	Hg1	Br1	110.98(12)		C4	C5	C6	123.2(6)
N2	Hg1	Br2	102.87(12)		C8	C9	C13	117.9(7)
N1	Hg1	I1	109.57(13)		C8	C9	C10	125.2(8)
N1	Hg1	I2	101.34(12)		C10	C9	C13	116.9(7)
N1	Hg1	Br1	101.34(12)		N1	C1	C2	123.0(7)
N1	Hg1	Br2	109.57(13)		N2	C13	C9	120.9(7)
Br1	Hg1	I1	140.79(2)		N3	C13	N2	115.3(6)
Br1	Hg1	I2	0.0		N3	C13	C9	123.8(7)
Br1	Hg1	Br2	140.79(2)		C7	C8	C9	120.7(7)
Br2	Hg1	I1	0.0		C2	C3	C4	118.8(7)
C6	N2	Hg1	120.6(5)		C8	C7	C6	118.3(7)
C6	N2	C13	120.6(6)		C3	C2	C1	118.3(7)
C13	N2	Hg1	118.4(5)		N3	C12	C11	125.0(8)
C5	N1	Hg1	117.3(4)		C3	C4	C5	121.0(7)
C1	N1	Hg1	123.9(4)		C11	C10	C9	119.7(8)
C1	N1	C5	118.8(6)		C10	C11	C12	118.2(8)
C12	N3	C13	116.4(7)					

Table S37. Crystal data and structure refinement for [Hg(phen)Br_2] (**9**).

Empirical formula	$C_{12}H_8Br_2HgN_2$
Formula weight	540.61
Temperature/K	293(2)
Crystal system	Triclinic
Space group	*P*-1
a/Å	7.885(4)
b/Å	9.159(4)
c/Å	9.703(2)
α/°	92.36(3)
β/°	112.06(4)
γ/°	101.02(4)
Volume/Å³	632.6(5)
Z	2
ρ_{calc}/g cm^{-3}	2.838
μ/mm^{-1}	18.459
F(000)	488.0
Crystal size/mm³	0.13 × 0.08 × 0.04
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.474 to 52.744
Index ranges	-9 ≤ h ≤ 9, -11 ≤ k ≤ 9, -11 ≤ l ≤ 12
Reflections collected	4931
Independent reflections	2581 [R_{int}= 0.0805, R_{sigma}= 0.2889]
Data/restraints/parameters	2581/212/154
Goodness-of-fit on F²	1.018
Final R indexes [I>=2σ (I)]	R_1= 0.0518, wR_2= 0.1079
Final R indexes [all data]	R_1= 0.0852, wR_2= 0.1137
Largest diff. peak/hole / e Å^{-3}	4.24/-2.48

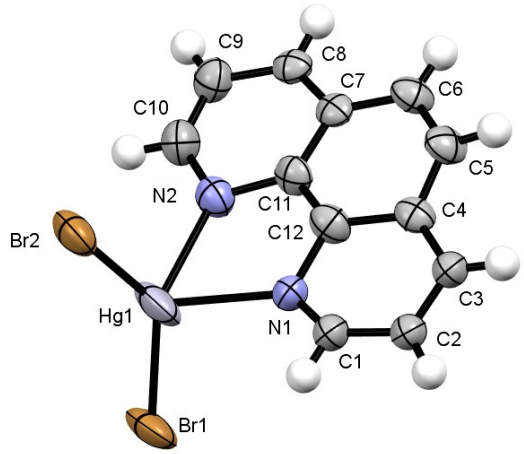

Figure S23. ORTEP plot of the asymmetric unit for [Hg(phen)Br_2] (**9**).

Table S38. Bond Lengths for [Hg(phen)Br_2] (**9**).

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Hg1	Br2	2.512(5)		C11	C12	1.32(4)
Hg1	Br1	2.477(4)		C11	C7	1.385(19)
Hg1	N2	2.40(3)		C12	C4	1.51(5)
Hg1	N1	2.33(3)		C8	C7	1.35(4)
N2	C10	1.38(4)		C8	C9	1.46(5)
N2	C11	1.46(4)		C3	C4	1.372(18)
N1	C1	1.18(3)		C3	C2	1.337(19)
N1	C12	1.43(4)		C4	C5	1.37(5)
C10	C9	1.29(5)		C7	C6	1.392(19)
C1	C2	1.39(5)		C6	C5	1.344(18)

Table S39. Bond Angles for [Hg(phen)Br_2] (**9**).

Atom	Atom	Atom	Angle/˚		Atom	Atom	Atom	Angle/˚
Br1	Hg1	Br2	137.08(17)		C7	C11	N2	124(3)
N2	Hg1	Br2	101.9(7)		N1	C12	C4	117(3)
N2	Hg1	Br1	114.2(7)		C11	C12	N1	119(4)
N1	Hg1	Br2	111.1(6)		C11	C12	C4	123(3)
N1	Hg1	Br1	102.9(6)		C7	C8	C9	128(3)
N1	Hg1	N2	69.8(10)		C2	C3	C4	118(3)
C10	N2	Hg1	130(3)		C3	C4	C12	120(3)
C10	N2	C11	115(3)		C5	C4	C12	112(3)
C11	N2	Hg1	113.8(19)		C5	C4	C3	127(3)
C1	N1	Hg1	131(3)		C11	C7	C6	123(3)
C1	N1	C12	112(3)		C8	C7	C11	112(3)
C12	N1	Hg1	117(2)		C8	C7	C6	125(3)
C9	C10	N2	126(4)		C5	C6	C7	117(3)
N1	C1	C2	137(4)		C3	C2	C1	115(3)
C12	C11	N2	118(3)		C10	C9	C8	114(4)
C12	C11	C7	118(3)		C6	C5	C4	126(3)

Table S40. Crystal data and structure refinement for [Hg(terpy)Br_2] (**10**).

Empirical formula	$C_{15}H_{11}Br_2HgN_3$
Formula weight	593.68
Temperature/K	293
Crystal system	Monoclinic
Space group	I2/a
a/Å	11.7090(6)
b/Å	9.5059(5)
c/Å	13.9720(10)
α/°	90
β/°	95.422(6)
γ/°	90
Volume/Å³	1548.19(16)
Z	4
ρ_{calc} / g cm^{-3}	2.547
μ/mm^{-1}	15.098
F(000)	1088.0
Crystal size/mm³	0.31 × 0.15 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.992 to 52.734
Index ranges	-14 ≤ h ≤ 14, -11 ≤ k ≤ 11, -17 ≤ l ≤ 17
Reflections collected	8803
Independent reflections	1587 [R_{int}= 0.0410, R_{sigma}= 0.0271]
Data/restraints/parameters	1587/0/97
Goodness-of-fit on F²	1.072
Final R indexes [I>=2σ (I)]	R_1= 0.0203, wR_2= 0.0459
Final R indexes [all data]	R_1= 0.0235, wR_2= 0.0473
Largest diff. peak/hole / e Å^{-3}	0.58/-0.84

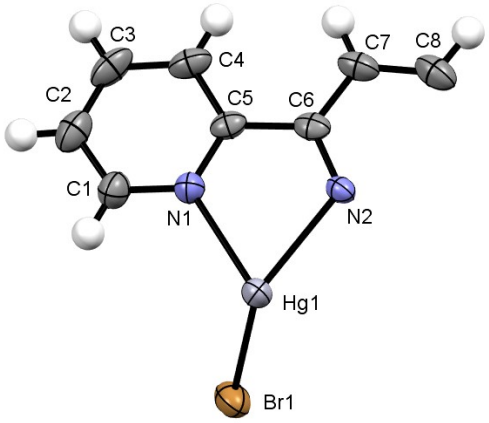

Figure S24. ORTEP plot of the asymmetric unit for [Hg(terpy)Br_2] (**10**).

Table S41. Bond Lenghts for [Hg(terpy)Br_2] (**10**).

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Hg1	Br1	2.5557(5)		N1	C1	1.334(5)
Hg1	$Br1^1$	2.5558(5)		C6	C7	1.378(5)
Hg1	N1	2.404(3)		C6	N2	1.332(4)
Hg1	$N1^1$	2.404(3)		C1	C2	1.371(6)
Hg1	N2	2.415(4)		C4	C3	1.392(6)
C5	N1	1.345(5)		C2	C3	1.362(7)
C5	C6	1.487(5)		C7	C8	1.374(5)
C5	C4	1.396(5)				
^{1}3/2-X,+Y,1-Z						

Table S42. Bond Angles for [Hg(terpy)Br_2] (**10**).

Atom	Atom	Atom	Angle/˚		Atom	Atom	Atom	Angle/˚
Br1	Hg1	$Br1^1$	122.08(2)		C1	N1	Hg1	120.9(3)
$N1^1$	Hg1	$Br1^1$	101.89(8)		C1	N1	C5	119.6(3)
$N1^1$	Hg1	Br1	99.31(7)		C7	C6	C5	122.7(3)
N1	Hg1	Br1	101.89(8)		N2	C6	C5	116.3(3)
N1	Hg1	$Br1^1$	99.31(7)		N2	C6	C7	121.0(4)
N1	Hg1	$N1^1$	135.35(15)		N1	C1	C2	122.7(4)
$N1^1$	Hg1	N2	67.67(7)		C3	C4	C5	119.1(4)
N1	Hg1	N2	67.67(8)		C3	C2	C1	118.8(4)
N2	Hg1	$Br1^1$	118.958(11)		C8	C7	C6	119.2(4)
N2	Hg1	Br1	118.959(12)		$C7^1$	C8	C7	119.2(6)
N1	C5	C6	116.8(3)		C2	C3	C4	119.5(4)
N1	C5	C4	120.2(4)		$C6^1$	N2	Hg1	119.8(2)
C4	C5	C6	123.0(4)		C6	N2	Hg1	119.8(2)
C5	N1	Hg1	119.5(2)		C6	N2	$C6^1$	120.4(5)
^{1} = 3/2-X,+Y,1-Z								