Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

β-$CsHg_2I_5$, a compound with rare [Hg_2I_5] dimers and large optical anisotropy

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Table S1. Crystal data and structure refinements of α-$CsHg_2I_5$ and β-$CsHg_2I_5$.

Empirical formula	α-$CsHg_2I_5$	β-$CsHg_2I_5$
Formula weight (Da)	1168.59	1168.59
Temperature/(K)	100	293
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/(Å)	14.0019(16)	8.8094(14)
b/(Å)	11.4545(14)	11.4931(17)
c/(Å)	19.067(3)	14.075(2)
α/°	90	90
β/°	117.911(4)	107.073(6)
γ/°	90	90
Volume/(Å^3)	2702.3(6)	1362.3(4)
Z	8	4
ρ_{calc}(g/cm^3)	5.745	5.698
μ/(mm^{-1})	36.718	36.418
F (000)	3840	1920
Completeness to θ (%)	99.7	94.7
2θ range for data collection/°	4.3 to 55.082	4.662 to 54.926
Max. and min. transmission	0.7456 and 0.4780	0.7455 and 0.4917
Index ranges	$-18 \le h \le 18$, $-14 \le k \le 14$, $-24 \le l \le 24$	$-11 \le h \le 10$, $-14 \le k \le 14$, $-17 \le l \le 18$
Reflections collected	71018	6897
Independent reflections	6199 [R_{int} = 0.0612, R_{sigma} = 0.0295]	2962 [R_{int} = 0.0646 R_{sigma} = 0.0833]
Data/restraints/parameters	6199/0/168	2962/0/91
Absorpt correction type	multi-scan	multi-scan
Goodness-of-fit on F^2	1.081	1.055
Final R indexes [$I \ge 2\sigma$ (I)][a]	R_1 = 0.0218, wR_2 = 0.0438	R_1 = 0.0620, wR_2 = 0.1299
Final R indexes [all data][a]	R_1 = 0.0250, wR_2 = 0.0449	R_1 = 0.1013, wR_2 = 0.1456
Largest diff. peak/hole/(e.Å^{-3})	1.87/-2.29	1.992/-2.414

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma wF_o^4]^{1/2}$ for $F_o^2 > 2\sigma(F_o^2)$

Table S2. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) and BVS of α-$CsHg_2I_5$.

Atoms	x	y	z	U_{eq}	Wyckoff positions	BVS[a]
Cs(1)	6479(1)	7454(1)	5317(1)	25(1)	4e	0.89
Cs(2)	8494(1)	2398(1)	-257(1)	30(1)	4e	0.88
Hg(1)	4891(7)	4131(9)	2635(5)	27(1)	4e	2.32
Hg(2)	4960(3)	4270(4)	2571(3)	21(1)	4e	
Hg(3)	7841(3)	6987(2)	3341(2)	22(1)	4e	2.33
Hg(4)	7971(7)	6771(11)	3333(3)	39(1)	4e	
Hg(5)	9201(1)	10234(1)	2731(1)	38(1)	4e	2.16
Hg(6)	7245(1)	3808(1)	1691(1)	31(1)	4e	2.17
I(1)	2775(1)	4444(1)	1496(1)	20(1)	4e	0.84
I(2)	5587(1)	4334(1)	4151(1)	19(1)	4e	1.10
I(3)	5762(1)	2436(1)	2032(1)	27(1)	4e	1.13
I(4)	5990(1)	6085(1)	2055(1)	13(1)	4e	0.94
I(5)	8606(1)	6079(1)	4803(1)	17(1)	4e	1.20
I(6)	9134(1)	7514(1)	2648(1)	25(1)	4e	0.93
I(7)	10592(1)	10556(1)	4215(1)	20(1)	4e	1.16
I(8)	7714(1)	10733(1)	1299(1)	18(1)	4e	1.13
I(9)	9016(1)	3971(1)	3064(1)	19(1)	4e	1.01
I(10)	6355(1)	4087(1)	138(1)	16(1)	4e	1.21

[a] The bond valence sum is calculated by bond-valence theory ($S_{ij} = \exp[(R_0-R)/B$, where R is an empirical constant, R_0 is the length of bond I (in angstroms), and $B = 0.37$).

Table S3. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) and BVS of β-$CsHg_2I_5$.

Atoms	x	y	z	U_{eq}	Wyckoff positions	BVS[a]
Cs(1)	10576(2)	2469(1)	8792(1)	49(1)	4e	0.84
Hg(1)	4540(2)	4750(2)	1486(2)	65(1)	4e	2.38
Hg(2)	4808(2)	4214(2)	2311(2)	48(1)	4e	
Hg(3)	6666(2)	3120(3)	5453(2)	54(1)	4e	2.28
Hg(4)	6612(2)	3806(2)	5515(2)	49(1)	4e	
I(1)	1637(1)	4389(1)	1403(1)	36(1)	4e	1.11
I(2)	7219(2)	4340(1)	1359(1)	45(1)	4e	1.07
I(3)	5574(3)	2464(1)	3620(1)	72(1)	4e	1.14
I(4)	4009(1)	3949(1)	6016(1)	32(1)	4e	0.85
I(5)	9656(1)	4004(1)	6202(1)	32(1)	4e	1.19

[a] The bond valence sum is calculated by bond-valence theory (S_{ij} = exp[(R_0-R)/B, where R is an empirical constant, R_0 is the length of bond I (in angstroms), and B = 0.37).

Table S4. Selected bond lengths of α-$CsHg_2I_5$.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cs(1)	I(2)$^{\#1}$	4.0417(7)	Hg(1)	I(2)	2.593(9)
Cs(1)	I(2)	4.0830(7)	Hg(1)	I(3)	2.809(10)
Cs(1)	I(3)$^{\#2}$	4.0929(8)	Hg(1)	I(4)	3.193(10)
Cs(1)	I(4)$^{\#3}$	4.0455(7)	Hg(2)	I(1)	2.780(4)
Cs(1)	I(5)	3.8801(6)	Hg(2)	I(2)	2.716(5)
Cs(1)	I(6)$^{\#3}$	4.2547(8)	Hg(2)	I(3)	2.795(5)
Cs(1)	I(7)$^{\#4}$	4.4039(7)	Hg(2)	I(4)	2.950(5)
Cs(1)	I(8)$^{\#3}$	4.0978(7)	Hg(3)	I(1)$^{\#2}$	3.002(2)
Cs(1)	I(10)$^{\#2}$	4.0950(7)	Hg(3)	I(4)	2.802(3)
Cs(1)	I(10)$^{\#3}$	3.9733(7)	Hg(3)	I(5)	2.684(3)
Cs(2)	I(1)$^{\#6}$	4.2291(7)	Hg(3)	I(6)	2.762(3)
Cs(2)	I(2)$^{\#7}$	4.1808(7)	Hg(4)	I(1)$^{\#2}$	3.300(14)
Cs(2)	I(5)$^{\#7}$	3.9853(7)	Hg(4)	I(4)	2.814(6)
Cs(2)	I(5)$^{\#5}$	4.0285(7)	Hg(4)	I(5)	2.635(6)
Cs(2)	I(6)$^{\#8}$	4.5089(9)	Hg(4)	I(6)	2.660(7)
Cs(2)	I(7)$^{\#8}$	4.2309(7)	Hg(5)	I(6)	3.1192(6)
Cs(2)	I(7)$^{\#5}$	4.0350(7)	Hg(5)	I(7)	2.6036(6)
Cs(2)	I(8)$^{\#9}$	4.0835(7)	Hg(5)	I(8)	2.6061(5)
Cs(2)	I(9)$^{\#7}$	3.9283(7)	Hg(6)	I(3)	2.9099(5)
Cs(2)	I(10)	3.9236(6)	Hg(6)	I(9)	2.6381(5)
Hg(1)	I(1)	2.757(9)	Hg(6)	I(10)	2.6402(6)

[1]1+X,3/2-Y,1/2+Z; [2]2-X,1/2+Y,3/2-Z; [3]+X,3/2-Y,1/2+Z; [4]1-X,1-Y,1-Z; [5]1+X, +Y,1+Z; [6]2-X,1-Y,1-Z; [7]1-X, -1/2+Y,1/2-Z, [8]+X,3/2-Y,-1/2+Z; [9]+X,-1+Y,+Z

Table S5. Selected bond lengths of β-$CsHg_2I_5$.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cs(1)	I(1)$^{\#1}$	4.075(2)	Hg(1)	I(2)	2.465(2)
Cs(1)	I(1)$^{\#2}$	4.312(2)	Hg(1)	I(3)$^{\#7}$	3.122(3)
Cs(1)	I(1)$^{\#3}$	4.151(2)	Hg(2)	I(1)	2.716(2)
Cs(1)	I(2)$^{\#4}$	4.341(2)	Hg(2)	I(2)	2.829(2)
Cs(1)	I(2)$^{\#5}$	4.184(2)	Hg(2)	I(3)	2.677(3)
Cs(1)	I(3)$^{\#4}$	4.342(3)	Hg(3)	I(3)	2.588(3)
Cs(1)	I(3)$^{\#2}$	4.481(33)	Hg(3)	I(4)	2.847(3)
Cs(1)	I(4)$^{\#2}$	4.0057(19)	Hg(3)	I(5)	2.729(2)
Cs(1)	I(5)$^{\#4}$	4.079(2)	Hg(4)	I(3)	2.984(3)
Cs(1)	I(5)$^{\#6}$	3.988(2)	Hg(4)	I(4)	2.594(3)
Cs(1)	I(5)	3.915(2)	Hg(4)	I(5)	2.580(2)
Hg(1)	I(1)	2.559(2)			

[1]1+X,3/2-Y,1/2+Z; [2]2-X,1/2+Y,3/2-Z; [3]+X,3/2-Y,1/2+Z; [4]1-X,1-Y,1-Z; [5]1+X, +Y,1+Z; [6]2-X,1-Y,1-Z; [7]1-X, -1/2+Y,1/2-Z

Table S6. Selected angles (°) of α-$CsHg_2I_5$.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
I(2)$^{\#1}$	Cs(1)	I(2)	67.716(13)	I(10)$^{\#2}$	Cs(1)	I(6)$^{\#3}$	120.244(13)
I(2)$^{\#1}$	Cs(1)	I(3)$^{\#2}$	89.996(14)	I(10)$^{\#3}$	Cs(1)	I(6)$^{\#3}$	93.602(11)
I(2)	Cs(1)	I(3)$^{\#2}$	61.134(11)	I(10)$^{\#3}$	Cs(1)	I(7)$^{\#4}$	60.017(10)
I(2)$^{\#1}$	Cs(1)	I(4)$^{\#3}$	65.742(11)	I(10)$^{\#2}$	Cs(1)	I(7)$^{\#4}$	121.633(15)
I(2)$^{\#1}$	Cs(1)	I(6)$^{\#3}$	96.917(15)	I(10)$^{\#3}$	Cs(1)	I(8)$^{\#3}$	156.876(15)
I(2)	Cs(1)	I(6)$^{\#3}$	118.111(13)	I(10)$^{\#2}$	Cs(1)	I(8)$^{\#3}$	131.574(13)
I(2)$^{\#1}$	Cs(1)	I(7)$^{\#4}$	156.884(14)	I(10)$^{\#3}$	Cs(1)	I(10)$^{\#2}$	61.782(12)
I(2)	Cs(1)	I(7)$^{\#4}$	125.566(13)	I(1)$^{\#6}$	Cs(2)	I(7)$^{\#8}$	63.287(12)
I(2)	Cs(1)	I(8)$^{\#3}$	54.921(12)	I(2)$^{\#7}$	Cs(2)	I(1)$^{\#6}$	98.849(14)
I(2)$^{\#1}$	Cs(1)	I(8)$^{\#3}$	68.423(12)	I(2)$^{\#7}$	Cs(2)	I(7)$^{\#8}$	153.550(16)
I(2)$^{\#1}$	Cs(1)	I(10)$^{\#2}$	63.174(12)	I(5)$^{\#7}$	Cs(2)	I(1)$^{\#6}$	150.600(16)
I(2)	Cs(1)	I(10)$^{\#2}$	105.399(14)	I(5)$^{\#5}$	Cs(2)	I(1)$^{\#6}$	123.960(13)
I(3)$^{\#2}$	Cs(1)	I(6)$^{\#3}$	172.091(14)	I(5)$^{\#5}$	Cs(2)	I(2)$^{\#7}$	129.470(14)
I(3)$^{\#2}$	Cs(1)	I(7)$^{\#4}$	112.856(13)	I(5)$^{\#7}$	Cs(2)	I(2)$^{\#7}$	63.493(11)
I(3)$^{\#2}$	Cs(1)	I(8)$^{\#3}$	116.037(12)	I(5)$^{\#7}$	Cs(2)	I(5)$^{\#5}$	66.198(12)
I(3)$^{\#2}$	Cs(1)	I(10)$^{\#2}$	66.422(12)	I(5)$^{\#5}$	Cs(2)	I(7)$^{\#8}$	61.110(12)
I(4)$^{\#3}$	Cs(1)	I(2)	133.022(13)	I(5)$^{\#7}$	Cs(2)	I(7)$^{\#5}$	151.932(17)
I(4)$^{\#3}$	Cs(1)	I(3)$^{\#2}$	124.159(15)	I(5)$^{\#7}$	Cs(2)	I(7)$^{\#8}$	122.533(14)
I(4)$^{\#3}$	Cs(1)	I(6)$^{\#3}$	62.690(13)	I(5)$^{\#5}$	Cs(2)	I(7)$^{\#5}$	100.082(14)
I(4)$^{\#3}$	Cs(1)	I(7)$^{\#4}$	96.804(13)	I(5)$^{\#7}$	Cs(2)	I(8)$^{\#9}$	62.145(10)
I(4)$^{\#3}$	Cs(1)	I(8)$^{\#3}$	101.026(14)	I(5)$^{\#5}$	Cs(2)	I(8)$^{\#9}$	104.723(14)
I(4)$^{\#3}$	Cs(1)	I(10)$^{\#2}$	57.737(10)	I(7)$^{\#5}$	Cs(2)	I(1)$^{\#6}$	57.451(12)
I(5)	Cs(1)	I(2)$^{\#1}$	125.587(14)	I(7)$^{\#5}$	Cs(2)	I(2)$^{\#7}$	127.073(13)
I(5)	Cs(1)	I(2)	65.307(12)	I(7)$^{\#5}$	Cs(2)	I(7)$^{\#8}$	61.644(12)
I(5)	Cs(1)	I(3)$^{\#2}$	90.421(15)	I(7)$^{\#5}$	Cs(2)	I(8)$^{\#9}$	101.079(15)
I(5)	Cs(1)	I(4)$^{\#3}$	144.992(15)	I(8)$^{\#9}$	Cs(2)	I(1)$^{\#6}$	128.313(14)
I(5)	Cs(1)	I(6)$^{\#3}$	82.441(15)	I(8)$^{\#9}$	Cs(2)	I(2)$^{\#7}$	54.305(11)
I(5)	Cs(1)	I(7)$^{\#4}$	60.576(12)	I(8)$^{\#9}$	Cs(2)	I(7)$^{\#8}$	152.050(16)
I(5)	Cs(1)	I(8)$^{\#3}$	62.880(11)	I(9)$^{\#7}$	Cs(2)	I(1)$^{\#6}$	94.372(15)
I(5)	Cs(1)	I(10)$^{\#3}$	113.014(13)	I(9)$^{\#7}$	Cs(2)	I(2)$^{\#7}$	96.858(13)
I(5)	Cs(1)	I(10)$^{\#2}$	156.101(15)	I(9)$^{\#7}$	Cs(2)	I(5)$^{\#5}$	58.124(11)
I(6)$^{\#3}$	Cs(1)	I(7)$^{\#4}$	60.555(11)	I(9)$^{\#7}$	Cs(2)	I(5)$^{\#7}$	66.692(11)
I(8)$^{\#3}$	Cs(1)	I(6)$^{\#3}$	63.567(10)	I(9)$^{\#7}$	Cs(2)	I(7)$^{\#8}$	67.209(12)
I(8)$^{\#3}$	Cs(1)	I(7)$^{\#4}$	102.411(14)	I(9)$^{\#7}$	Cs(2)	I(7)$^{\#5}$	128.449(14)
I(10)$^{\#3}$	Cs(1)	I(2)	146.709(15)	I(9)$^{\#7}$	Cs(2)	I(8)$^{\#9}$	128.370(15)
I(10)$^{\#3}$	Cs(1)	I(2)$^{\#1}$	121.286(13)	I(10)	Cs(2)	I(1)$^{\#6}$	61.750(11)
I(10)$^{\#3}$	Cs(1)	I(3)$^{\#2}$	86.031(11)	I(10)	Cs(2)	I(2)$^{\#7}$	63.367(13)
I(10)$^{\#3}$	Cs(1)	I(4)$^{\#3}$	68.927(10)	I(10)	Cs(2)	I(5)$^{\#7}$	120.713(14)

I(10)	Cs(2)	I(5)$^{\#5}$	157.970(16)	I(5)	Hg(3)	I(1)$^{\#2}$	104.50(9)
I(10)	Cs(2)	I(7)$^{\#5}$	63.791(12)	I(5)	Hg(3)	I(4)	121.47(11)
I(10)	Cs(2)	I(7)$^{\#8}$	116.744(14)	I(5)	Hg(3)	I(6)	123.33(11)
I(10)	Cs(2)	I(8)$^{\#9}$	66.596(12)	I(6)	Hg(3)	I(1)$^{\#2}$	97.42(8)
I(10)	Cs(2)	I(9)$^{\#7}$	143.450(16)	I(6)	Hg(3)	I(4)	101.90(10)
I(1)	Hg(1)	I(3)	106.3(3)	I(4)	Hg(4)	I(1)$^{\#2}$	96.7(3)
I(1)	Hg(1)	I(4)	98.7(3)	I(5)	Hg(4)	I(1)$^{\#2}$	98.0(3)
I(2)	Hg(1)	I(1)	124.8(4)	I(5)	Hg(4)	I(4)	122.8(2)
I(2)	Hg(1)	I(3)	120.6(3)	I(5)	Hg(4)	I(6)	129.7(3)
I(2)	Hg(1)	I(4)	109.4(3)	I(6)	Hg(4)	I(1)$^{\#2}$	92.7(3)
I(3)	Hg(1)	I(4)	88.3(3)	I(6)	Hg(4)	I(4)	104.2(2)
I(1)	Hg(2)	I(3)	106.03(15)	I(7)	Hg(5)	I(6)	100.710(15)
I(1)	Hg(2)	I(4)	104.15(14)	I(7)	Hg(5)	I(8)	158.745(19)
I(2)	Hg(2)	I(1)	119.27(18)	I(8)	Hg(5)	I(6)	100.097(16)
I(2)	Hg(2)	I(3)	116.83(16)	I(9)	Hg(6)	I(3)	104.727(18)
I(2)	Hg(2)	I(4)	113.33(15)	I(9)	Hg(6)	I(10)	146.669(18)
I(3)	Hg(2)	I(4)	93.64(14)	I(10)	Hg(6)	I(3)	107.713(17)
I(4)	Hg(3)	I(1)$^{\#2}$	104.10(9)				

[1]1+X,3/2-Y,1/2+Z; [2]2-X,1/2+Y,3/2-Z; [3]+X,3/2-Y,1/2+Z; [4]1-X,1-Y,1-Z; [5]1+X, +Y,1+Z; [6]2-X,1-Y,1-Z; [7]1-X, -1/2+Y,1/2-Z, [8]+X,3/2-Y,-1/2+Z; [9]+X,-1+Y,+Z

Table S7. Selected angles (°) of β-$CsHg_2I_5$.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
I(1)$^{\#1}$	Cs(1)	I(1)$^{\#3}$	64.37(4)	I(5)$^{\#6}$	Cs(1)	I(2)$^{\#4}$	60.00(3)
I(1)$^{\#3}$	Cs(1)	I(1)$^{\#2}$	155.46(5)	I(5)$^{\#6}$	Cs(1)	I(2)$^{\#5}$	154.18(5)
I(1)$^{\#1}$	Cs(1)	I(1)$^{\#2}$	126.55(4)	I(5)	Cs(1)	I(2)$^{\#4}$	64.82(4)
I(1)$^{\#3}$	Cs(1)	I(2)$^{\#5}$	65.91(4)	I(5)$^{\#4}$	Cs(1)	I(2)$^{\#4}$	101.62(4)
I(1)$^{\#3}$	Cs(1)	I(2)$^{\#4}$	151.31(5)	I(5)$^{\#6}$	Cs(1)	I(3)$^{\#4}$	88.06(4)
I(1)$^{\#2}$	Cs(1)	I(2)$^{\#4}$	53.20(3)	I(5)	Cs(1)	I(3)$^{\#4}$	90.62(4)
I(1)$^{\#1}$	Cs(1)	I(2)$^{\#5}$	55.94(4)	I(5)$^{\#4}$	Cs(1)	I(3)$^{\#4}$	66.91(4)
I(1)$^{\#1}$	Cs(1)	I(2)$^{\#4}$	99.78(4)	I(5)	Cs(1)	I(4)$^{\#2}$	144.44(5)
I(1)$^{\#3}$	Cs(1)	I(3)$^{\#4}$	90.07(4)	I(5)$^{\#6}$	Cs(1)	I(4)$^{\#2}$	67.62(3)
I(1)$^{\#1}$	Cs(1)	I(3)$^{\#4}$	61.50(3)	I(5)	Cs(1)	I(5)$^{\#6}$	117.10(4)
I(1)$^{\#2}$	Cs(1)	I(3)$^{\#4}$	114.47(4)	I(5)	Cs(1)	I(5)$^{\#4}$	157.52(6)
I(1)$^{\#1}$	Cs(1)	I(5)$^{\#4}$	102.47(5)	I(5)$^{\#6}$	Cs(1)	I(5)$^{\#4}$	63.94(4)
I(2)$^{\#5}$	Cs(1)	I(1)$^{\#2}$	100.62(5)	I(1)	Hg(1)	I(3)$^{\#7}$	98.19(9)
I(2)$^{\#5}$	Cs(1)	I(2)$^{\#4}$	126.77(4)	I(2)	Hg(1)	I(1)	158.60(12)
I(2)$^{\#5}$	Cs(1)	I(3)$^{\#4}$	117.40(4)	I(2)	Hg(1)	I(3)$^{\#7}$	101.86(9)
I(2)$^{\#4}$	Cs(1)	I(3)$^{\#4}$	61.28(4)	I(1)	Hg(2)	I(2)	125.77(9)
I(4)$^{\#2}$	Cs(1)	I(1)$^{\#3}$	66.55(3)	I(1)	Hg(2)	I(4)$^{\#1}$	112.12(8)
I(4)$^{\#2}$	Cs(1)	I(1)$^{\#1}$	130.52(5)	I(2)	Hg(2)	I(4)$^{\#1}$	101.11(6)
I(4)$^{\#2}$	Cs(1)	I(1)$^{\#2}$	96.96(4)	I(3)	Hg(2)	I(1)	113.33(9)
I(4)$^{\#2}$	Cs(1)	I(2)$^{\#4}$	127.20(4)	I(3)	Hg(2)	I(2)	106.96(8)
I(4)$^{\#2}$	Cs(1)	I(2)$^{\#5}$	98.11(4)	I(3)	Hg(2)	I(4)$^{\#1}$	91.65(7)
I(4)$^{\#2}$	Cs(1)	I(3)$^{\#4}$	124.88(5)	I(3)	Hg(3)	I(2)$^{\#4}$	96.45(9)
I(4)$^{\#2}$	Cs(1)	I(5)$^{\#4}$	58.00(3)	I(3)	Hg(3)	I(4)	106.24(9)
I(5)$^{\#6}$	Cs(1)	I(1)$^{\#1}$	149.48(5)	I(3)	Hg(3)	I(5)	121.86(11)
I(5)	Cs(1)	I(1)$^{\#2}$	61.96(4)	I(4)	Hg(3)	I(2)$^{\#4}$	103.58(9)
I(5)	Cs(1)	I(1)$^{\#1}$	64.78(4)	I(5)	Hg(3)	I(2)$^{\#4}$	99.47(8)
I(5)$^{\#6}$	Cs(1)	I(1)$^{\#3}$	121.81(4)	I(5)	Hg(3)	I(4)	123.17(10)
I(5)	Cs(1)	I(1)$^{\#3}$	121.08(5)	I(3)	Hg(4)	I(4)$^{\#1}$	82.64(7)
I(5)$^{\#4}$	Cs(1)	I(1)$^{\#2}$	125.76(4)	I(4)	Hg(4)	I(3)	102.27(8)
I(5)$^{\#4}$	Cs(1)	I(1)$^{\#3}$	62.14(4)	I(4)	Hg(4)	I(4)$^{\#1}$	97.91(8)
I(5)$^{\#6}$	Cs(1)	I(1)$^{\#2}$	61.98(3)	I(5)	Hg(4)	I(3)	113.12(11)
I(5)	Cs(1)	I(2)$^{\#5}$	61.97(4)	I(5)	Hg(4)	I(4)$^{\#1}$	97.47(8)
I(5)$^{\#4}$	Cs(1)	I(2)$^{\#5}$	127.92(5)	I(5)	Hg(4)	I(4)	142.85(12)

[1]1+X,3/2-Y,1/2+Z; [2]2-X,1/2+Y,3/2-Z; [3]+X,3/2-Y,1/2+Z; [4]1-X,1-Y,1-Z; [5]1+X, +Y,1+Z; [6]2-X,1-Y,1-Z; [7]1-X, -1/2+Y,1/2-Z

Table S8. Anisotropic displacement parameters ($Å^2 \times 10^3$) for α-$CsHg_2I_5$. The anisotropic displacement factor exponent takes the form:$-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$

Atom	U11	U22	U33	U23	U13	U12
Cs(1)	28(1)	17(1)	33(1)	-2(1)	17(1)	3(1)
Cs(2)	35(1)	17(1)	52(1)	-3(1)	31(1)	0(1)
Hg(1)	37(2)	32(2)	14(1)	3(1)	14(1)	2(1)
Hg(2)	25(1)	24(1)	13(1)	2(1)	9(1)	-1(1)
Hg(3)	23(1)	26(1)	15(1)	2(1)	7(1)	-3(1)
Hg(4)	30(2)	68(3)	16(1)	6(2)	8(1)	-14(2)
Hg(5)	32(1)	50(1)	16(1)	3(1)	-2(1)	-3(1)
Hg(6)	25(1)	46(1)	16(1)	5(1)	5(1)	-4(1)
I(1)	18(1)	16(1)	20(1)	5(1)	5(1)	-3(1)
I(2)	23(1)	15(1)	14(1)	1(1)	4(1)	-2(1)
I(3)	38(1)	11(1)	46(1)	-2(1)	33(1)	-3(1)
I(4)	14(1)	10(1)	14(1)	-1(1)	7(1)	0(1)
I(5)	19(1)	14(1)	16(1)	1(1)	7(1)	1(1)
I(6)	30(1)	16(1)	41(1)	-2(1)	26(1)	0(1)
I(7)	20(1)	19(1)	15(1)	1(1)	4(1)	-1(1)
I(8)	20(1)	17(1)	14(1)	0(1)	4(1)	3(1)
I(9)	19(1)	20(1)	16(1)	-2(1)	5(1)	6(1)
I(10)	17(1)	15(1)	15(1)	0(1)	7(1)	2(1)

Table S9. Anisotropic displacement parameters ($Å^2 \times 10^3$) for β-$CsHg_2I_5$. The anisotropic displacement factor exponent takes the form:$-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U11	U22	U33	U23	U13	U12
Cs(1)	65(1)	38(1)	42(1)	10(1)	12(1)	6(1)
Hg(1)	25(1)	84(2)	90(2)	0(1)	21(1)	3(1)
Hg(2)	24(1)	60(1)	57(1)	10(1)	5(1)	4(1)
Hg(3)	25(1)	75(2)	57(1)	-24(1)	7(1)	-8(1)
Hg(4)	23(1)	62(1)	61(1)	-9(1)	9(1)	-8(1)
I(1)	23(1)	35(1)	50(1)	-4(1)	10(1)	-3(1)
I(2)	50(1)	41(1)	50(1)	-17(1)	24(1)	-19(1)
I(3)	147(2)	25(1)	53(1)	-6(1)	43(1)	-7(1)
I(4)	32(1)	28(1)	37(1)	4(1)	12(1)	-1(1)
I(5)	25(1)	36(1)	34(1)	3(1)	5(1)	4(1)

Table S10. Atomic occupancy for α-$CsHg_2I_5$.

Atom	Occupancy	Atom	Occupancy
Hg(1)	0.5	Hg(3)	0.5
Hg(2)	0.5	Hg(4)	0.5

Table S11. Atomic occupancy for β-$CsHg_2I_5$.

Atom	Occupancy	Atom	Occupancy
Hg(1)	0.5	Hg(3)	0.5
Hg(2)	0.5	Hg(4)	0.5

Table S12. Cs, Hg and I elements in β-$CsHg_2I_5$ with an atomic ratio.

Element	Wt%	Wt% Sigma	Atomic %
Cs	12.82	0.22	13.95
Hg	31.64	0.22	22.80
I	55.54	0.23	63.26
Total	100.00		100.00

Table S13. Bulk modulus of β-$CsHg_2I_5$

Element	Voigt	Reuss	Hill
Bulk modulus	9.89422	7.99758	8.94950

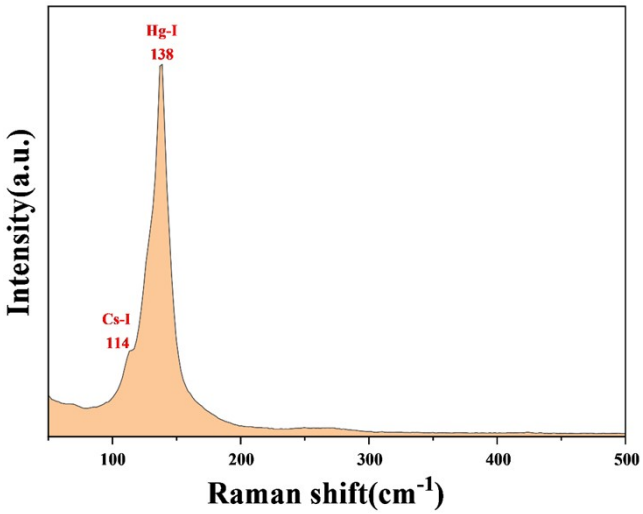

Figure S1. Raman spectrum of β-$CsHg_2I_5$.

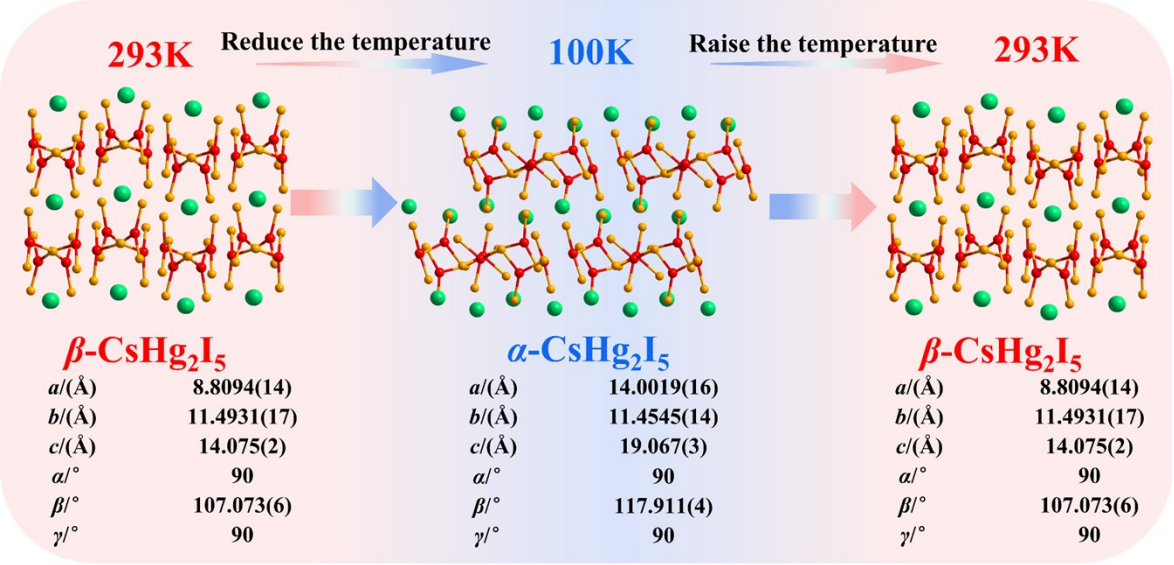

Figure S2. Reversible phase transition process.

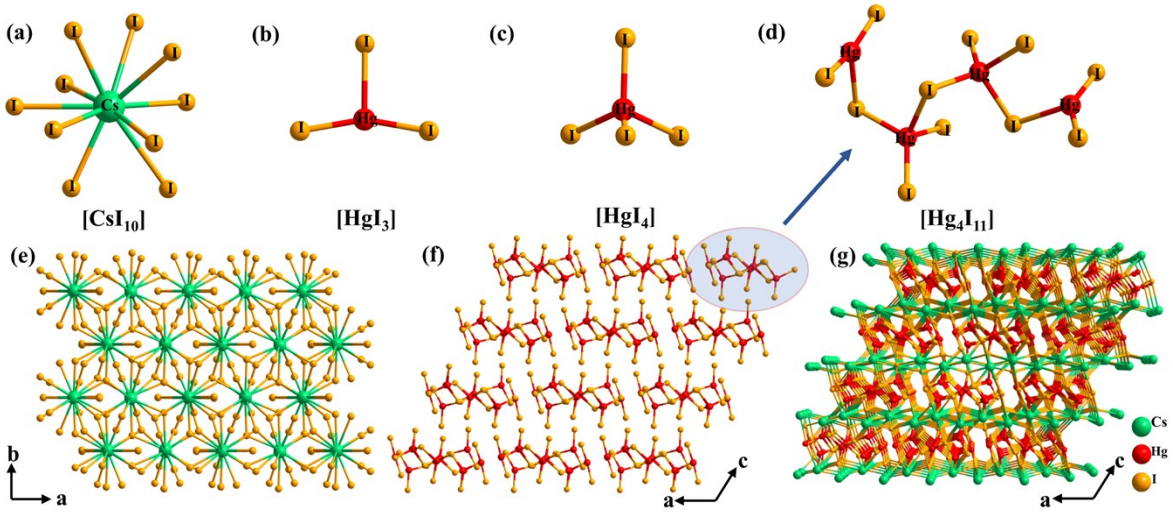

Figure S3. (a – c) Coordination modes of Cs and Hg; (d) The formed $[Hg_4I_{11}]$ multimer; (e) The structure of Cs-I framework; (f) The resulted $[Hg_4I_{11}]$ pseudo-layer; (g) The 3D crystal structure of α-$CsHg_2I_5$.

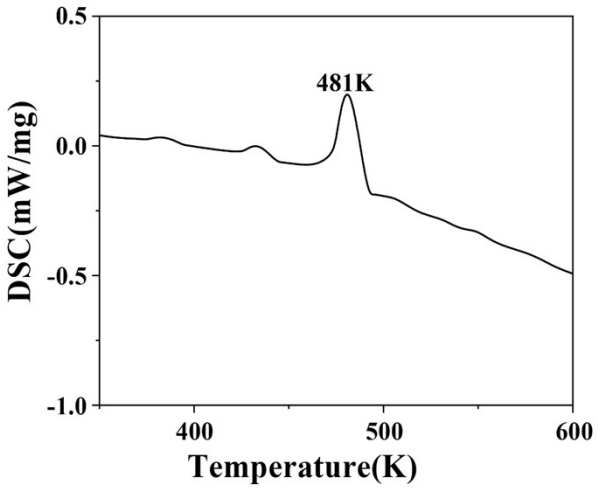

Figure S4. The DSC curve of β-$CsHg_2I_5$.

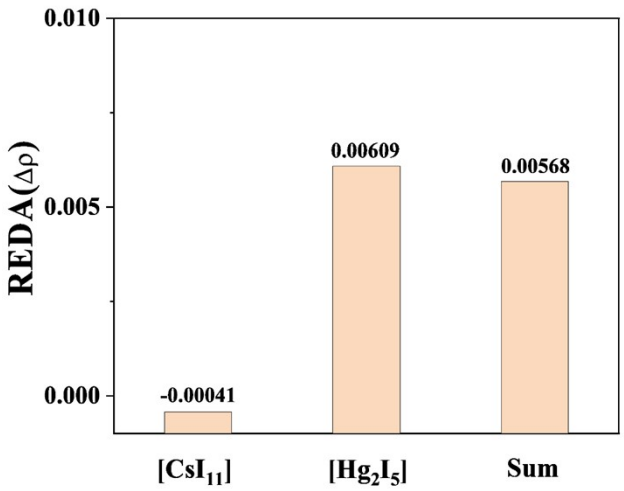

Figure S5. Bonding electron density difference ($\Delta\rho$) of each tiny units in β-$CsHg_2I_5$.

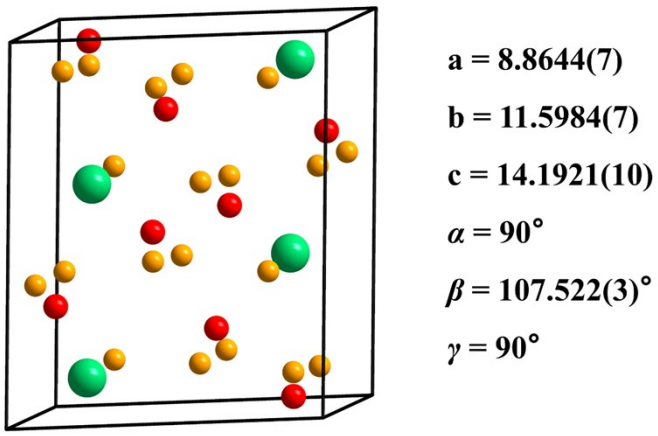

Figure S6. The optimized structure model and unit-cell parameters of β-$CsHg_2I_5$.