Crystals

Article

Synthesis, Single-Crystal X-ray Structures, Hirshfeld Surface Analysis, and Quantum Chemical Study of Novel Hexachloroplatinate, Tetrachloroaurate, Tetrachlorocuprate and Tetrabromocuprate Benzyltrimethylammonium Salts: Non-classical Synthon Preferences

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SUPPLEMENTARY MATERIALS

FIGURES

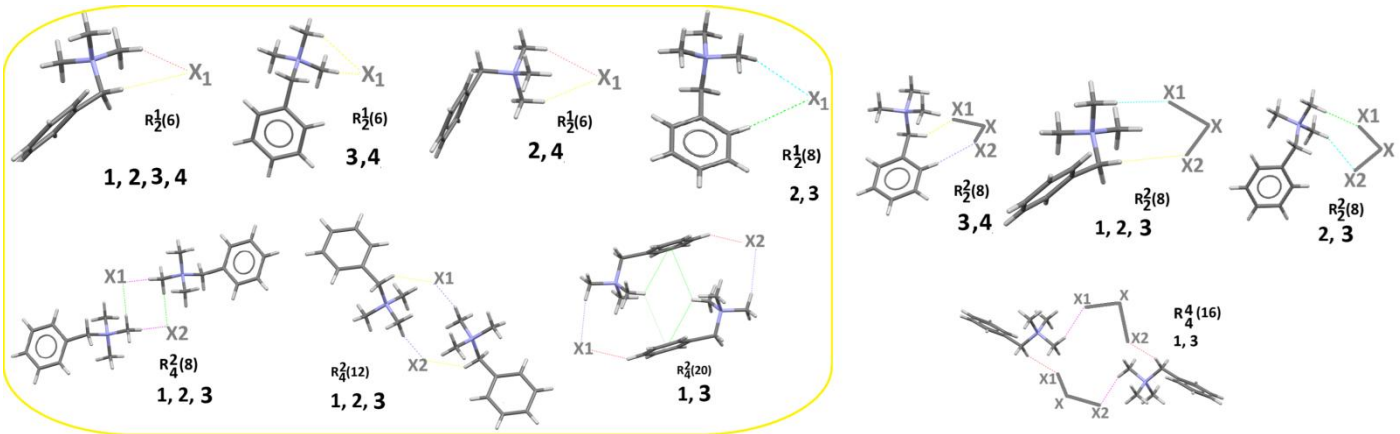


Figure S1. Equivalent/interchangeable H-bonding synthons observed in analyzed crystals **1**-**4** (X1, X2 = Cl, Br). Bifurcated synthons – in yellow frame.

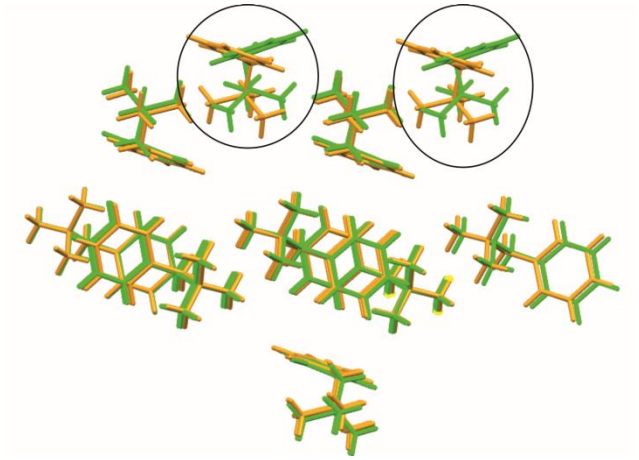


Figure S2. Crystal packing similarity between **3** (green) and **4** (orange). The black circles show the differences.

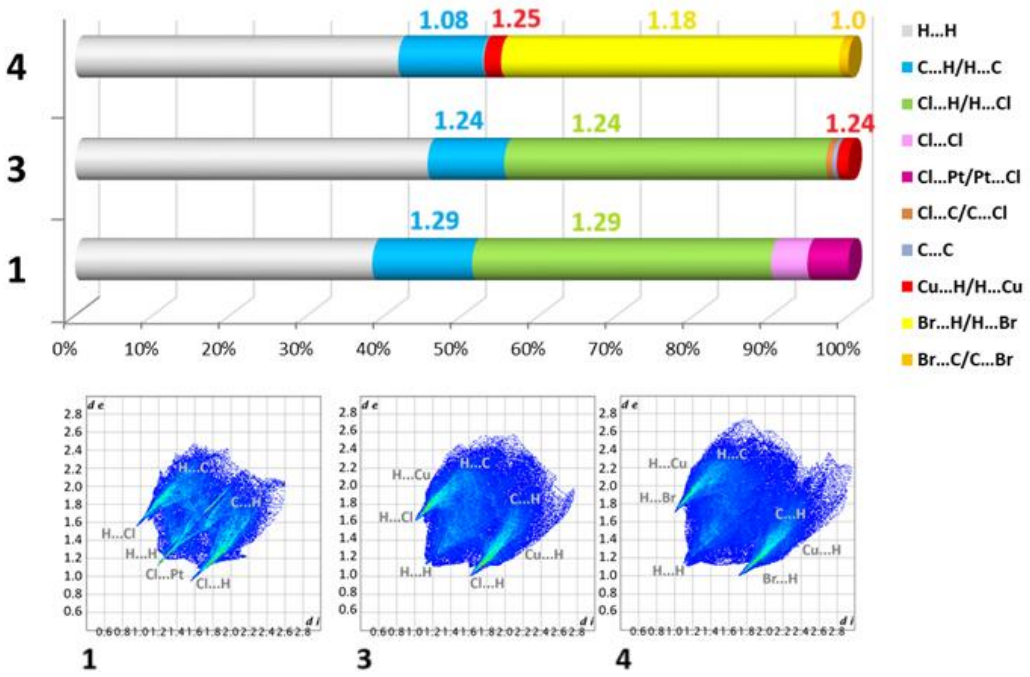
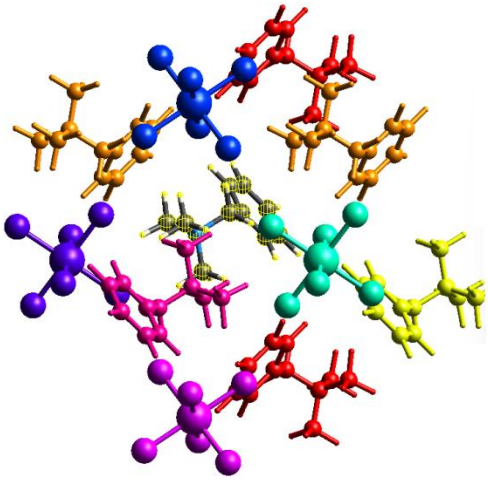


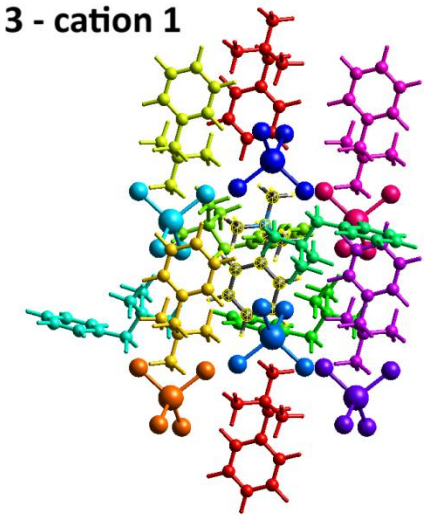
Figure S3. Upper: Percentage contributions of intercontacts in crystals **1**–**4** (above 1%) – calculations for entire salt; Below: fingerprint plots for overall interactions for **1**–**4**. The enrichment ratio values are signifies in the diagram by the same colours as corresponding interactions.



N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
2	-x, y+1/2, -z+1/2	7.02	HF/3-21G	-4.8	-4.6	-10.7	3.1	-15.1
2	x, -y+1/2, z+1/2	5.72	HF/3-21G	7.5	-14.6	-25.1	12.6	-14.3
1	-x, -y, -z	8.25	HF/3-21G	1.2	-2.6	-7.7	3.2	-4.9
1	-x, -y, -z	4.77	HF/3-21G	-54.2	-18.4	-31.9	14.7	-84.0
1	-	7.83	HF/3-21G	0.0	nan	0.0	0.0	nan
1	-	5.74	HF/3-21G	-4.0	-0.5	-0.7	0.0	-5.1
1	-	8.35	HF/3-21G	0.0	-0.1	0.0	0.0	-0.0
1	-	6.18	HF/3-21G	-4.8	-4.6	-10.7	3.1	-15.1
1	-	7.34	HF/3-21G	0.0	-0.2	0.0	0.0	-0.1
1	-	8.58	HF/3-21G	-4.8	-4.6	-10.7	3.1	-15.1
1	-x, -y, -z	8.94	HF/3-21G	17.9	-5.2	-16.2	9.9	8.4

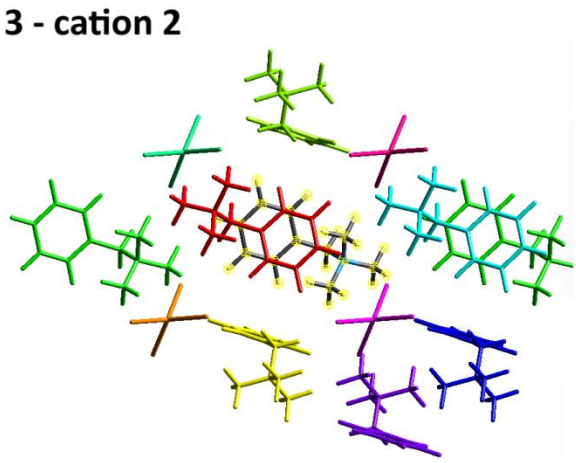
Energy Model	k_ele	k_pol	k_disp	k_rep
CE-HF ... HF/3-21G electron densities	1.019	0.651	0.901	0.811
CE-B3LYP ... B3LYP/6-31G(d,p) electron densities	1.057	0.740	0.871	0.618

Figure S4. Energy frameworks calculation for cation in **1** (R – molecular centroids distance, N – number of moieties at that distance).



N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
2	x, y, z	9.02	HF/3-21G	-11.5	-3.3	-9.5	5.5	-18.0
1	-	8.60	HF/3-21G	0.0	nan	0.0	0.0	nan
1	-x, -y, -z	5.35	HF/3-21G	0.0	-11.6	0.0	0.0	-7.5
1	-x, -y, -z	8.39	HF/3-21G	10.8	-3.7	-10.2	2.4	1.3
1	-	6.22	HF/3-21G	0.0	nan	0.0	0.0	nan
1	-	6.27	HF/3-21G	0.0	-0.2	0.0	0.0	-0.1
1	-	8.81	HF/3-21G	0.0	-0.0	0.0	0.0	-0.0
1	-	9.71	HF/3-21G	0.0	-0.0	0.0	0.0	-0.0
1	-	5.13	HF/3-21G	-11.5	-3.3	-9.5	5.5	-18.0
1	-	6.12	HF/3-21G	0.0	-0.2	0.0	0.0	-0.1
1	-	6.75	HF/3-21G	-39.5	-11.7	-24.6	13.3	-59.2
1	-	8.91	HF/3-21G	7.6	-0.3	-0.7	0.0	6.9
1	-x, -y, -z	6.59	HF/3-21G	-21.4	-3.4	-12.3	2.7	-32.9
1	-x, -y, -z	9.23	HF/3-21G	11.2	-2.8	-5.9	0.9	5.0
1	-	5.63	HF/3-21G	0.0	-0.1	0.0	0.0	-0.1

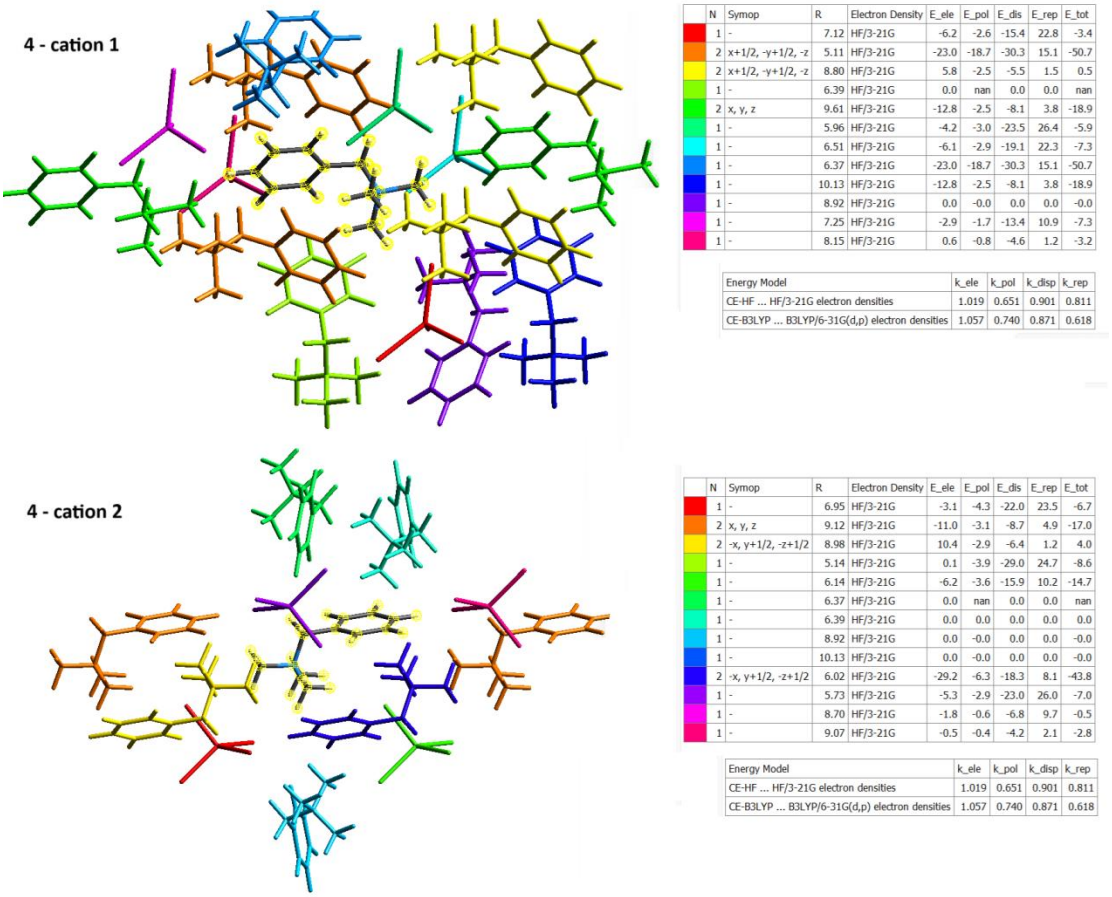
Energy Model	k_ele	k_pol	k_disp	k_rep
CE-HF ... HF/3-21G electron densities	1.019	0.651	0.901	0.811
CE-B3LYP ... B3LYP/6-31G(d,p) electron densities	1.057	0.740	0.871	0.618



N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
2	-x+1/2, y+1/2, -z+1/2	5.19	HF/3-21G	-16.7	-18.6	-30.4	16.5	-43.1
1	-	8.23	HF/3-21G	0.0	nan	0.0	0.0	nan
1	-	6.27	HF/3-21G	0.0	nan	0.0	0.0	nan
1	-	6.22	HF/3-21G	-16.7	-18.6	-30.4	16.5	-43.1
2	x, y, z	9.49	HF/3-21G	-13.1	-2.7	-9.6	5.5	-19.3
1	-	7.08	HF/3-21G	0.0	-0.2	0.0	0.0	-0.2
2	-x+1/2, y+1/2, -z+1/2	8.46	HF/3-21G	5.1	-3.1	-7.4	2.9	-1.1
1	-	6.17	HF/3-21G	-13.1	-2.7	-9.6	5.5	-19.3
1	-	9.71	HF/3-21G	-13.1	-2.7	-9.6	5.5	-19.3
1	-	8.81	HF/3-21G	0.0	-0.1	0.0	0.0	-0.0
1	-	6.82	HF/3-21G	0.0	-0.2	0.0	0.0	-0.1
1	-	5.85	HF/3-21G	-16.7	-18.6	-30.4	16.5	-43.1

Energy Model	k_ele	k_pol	k_disp	k_rep
CE-HF ... HF/3-21G electron densities	1.019	0.651	0.901	0.811
CE-B3LYP ... B3LYP/6-31G(d,p) electron densities	1.057	0.740	0.871	0.618

Figure S5. Energy frameworks calculation for cations in **3** (R – molecular centroids distance, N – number of moieties at that distance).



	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
	1	-	7.12	HF/3-21G	-6.2	-2.6	-15.4	22.8	-3.4
	2	x+1/2, -y+1/2, -z	5.11	HF/3-21G	-23.0	-18.7	-30.3	15.1	-50.7
	2	x+1/2, -y+1/2, -z	8.80	HF/3-21G	5.8	-2.5	-5.5	1.5	0.5
	1	-	6.39	HF/3-21G	0.0	nan	0.0	0.0	nan
	2	x, y, z	9.61	HF/3-21G	-12.8	-2.5	-8.1	3.8	-18.9
	1	-	5.96	HF/3-21G	-4.2	-3.0	-23.5	26.4	-5.9
	1	-	6.51	HF/3-21G	-6.1	-2.9	-19.1	22.3	-7.3
	1	-	6.37	HF/3-21G	-23.0	-18.7	-30.3	15.1	-50.7
	1	-	10.13	HF/3-21G	-12.8	-2.5	-8.1	3.8	-18.9
	1	-	8.92	HF/3-21G	0.0	-0.0	0.0	0.0	-0.0
	1	-	7.25	HF/3-21G	-2.9	-1.7	-13.4	10.9	-7.3
	1	-	8.15	HF/3-21G	0.6	-0.8	-4.6	1.2	-3.2

Energy Model	k_ele	k_pol	k_disp	k_rep
CE-HF ... HF/3-21G electron densities	1.019	0.651	0.901	0.811
CE-B3LYP ... B3LYP/6-31G(d,p) electron densities	1.057	0.740	0.871	0.618

	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
	1	-	6.95	HF/3-21G	-3.1	-4.3	-22.0	23.5	-6.7
	2	x, y, z	9.12	HF/3-21G	-11.0	-3.1	-8.7	4.9	-17.0
	2	-x, y+1/2, -z+1/2	8.98	HF/3-21G	10.4	-2.9	-6.4	1.2	4.0
	1	-	5.14	HF/3-21G	0.1	-3.9	-29.0	24.7	-8.6
	1	-	6.14	HF/3-21G	-6.2	-3.6	-15.9	10.2	-14.7
	1	-	6.37	HF/3-21G	0.0	nan	0.0	0.0	nan
	1	-	6.39	HF/3-21G	0.0	0.0	0.0	0.0	0.0
	1	-	8.92	HF/3-21G	0.0	-0.0	0.0	0.0	-0.0
	1	-	10.13	HF/3-21G	0.0	-0.0	0.0	0.0	-0.0
	2	-x, y+1/2, -z+1/2	6.02	HF/3-21G	-29.2	-6.3	-18.3	8.1	-43.8
	1	-	5.73	HF/3-21G	-5.3	-2.9	-23.0	26.0	-7.0
	1	-	8.70	HF/3-21G	-1.8	-0.6	-6.8	9.7	-0.5
	1	-	9.07	HF/3-21G	-0.5	-0.4	-4.2	2.1	-2.8

Energy Model	k_ele	k_pol	k_disp	k_rep
CE-HF ... HF/3-21G electron densities	1.019	0.651	0.901	0.811
CE-B3LYP ... B3LYP/6-31G(d,p) electron densities	1.057	0.740	0.871	0.618

Figure S6. Energy frameworks calculation for cations in **4** (R – molecular centroids distance, N – number of moieties at that distance).

TABLES

Table S1. Bond lengths for **1**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.393(5)	C10	N8	1.518(4)
C1	C6	1.395(5)	C11	N8	1.492(4)
C1	C7	1.505(4)	Cl13	Pt12	2.3181(7)
C2	C3	1.392(5)	Cl14	Pt12	2.3237(7)
C3	C4	1.383(6)	Cl15	Pt12	2.3174(7)
C4	C5	1.382(6)	Pt12	Cl13[1]	2.3181(7)
C5	C6	1.385(5)	Pt12	Cl14[1]	2.3237(7)
C7	N8	1.521(4)	Pt12	Cl15[1]	2.3173(7)
C9	N8	1.489(5)			

[1]2-X,1-Y,1-Z

Table S2. Valence angles for **1**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	C1	C6	118.7(3)	Cl13	Pt12	Cl13[1]	180.00(3)
C2	C1	C7	120.6(3)	Cl13	Pt12	Cl14[1]	90.63(3)
C6	C1	C7	120.4(3)	Cl13	Pt12	Cl14	89.37(3)
C3	C2	C1	120.6(4)	Cl13[1]	Pt12	Cl14	90.63(3)
C4	C3	C2	120.1(4)	Cl13[1]	Pt12	Cl14[1]	89.37(3)

C5	C4	C3	119.6(3)	Cl14	Pt12	Cl14[1]	180.0
C4	C5	C6	120.8(4)	Cl15	Pt12	Cl13	89.70(3)
C5	C6	C1	120.3(3)	Cl15	Pt12	Cl13[1]	90.30(3)
C1	C7	N8	115.3(2)	Cl15[1]	Pt12	Cl13	90.30(3)
C9	N8	C7	111.1(3)	Cl15[1]	Pt12	Cl13[1]	89.70(3)
C9	N8	C10	110.8(3)	Cl15[1]	Pt12	Cl14[1]	91.03(3)
C9	N8	C11	110.0(3)	Cl15	Pt12	Cl14	91.03(3)
C10	N8	C7	106.8(2)	Cl15	Pt12	Cl14[1]	88.97(3)
C11	N8	C7	111.9(3)	Cl15[1]	Pt12	Cl14	88.97(3)
C11	N8	C10	106.1(3)	Cl15[1]	Pt12	Cl15	180.0

[1]2-X,1-Y,1-Z

Table S3. Torsion angles for **1**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C1	C2	C3	C4	-1.1(5)	C3	C4	C5	C6	-0.3(5)
C1	C7	N8	C9	71.6(4)	C4	C5	C6	C1	-0.3(5)
C1	C7	N8	C10	-167.5(3)	C6	C1	C2	C3	0.5(5)
C1	C7	N8	C11	-51.8(4)	C6	C1	C7	N8	-95.1(3)
C2	C1	C6	C5	0.2(5)	C7	C1	C2	C3	174.8(3)
C2	C1	C7	N8	90.7(4)	C7	C1	C6	C5	-174.1(3)
C2	C3	C4	C5	1.0(6)					

Table S4. Bond lengths for **2**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Au12	Cl13	2.2752(5)	C1	C7	1.500(3)
Au12	Cl13[1]	2.2753(5)	C2	C3	1.389(3)
Au12	Cl14	2.2778(5)	C3	C4	1.379(4)
Au12	Cl14[1]	2.2778(5)	C4	C5	1.380(4)
Au15	Cl16	2.2761(5)	C5	C6	1.379(3)
Au15	Cl16[2]	2.2761(5)	C7	N8	1.532(2)
Au15	Cl17[2]	2.2815(6)	C9	N8	1.508(3)
Au15	Cl17	2.2816(6)	C10	N8	1.499(3)
C1	C2	1.392(3)	C11	N8	1.497(3)
C1	C6	1.388(3)			

[1]1-X,+Y,3/2-Z; [2]1-X,2-Y,1-Z

Table S5. Valence angles for **2**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Cl13	Au12	Cl13[1]	179.10(3)	C6	C1	C7	121.0(2)
Cl13	Au12	Cl14[1]	89.81(2)	C3	C2	C1	119.9(2)
Cl13[1]	Au12	Cl14[1]	90.21(2)	C4	C3	C2	120.4(2)
Cl13	Au12	Cl14	90.21(2)	C3	C4	C5	119.8(2)
Cl13[1]	Au12	Cl14	89.81(2)	C6	C5	C4	120.1(2)
Cl14[1]	Au12	Cl14	177.94(3)	C5	C6	C1	120.6(2)
Cl16[2]	Au15	Cl16	180.0	C1	C7	N8	114.69(17)
Cl16[2]	Au15	Cl17[2]	88.99(2)	C9	N8	C7	110.59(16)
Cl16	Au15	Cl17[2]	91.00(2)	C10	N8	C7	107.60(16)

Cl16[2]	Au15	Cl17	91.00(2)	C10	N8	C9	109.31(16)
Cl16	Au15	Cl17	89.00(2)	C11	N8	C7	112.07(16)
Cl17[2]	Au15	Cl17	180.0	C11	N8	C9	108.21(17)
C2	C1	C7	119.8(2)	C11	N8	C10	109.02(17)
C6	C1	C2	119.1(2)				

[1]1-X,+Y,3/2-Z; [2]1-X,2-Y,1-Z

Table S6. Torsion angles for **2**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C1	C2	C3	C4	-1.0(4)	C3	C4	C5	C6	0.2(4)
C1	C7	N8	C9	63.0(2)	C4	C5	C6	C1	0.4(4)
C1	C7	N8	C10	-177.69(19)	C6	C1	C2	C3	1.6(3)
C1	C7	N8	C11	-57.8(2)	C6	C1	C7	N8	-93.2(2)
C2	C1	C6	C5	-1.3(3)	C7	C1	C2	C3	178.6(2)
C2	C1	C7	N8	89.8(2)	C7	C1	C6	C5	-178.3(2)
C2	C3	C4	C5	0.1(4)					

Table S7. Bond lengths for **3**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1A	C2A	1.396(4)	C1B	C7B	1.502(4)
C1A	C6A	1.394(4)	C2B	C3B	1.389(4)
C1A	C7A	1.503(4)	C3B	C4B	1.381(5)
C2A	C3A	1.386(5)	C4B	C5B	1.386(5)
C3A	C4A	1.382(5)	C5B	C6B	1.390(4)
C4A	C5A	1.384(5)	C7B	N8B	1.530(4)
C5A	C6A	1.388(4)	C9B	N8B	1.499(4)
C7A	N8A	1.527(4)	C10B	N8B	1.498(4)
C9A	N8A	1.494(4)	C11B	N8B	1.500(4)
C10A	N8A	1.502(4)	Cl13	Cu12	2.2643(8)
C11A	N8A	1.500(4)	Cl14	Cu12	2.2290(8)
C1B	C2B	1.392(4)	Cl15	Cu12	2.2650(8)
C1B	C6B	1.384(4)	Cl16	Cu12	2.2546(8)

Table S8. Valence angles for **3**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2A	C1A	C7A	119.9(3)	C3B	C2B	C1B	120.3(3)
C6A	C1A	C2A	119.4(3)	C4B	C3B	C2B	120.2(3)
C6A	C1A	C7A	120.7(3)	C3B	C4B	C5B	119.9(3)
C3A	C2A	C1A	120.1(3)	C4B	C5B	C6B	119.8(3)
C4A	C3A	C2A	120.1(3)	C1B	C6B	C5B	120.7(3)
C3A	C4A	C5A	120.2(3)	C1B	C7B	N8B	113.3(2)
C4A	C5A	C6A	120.1(3)	C9B	N8B	C7B	111.5(2)
C5A	C6A	C1A	120.0(3)	C9B	N8B	C11B	109.2(2)
C1A	C7A	N8A	114.0(2)	C10B	N8B	C7B	107.6(2)
C9A	N8A	C7A	111.2(2)	C10B	N8B	C9B	108.5(2)
C9A	N8A	C10A	109.0(2)	C10B	N8B	C11B	108.9(2)
C9A	N8A	C11A	109.5(3)	C11B	N8B	C7B	111.0(2)

C10A	N8A	C7A	107.2(2)	Cl13	Cu12	Cl15	99.32(3)
C11A	N8A	C7A	111.2(2)	Cl14	Cu12	Cl13	99.24(3)
C11A	N8A	C10A	108.6(2)	Cl14	Cu12	Cl15	131.39(3)
C2B	C1B	C7B	120.5(3)	Cl14	Cu12	Cl16	99.99(3)
C6B	C1B	C2B	119.1(3)	Cl16	Cu12	Cl13	133.43(3)
C6B	C1B	C7B	120.4(3)	Cl16	Cu12	Cl15	98.91(3)

Table S9. Torsion angles for **3**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C1A	C2A	C3A	C4A	-0.5(5)	C1B	C2B	C3B	C4B	0.5(5)
C1A	C7A	N8A	C9A	62.5(3)	C1B	C7B	N8B	C9B	63.7(3)
C1A	C7A	N8A	C10A	-178.4(3)	C1B	C7B	N8B	C10B	-177.4(2)
C1A	C7A	N8A	C11A	-59.7(3)	C1B	C7B	N8B	C11B	-58.4(3)
C2A	C1A	C6A	C5A	-1.5(4)	C2B	C1B	C6B	C5B	-2.4(5)
C2A	C1A	C7A	N8A	92.0(3)	C2B	C1B	C7B	N8B	92.2(3)
C2A	C3A	C4A	C5A	0.0(5)	C2B	C3B	C4B	C5B	-1.6(5)
C3A	C4A	C5A	C6A	-0.2(5)	C3B	C4B	C5B	C6B	0.7(5)
C4A	C5A	C6A	C1A	1.0(5)	C4B	C5B	C6B	C1B	1.3(5)
C6A	C1A	C2A	C3A	1.3(5)	C6B	C1B	C2B	C3B	1.5(5)
C6A	C1A	C7A	N8A	-90.3(3)	C6B	C1B	C7B	N8B	-86.4(3)
C7A	C1A	C2A	C3A	179.0(3)	C7B	C1B	C2B	C3B	-177.1(3)
C7A	C1A	C6A	C5A	-179.2(3)	C7B	C1B	C6B	C5B	176.2(3)

Table S10. Bond lengths for **4**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br13	Cu12	2.3875(7)	C10A	N8A	1.507(6)
Br14	Cu12	2.4070(7)	C11A	N8A	1.504(5)
Br15	Cu12	2.3844(7)	C1B	C2B	1.393(7)
Br16	Cu12	2.3585(7)	C1B	C6B	1.383(6)
C1A	C2A	1.391(6)	C1B	C7B	1.511(6)
C1A	C6A	1.391(7)	C2B	C3B	1.370(7)
C1A	C7A	1.497(6)	C3B	C4B	1.379(7)
C2A	C3A	1.388(7)	C4B	C5B	1.379(7)
C3A	C4A	1.379(8)	C5B	C6B	1.402(6)
C4A	C5A	1.388(7)	C7B	N8B	1.532(5)
C5A	C6A	1.377(7)	C9B	N8B	1.493(6)
C7A	N8A	1.528(5)	C10B	N8B	1.507(6)
C9A	N8A	1.499(5)	C11B	N8B	1.495(6)

Table S11. Valence angles for **4**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Br13	Cu12	Br14	131.97(3)	C10A	N8A	C7A	107.7(3)
Br15	Cu12	Br13	99.38(3)	C11A	N8A	C7A	110.7(3)
Br15	Cu12	Br14	99.50(3)	C11A	N8A	C10A	109.3(3)
Br16	Cu12	Br13	100.20(3)	C2B	C1B	C7B	119.5(4)
Br16	Cu12	Br14	99.77(3)	C6B	C1B	C2B	119.9(4)
Br16	Cu12	Br15	131.02(3)	C6B	C1B	C7B	120.6(4)

C2A	C1A	C6A	118.6(4)	C3B	C2B	C1B	120.2(4)
C2A	C1A	C7A	120.7(4)	C2B	C3B	C4B	120.7(5)
C6A	C1A	C7A	120.6(4)	C3B	C4B	C5B	119.5(4)
C3A	C2A	C1A	120.5(5)	C4B	C5B	C6B	120.7(4)
C4A	C3A	C2A	120.2(4)	C1B	C6B	C5B	119.0(4)
C3A	C4A	C5A	119.5(5)	C1B	C7B	N8B	113.9(3)
C6A	C5A	C4A	120.4(5)	C9B	N8B	C7B	111.3(3)
C5A	C6A	C1A	120.7(4)	C9B	N8B	C10B	108.6(4)
C1A	C7A	N8A	113.9(3)	C9B	N8B	C11B	109.7(4)
C9A	N8A	C7A	111.5(3)	C10B	N8B	C7B	107.4(3)
C9A	N8A	C10A	108.4(3)	C11B	N8B	C7B	111.2(3)
C9A	N8A	C11A	109.2(3)	C11B	N8B	C10B	108.4(4)

Table S12. Torsion angles for **4**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C1A	C2A	C3A	C4A	0.8(7)	C1B	C2B	C3B	C4B	0.6(7)
C1A	C7A	N8A	C9A	65.6(4)	C1B	C7B	N8B	C9B	68.9(5)
C1A	C7A	N8A	C10A	-175.6(3)	C1B	C7B	N8B	C10B	-172.3(4)
C1A	C7A	N8A	C11A	-56.2(5)	C1B	C7B	N8B	C11B	-53.8(5)
C2A	C1A	C6A	C5A	-3.4(7)	C2B	C1B	C6B	C5B	-1.4(6)
C2A	C1A	C7A	N8A	94.2(5)	C2B	C1B	C7B	N8B	91.6(5)
C2A	C3A	C4A	C5A	-1.9(7)	C2B	C3B	C4B	C5B	-1.5(7)
C3A	C4A	C5A	C6A	0.4(7)	C3B	C4B	C5B	C6B	0.9(6)
C4A	C5A	C6A	C1A	2.3(7)	C4B	C5B	C6B	C1B	0.5(6)
C6A	C1A	C2A	C3A	1.9(7)	C6B	C1B	C2B	C3B	0.8(6)
C6A	C1A	C7A	N8A	-86.0(5)	C6B	C1B	C7B	N8B	-89.5(5)
C7A	C1A	C2A	C3A	-178.3(4)	C7B	C1B	C2B	C3B	179.8(4)
C7A	C1A	C6A	C5A	176.8(4)	C7B	C1B	C6B	C5B	179.7(4)

Table S13. Π-based intercontacts in **1**-**4** (<4 Å).

Cg-Cg / Y-X···Cg	Cg···Cg / X···Cg	P	Q	R	S	apha / X-perp	beta	gamma	CgI-perp / Y-X…Cg	CgJ-perp / Y…Cg
2										
Cg1-Cg1 [i]	3.9323(15)	-0.4632	-0.2894	-0.8377	-18.7009	0.03(12)	21.7	21.7	3.6525(10)	3.6525(10)
Symmetry code: (i) *3/2-x, 3/2-y, 2-z*										
4										
Cu12-Br16···Cg2 [i]	3.9085(18)	-0.0832	0.3236	0.9425	4.8313	3.672	-	20.05	152.45(4)	6.0979(18)
Symmetry code: (i) *3/2-x, 1-y, -1/2+z*										

Table S14. Aromatic Analyser results.

Centroid-Centroid distance	Relative orientation	AA score
1		
5.32	74.01	5.8
2		
3.93	0	8.9

4.54	33.64	5.3
3		
4.63	32.46	4.4
5.42	78.95	4.3
5.17	88.12	4.3
4		
5.35	88.41	4.5
5.53	82.39	4.2
4.75	31.08	4.1

Table S15. Library of H-bonding synthons (< 20-membered) in **1**-**4**.

1	
D(2)	$_{*(arom)}$C4-H4···Cl13
	$_{*(arom)}$C5-H5···Cl15
	$_{*(CH2)}$C7-H7A···Cl15
	$_{*(CH2)}$C7-H7B···Cl13
	$_{*(CH2)}$C7-H7B···Cl15
	$_{*(CH3)}$C9-H9C···Cl14
	$_{*(CH3)}$C10-H10A···Cl13
	$_{*(CH3)}$C10-H10B···Cl14
	$_{*(CH3)}$C10-H10B···Cl13
	$_{*(CH3)}$C11-H11B···Cl15
$D^2_2(5)$	$_{[(arom)}$C4-H4···Cl13$_{]2}$
	$_{*[(arom)}$C5-H5···Cl15$_{]2}$
	$_{*([(CH2)}$C7-H7A···Cl15$_{]2}$
	$_{*[(CH2)}$C7-H7B···Cl13$_{]2}$
	$_{*[(CH2)}$C7-H7B···Cl15$_{]2}$
	$_{*[(CH3)}$C9-H9C···Cl14$_{]2}$
	$_{*[(CH3)}$C10-H10A···Cl13$_{]2}$
	$_{*[(CH3)}$C10-H10B···Cl14$_{]2}$
	$_{*[(CH3)}$C10-H10B···Cl13$_{]2}$
	$_{*[(CH3)}$C11-H11B···Cl15$_{]2}$
Level 2	
$R^1_2(6)$	$_{(CH2)}$C7-H7B···Cl13 & $_{(CH3)}$C10-H10A···Cl13
$R^2_1(4)$	$_{*(CH2)}$C7-H7B···Cl15 & $_{(CH2)}$C7-H7B···Cl13
	$_{*(CH3)}$C10-H10B···Cl14 & $_{(CH3)}$C10-H10B···Cl13
$R^2_2(7)$	$_{(arom)}$C4-H4···Cl13 & $_{(arom)}$C5-H5···Cl15
$R^2_2(8)$	$_{*(CH3)}$C9-H9C···Cl14 & $_{(CH2)}$C7-H7B···Cl13
	$_{*(CH2)}$C7-H7B···Cl15 & $_{(CH3)}$C9-H9C···Cl14
	$_{*(CH2)}$C7-H7B···Cl15 & $_{(CH3)}$C10-H10A···Cl13
	$_{*(CH3)}$C9-H9C···Cl14 & $_{(CH3)}$C10-H10A···Cl13
	$_{*(CH3)}$C10-H10B···Cl14 & $_{(CH3)}$C11-H11B···Cl15
	$_{*(CH3)}$C10-H10B···Cl13 & $_{(CH3)}$C11-H11B···Cl15
$R^2_4(8)$	$_{*(CH3)}$C10-H10A···Cl13 & $_{(CH3)}$C10-H10B···Cl13
$R^2_4(12)$	$_{*[(CH3)}$C10-H10B···Cl13$_{]2}$ & $_{[(arom)}$C7-H7B···Cl13$_{]2}$
	$_{*(CH3)}$C9-H9C···Cl14 & $_{(CH3)}$C10-H10B···Cl14$_{]2}$
$R^2_4(18)$	$_{[(arom)}$C5-H5···Cl15$_{]2}$ & $_{[(CH3)}$C11-H11B···Cl15$_{]2}$
$R^4_4(12)$	$_{(CH3)}$C10-H10A···Cl13 & $_{(CH3)}$C10-H10B···Cl14$_{]2}$
$R^4_4(14)$	$_{(arom)}$C5-H5···Cl15$_{]2}$ & $_{(CH2)}$C7-H7B···Cl13$_{]2}$
$R^4_4(16)$	$_{*[(CH2)}$C7-H7B···Cl13$_{]2}$ & $_{(CH3)}$C10-H10B···Cl14$_{]2}$
	$_{*(CH2)}$C7-H7B···Cl13$_{]2}$ & $_{(CH3)}$C11-H11B···Cl15$_{]2}$
	$_{*(CH2)}$C7-H7B···Cl15$_{]2}$ & $_{(CH3)}$C10-H10B···Cl14$_{]2}$
	$_{*(CH2)}$C7-H7B···Cl15$_{]2}$ & $_{(CH3)}$C10-H10B···Cl13$_{]2}$
	$_{*(CH2)}$C7-H7B···Cl15$_{]2}$ & $_{(CH3)}$C11-H11B···Cl15$_{]2}$
	$_{*(CH3)}$C10-H10B···Cl13$_{]2}$ & $_{(CH3)}$C9-H9C···Cl14$_{]2}$
	$_{*(CH3)}$C9-H9C···Cl14$_{]2}$ & $_{(CH3)}$C11-H11B···Cl15$_{]2}$

	*(CH3)C10-H10A···Cl13]2 & (CH3)C11-H11B···Cl15]2
R^4_4(18)	[(arom)C5-H5…Cl15]2 & [(CH2)C7-H7A…Cl15]2
R^4_4(20)	[(CH2)C7-H7B…Cl13]2 & [(arom)C4-H4…Cl13]2
	*[(CH2)C7-H7B…Cl13]2 & [(arom)C4-H4…Cl13]2
	*[(arom)C4-H4…Cl13]2 & [(CH3)C10-H10B…Cl13]2
C^1_2(4)	(CH2)C7-H7A…Cl15 & (CH2)C7-H7B…Cl13
C^1_2(6)	(CH2)C7-H7A…Cl15 & (CH3)C11-H11B…Cl15
	*(CH2)C7-H7B…Cl15 & (CH3)C11-H11B…Cl15
C^1_2(7)	(arom)C5-H5…Cl15 & (CH2)C7-H7A…Cl15
C^1_2(8)	(CH2)C7-H7B…Cl13 & (arom)C4-H4…Cl13
C^1_2(10)	(arom)C4-H4…Cl13 & (CH3)C10-H10A…Cl13
C^2_2(6)	(CH2)C7-H7B…Cl13 & (CH2)C7-H7A…Cl15
	*(CH2)C7-H7A…Cl15 & (CH2)C7-H7B…Cl13
	*(CH3)C10-H10A…Cl13 & (CH3)C10-H10B…Cl14
	*(CH3)C10-H10A…Cl13 & (CH3)C10-H10B…Cl13
C^2_2(8)	(CH2)C7-H7A…Cl15 & (CH3)C9-H9C…Cl14
	*(CH2)C7-H7A…Cl15 & (CH3)C10-H10A…Cl13
	*(CH2)C7-H7A…Cl15 & (CH3)C10-H10B…Cl14
	*(CH2)C7-H7A…Cl15 & (CH3)C10-H10B…Cl13
	*(CH2)C7-H7A…Cl15 & (CH3)C11-H11B…Cl15
	(CH2)C7-H7B…Cl13 & (CH3)C10-H10B…Cl14
	*[(CH2)C7-H7B…Cl13 & (CH3)C10-H10B…Cl14
	*(CH2)C7-H7B…Cl13 & (CH3)C11-H11B…Cl15
	*(CH2)C7-H7B…Cl15 & (CH3)C10-H10B…Cl14
	*(CH2)C7-H7B…Cl15 & (CH3)C10-H10B…Cl13
	*(CH3)C9-H9C…Cl14 & (CH3)C10-H10B…Cl14
	*(CH3)C9-H9C…Cl14 & (CH3)C10-H10B…Cl13
	*(CH3)C9-H9C…Cl14 & (CH3)C11-H11B…Cl15
	*(CH3)C10-H10A…Cl13 & (CH3)C11-H11B…Cl15
C^2_2(9)	(arom)C5-H5…Cl15 & (CH2)C7-H7A…Cl15
C^2_2(11)	(arom)C5-H5…Cl15 & (CH2)C7-H7B…Cl13
	*(arom)C5-H5…Cl15 & (CH3)C10-H10A…Cl13
	*(arom)C5-H5…Cl15 & (CH3)C10-H10B…Cl14
	*(arom)C5-H5…Cl15 & (CH3)C10-H10B…Cl13
	*(arom)C5-H5…Cl15 & (CH3)C11-H11B…Cl15
C^2_2(12)	(arom)C4-H4…Cl13 & (CH3)C9-H9C…Cl14
	*(arom)C4-H4…Cl13 & (CH3)C10-H10B…Cl14
	*(arom)C4-H4…Cl13 & (CH3)C10-H10B…Cl13
	*(arom)C4-H4…Cl13 & (CH3)C11-H11B…Cl15
C^2_2(10)	(arom)C4-H4…Cl13 & (CH2)C7-H7A…Cl15
	*[(CH2)C7-H7B…Cl13]2 & [(arom)C4-H4…Cl13
C^4_4(12)	[CH2)C7-H7A…Cl15]2 & [(CH2)C7-H7B…Cl15]2
	*(CH3)C10-H10A…Cl13 & (CH3)C10-H10B…Cl14
	*(CH3)C10-H10A…Cl13 & (CH3)C10-H10B…Cl13
C^4_4(16)	(CH3)C9-H9C…Cl14]2 & (CH2)C7-H7A…Cl15]2
	*[(CH2)C7-H7A…Cl15]2 & (CH3)C10-H10A…Cl13]2
	*[(CH2)C7-H7A…Cl15]2 & (CH3)C10-H10B…Cl14]2
	*(CH2)C7-H7A…Cl15]2 & (CH3)C10-H10B…Cl13]2
	*(CH2)C7-H7A…Cl15]2 & (CH3)C11-H11B…Cl15]2
	*[(CH2)C7-H7B…Cl13]2 & (CH3)C10-H10B…Cl14]2
	*[(CH2)C7-H7B…Cl13]2 & (CH3)C10-H10B…Cl13]2
	*(CH2)C7-H7B…Cl13]2 & (CH3)C11-H11B…Cl15]2
	*(CH2)C7-H7B…Cl15]2 & (CH3)C10-H10B…Cl14]2
	*(CH2)C7-H7B…Cl15 & (CH3)C10-H10B…Cl13]2
	*(CH2)C7-H7B…Cl15]2 & (CH3)C11-H11B…Cl15]2
	*(CH3)C9-H9C…Cl14 & (CH3)C10-H10B…Cl14]2
	*(CH3)C9-H9C…Cl14 & (CH3)C10-H10B…Cl13]2
	*(CH3)C9-H9C…Cl14]2 & (CH3)C11-H11B…Cl15]2
	*(CH3)C10-H10A…Cl13 & (CH3)C11-H11B…Cl15]2
C^4_4(18)	*[(arom)C5-H5…Cl15]2 & (CH2)C7-H7A…Cl15]2
	*[(arom)C5-H5…Cl15]2 & [(CH2)C7-H7B…Cl13]2
C^4_4(20)	[(arom)C4-H4…Cl13]2 & [(CH2)C7-H7B…Cl13]2
	*[(CH2)C7-H7B…Cl13]2 & [(arom)C4-H4…Cl13]2

2

D(2)	(arom)C3-H3…Cl13
	*(arom)C6-H6…Cl16
	*(CH2)C7-H7A…Cl16
	*(CH3)C9-H9B…Cl13
	*(CH3)C9-H9C…Cl14
	*(CH3)C9-H9C…Cl16
	*(CH3)C10-H10B…Cl14
	*(CH3)C10-H10C…Cl17
	*(CH3)C11-H11A…Cl16
D22(5)	(arom)C3-H3…Cl13]2
	*(arom)C6-H6…Cl16]2
	*(CH2)C7-H7A…Cl16]2
	*(CH3)C9-H9B…Cl14]2
	*(CH3)C9-H9C…Cl14]2
	*(CH3)C9-H9C…Cl16]2
	*(CH3)C10-H10B…Cl14]2
	*(CH3)C10-H10C…Cl17]2
	*(CH3)C11-H11A…Cl16]2
Level 2	
R12(6)	(CH2)C7-H7A…Cl16 & (CH3)C11-H11A…Cl16
	* C9-H9B…Cl14 & C10-H10B…Cl14
R12(8)	* C9-H9C…Cl16 & (arom)C6-H6…Cl16
R22(8)	(CH2)C7-H7A…Cl16 & C10-H10C…Cl17
	C10-H10C…Cl17 & (CH3)C11-H11A…Cl16
R24(8)	(CH3)C9-H9C…Cl14]2 & [C9-H9B…Cl14]2
R24(12)	C10-H10B…Cl14]2 & C9-H9C…Cl14]2
D21(3)	C9-H9C…Cl14 & C9-H9C…Cl16
D22(5)	C9-H9C…Cl16 & C9-H9B…Cl14
	* C10-H10B…Cl14 & C10-H10C…Cl17
D22(7)	(CH2)C7-H7A…Cl16 & C9-H9B…Cl14
	*(CH2)C7-H7A…Cl16 & C9-H9C…Cl14
	*(CH2)C7-H7A…Cl16 & C10-H10B…Cl14
	C9-H9B…Cl14 & C10-H10C…Cl17
	* C9-H9B…Cl14 & (CH3)C11-H11A…Cl16
	C10-H10C…Cl17 & C9-H9C…Cl14
	C9-H9C…Cl14 & (CH3)C11-H11A…Cl16
	(CH2)C9-H9C…Cl16 & C10-H10B…Cl14
	C10-H10B…Cl14 & (CH3)C11-H11A…Cl16
D22(8)	(arom)C3-H3…Cl13 & (arom)C6-H6…Cl16
	*(arom)C3-H3…Cl13 & (CH2)C7-H7A…Cl16
D22(9)	(arom)C6-H6…Cl16 & C9-H9B…Cl14
	*(arom)C6-H6…Cl16 & *(CH3)C10-H10B…Cl14
D22(10)	*(arom)C3-H3…Cl13]2 & C9-H9C…Cl16
	*(arom)C3-H3…Cl13 & C10-H10C…Cl17
	*(arom)C3-H3…Cl13 & (CH3)C11-H11A…Cl16
D32(6)	C9-H9C…Cl14]2 & C9-H9C…Cl16
D33(8)	C9-H9B…Cl14]2 & C9-H9C…Cl16
	*C10-H10B…Cl14 & C10-H10C…Cl17
D33(10)	(CH2)C7-H7A…Cl16 & C9-H9B…Cl14
	*(CH2)C7-H7A…Cl16 & C9-H9C…Cl14
	*(CH2)C7-H7A…Cl16 & C10-H10B…Cl14
	C9-H9B…Cl14]2 & C10-H10C…Cl17
	* C9-H9B…Cl14 & C9-H9B…Cl14
	*(CH3)C11-H11A…Cl16 & C9-H9B…Cl14
	C10-H10C…Cl17 & C9-H9C…Cl14]2
	C9-H9C…Cl14 & (CH3)C11-H11A…Cl16
	(CH2)C9-H9C…Cl16 & C10-H10B…Cl14
	C10-H10B…Cl14 & (CH3)C11-H11A…Cl16
D33(11)	(arom)C3-H3…Cl13]2 & (arom)C6-H6…Cl16]2
	*(arom)C3-H3…Cl13]2 & (CH2)C7-H7A…Cl16]2
D33(12)	(arom)C6-H6…Cl16 & C9-H9B…Cl14B

	*(arom)C6-H6…Cl16 & *(CH3)C10-H10B…Cl14
D33(13)	*(arom)C3-H3…Cl13]2 & C9-H9C…Cl16]2
	*(arom)C3-H3…Cl13]2 & *(CH3)C10-H10C…Cl17
	*(arom)C3-H3…Cl13 & (CH3)C11-H11A…Cl16]2
C12(6)	(arom)C6-H6…Cl16 & (CH2)C7-H7A…Cl16
	*(CH2)C7-H7A…Cl16 & C9-H9C…Cl16
	C9-H9C…Cl16 & (CH3)C11-H11A…Cl16
C12(8)	(arom)C6-H6…Cl16 & (CH3)C11-H11A…Cl16
C22(6)	C9-H9B…Cl14 & C9-H9C…Cl14
C22(8)	(arom)C6-H6…Cl16 & (CH2)C7-H7A…Cl16
	*(CH2)C7-H7A…Cl16 & C9-H9C…Cl16
	C9-H9C…Cl16 & (CH3)C10-H10C…Cl17
	(CH3) C9-H9C…Cl16 & (CH3)C11-H11A…Cl16
C22(10)	(arom)C6-H6…Cl16 & (CH3)C10-H10C…Cl17
	(arom)C6-H6…Cl16 & (CH3)C11-H11A…Cl16
C22(11)	*(arom)C3-H3…Cl13 & C9-H9B…Cl14
	*(arom)C3-H3…Cl13 & C9-H9C…Cl14
	*(arom)C3-H3…Cl13 & C10-H10B…Cl14
C42(8)	(CH3)C9-H9C…Cl14]2 & C9-H9C…Cl16
	*(CH3)C9-H9C…Cl14]2 & C10-H10C…Cl14
C44(12)	(CH3)C9-H9C…Cl14]2 & [C9-H9B…Cl14]2
	*C9-H9B…Cl14]2 & C9-H9C…Cl16]2
	C10-H10B…Cl14 & C10-H10C…Cl17
C44(16)	(arom)C6-H6…Cl16 & (CH2)C7-H7A…Cl16
	(CH2)C7-H7A…Cl16 & C9-H9B…Cl14
	*(CH2)C7-H7A…Cl16 & C9-H9C…Cl14
	(CH2)C7-H7A…Cl16 & C9-H9C…Cl16
	*(CH2)C7-H7A…Cl16 & C10-H10B…Cl14
	C9-H9B…Cl14]2 & C10-H10C…Cl17]2
	*(CH3)C11-H11A…Cl16 & C9-H9B…Cl14]2
	C10-H10B…Cl14]2 & C9-H9C…Cl14]2
	C10-H10C…Cl17 & C9-H9C…Cl14]2
	C9-H9C…Cl14 & (CH3)C11-H11A…Cl16
	(CH2)C9-H9C…Cl16 & C10-H10B…Cl14
	C9-H9C…Cl16 & (CH3)C10-H10C…Cl17
	(CH3) C9-H9C…Cl16 & (CH3)C11-H11A…Cl16
	C10-H10B…Cl14 & (CH3)C11-H11A…Cl16
C44(18)	arom)C3-H3…Cl13]2 & (arom)C6-H6…Cl16]2
	*(arom)C3-H3…Cl13]2 & (CH2)C7-H7A…Cl16]2
C44(20)	(arom)C6-H6…Cl16 & C9-H9B…Cl14]2
	* C9-H9C…Cl14 & (arom)C6-H6…Cl16]2
	*(arom)C6-H6…Cl16 & *(CH3)C10-H10B…Cl14
	(arom)C6-H6…Cl16 & (CH3)C10-H10C…Cl17]2
	(arom)C6-H6…Cl16 & (CH3)C11-H11A…Cl16

3

D(2)	(arom)C2A-H2A…Cl16
	*C4A-H4A…Cl15
	*C6A-H6A…Cl14
	*(CH2)C7A-H7AB…Cl13
	*(CH3)C9A-H9AA…Cl14
	*(CH3)C9A-H9AB…Cl13
	*(CH3)C9A-H9AC…Cl14
	*(CH3)C10-H10A…Cl13
	*(CH3)C10-H10B…Cl13
	*(CH3)C11A-H11B…Cl15
	*(CH3)C11A-H11C…Cl15
	*(arom)C3B-H3B…Cl13
	*(CH2)C7B-H7BA…Cl16
	*(CH2)C7B-H7BB…Cl13
	*(CH3)C9B-H9BB…Cl16
	*(CH3)C9B-H9BC…Cl13

Level 2	
R12(6)	(arom)C7A-H7AB…Cl13 & (CH3)C10-H10A…Cl13
	*(CH3)C9A-H9AB…Cl13 & (CH3)C10A-H10B…Cl13
	arom)C7B-H7BA…Cl16 & (CH3)C10B-H10F…Cl16
R12(8)	(arom) C6A-H6A…Cl14 & (CH3)C9A-H9AC…Cl14
R22(8)	*(arom)C6A-H6A…Cl14 & (arom)C7A-H7AB…Cl13
	(arom)C7A-H7AB…Cl13 & (CH3)C9A-H9AC…Cl14
	*(CH3)C9A-H9AB…Cl13 & (CH3)C11A-H11C…Cl15
	*(CH3)C9A-H9AC…Cl14 & (CH3)C10A-H10A…Cl13
	(CH3)C10A-H10B…Cl13 & (CH3)C11-H11C…Cl15
R22(10)	(arom) C2A-H2A…Cl16 & (CH3)C11-H11B…Cl15
	(arom) C6A-H6A…Cl14 & (CH3)C10-H10A…Cl13
R24(8)	(CH3)C9A-H9AA…Cl14]2 & (CH3)C9A-H9AC…Cl14
	*(CH3)C10-H10A…Cl13 & (CH3)C10A-H10B…Cl13
	*(CH3)C11-H11C…Cl15 & (CH3)C11A-H11B…Cl15
R24(12)	(arom)C7A-H7AB…Cl13 & (CH3)C9A-H9AB…Cl13
	(arom)C7A-H7AB…Cl13 & (CH3)C10-H10B…Cl13
R24(16)	*(arom)C6A-H6A…Cl14 & (CH3)C9A-H9AA…Cl14
R24(20)	(arom)C4A-H4A…Cl15 & (CH3)C11-H11C…Cl15
R44(12)	(CH3)C9A-H9AB…Cl13]2 & (CH3)C9A-H9AC…Cl14]
R44(16)	(arom)C7A-H7AB…Cl13 & (CH3)C9A-H9AA…Cl14
	*(CH3)C11-H11C…Cl15 & (arom)C7A-H7AB…Cl13
R44(20)	(CH3)C9A-H9AA…Cl14]2 & (arom)C2A-H2A…Cl16]2
	*(arom)C2A-H2A…Cl16 & (CH3)C10-H10B…Cl13
	*(arom)C2A-H2A…Cl16 & (CH3)C11-H11C…Cl15
	*(arom)C6A-H6A…Cl14 & (CH3)C9A-H9AB…Cl13
C12(10)	(arom)C4A-H4A…Cl15 & (CH3)C11A-H11B…Cl15
C22(8)	(arom)C4A-H4A…Cl15 & (arom)C2A-H2A…Cl16
	*(arom)C6A-H6A…Cl14 & (arom)C2A-H2A…Cl16
	(arom)C7A-H7AB…Cl13 & (arom)C2A-H2A…Cl16
	(arom)C4A-H4A…Cl15 & (arom)C6A-H6A…Cl14
C22(10)	(arom)C2A-H2A…Cl16 & (CH3)C9A-H9AC…Cl14
	(arom)C7A-H7AB…Cl13 & (arom)C4A-H4A…Cl15
	*(arom)C6A-H6A…Cl14 & (CH3)C11-H11BB…Cl15
C22(12)	(arom)C4A-H4A…Cl15 & (CH3)C9A-H9AC---Cl14
D12(3)	(arom)C2A-H2A…Cl16 & (arom)C7B-H7BA…Cl16
	*(arom)C2A-H2A…Cl16 & (CH3)C9B-H9BB…Cl16
	*(arom)C2A-H2A…Cl16 & (CH3)C10B-H10E…Cl16
D22(5)	(arom)C2A-H2A…Cl16 & (arom)C3B-H3B…Cl13
	*(arom)C2A-H2A…Cl16 & (arom)C7B-H7BB…Cl13
	*(arom)C2A-H2A…Cl16 & (arom)C9B-H9BC…Cl13
	(arom)C4A-H4A…Cl15 & (arom)c3b-h3b…cL13
	*(arom)C6A-H6A…Cl14 & (arom)C3B-H3B…Cl13
4	
D(2)	$_{(CH2)}$C7A-H7AA…Br13
Level 2	
$R^1_2(6)$	$_{(CH2)}$C7A-H7AA…Br13 & $_{(CH3)}$C11-H11A…Br13
$R^2_2(8)$	$_{(arom)}$C7B-H7B…Br14 & $_{(arom)}$C6B-H6B…Br16
$C^1_2(4)$	$_{(CH3)}$C11A-H11A…Br13 & $_{(CH3)}$C11A-H11B…Br13
$C^1_2(6)$	$_{(CH2)}$C7A-H7AA…Br13 & $_{(CH3)}$C9A-H9AA…Br13
	$^{*}{}_{(CH2)}$C7A-H7AA…Br13 & $_{(CH3)}$C11-H11A…Br13
	$_{(arom)}$C7B-H7B…Br14 & $_{(CH3)}$C11B-H11D…Br14
$C^1_2(8)$	$_{(arom)}$C6B-H6B…Br16 & $_{(CH3)}$C9B-H9BB…Br16
$C^2_2(8)$	$_{(CH2)}$C7A-H7AA…Br13 & $_{(CH3)}$C10A-H10A…Br13
	$^{*}{}_{(CH3)}$C10A-H10B…Br13 & $_{(CH3)}$C9A-H9AB…Br14
	$_{(arom)}$C7B-H7BB…Br14 & $_{(CH3)}$C9B-H9BB…Br16
$C^2_2(10)$	$_{(CH3)}$C9B-H9BB…Br16 & $_{(arom)}$C2B-H2B…Br13
	$_{(arom)}$C6B-H6B…Br16 & $_{(CH3)}$C11B-H11D…Br14
$C^2_2(12)$	$_{(arom)}$C4B-H4B…Br15 & $_{(CH3)}$C9B-H9BB…Br16
$D^1_2(3)$	$_{(CH2)}$C7A-H7AA…Br13 & $_{(arom)}$C2B-H2B…Br13
$D^2_2(5)$	$_{(CH2)}$C7A-H7AA…Br13 & $_{(arom)}$C4B-H4B…Br15

*(CH2)C7A-H7AA…Br13 & (arom)C7B-H7B…Br14

Table S16. Enrichment ratio for cation in **1** (>0.9).

	Contacts (%)		
atoms	H	C	Cl
H	55.2		
C	18.8		
Cl	26		
Surface (%)	77.6	9.4	13
	Random contacts (%)		
H	60.22		
C	14.59		
Cl	20.18		
Enrichment ratio E_{XY}			
H	0.92		
C	**1.29**		
Cl	**1.29**		

Table S17. Enrichment ratio for cation no. 1 in **3** (>0.9).

	Contacts (%)			
Atoms	H	C	Cl	Cu
H	61.7			
C	10.9			
Cl	25			
Cu	1.5			
Surface (%)	80.4	5.45	12.5	0.75
		Random contacts (%)		
H	64.64			
C	8.76			
Cl	20.1			
Cu	1.21			
Enrichment ratio E_{XY}				
H	0.95			
C	**1.24**			
Cl	**1.24**			
Cu	**1.24**			

Table S18. Enrichment ratio for cation no. 2 in **3** (>0.9).

	Contacts (%)		
atoms	H	C	Cl
H	57.9		
C	20.7	1.3	
Cl	19.4		
Surface (%)	77.95	11.65	9.7
		Random contacts (%)	
H	60.76		

C	18.16	1.35	
Cl	15.12		
H	0.95		
C	**1.14**	0.96	
Cl	**1.28**		

Table S19. Enrichment ratio for cation no. 1 in **4** (>0.9).

	Contacts (%)		
atoms	H	C	Br
H	56.9		
C	21.9		
Br	20.1		
Surface (%)	77.9	10.95	10.05
		Random contacts (%)	
H	60.68		
C	17.06		
Br	15.66		
Enrichment ratio E_{XY}			
H	0.94		
C	**1.28**		
Br	**1.28**		

Table S20. Enrichment ratio for cation no. 2 in **4** (>0.9).

	Contacts (%)			
atoms	H	C	Cu	Br
H	61.6			
C	9.5			
Cu	1.7			
Br	25.6	1.5		
Surface (%)	80	5.5	0.85	13.55
		Random contacts (%)		
H	64			
C	8.8			
Cu	1.36			
Br	21.68	1.49		
Enrichment ratio E_{XY}				
H	0.96			
C	**1.08**			
Cu	**1.25**			
Br	**1.18**	**1.0**		

Table S21. The total interaction energies fof **1**-**4** via energy framework calculations.

	Eele	Edis	Erep	Etot
1	-46	-113.7	49.7	-145.3
3 cation 1	-54.3	-72.7	30.3	-122.7

3 cation 2	-84.3	-127.4	68.9	-188.5
4 cation 1	-84.6	-158.3	122.9	165.8
4 cation 2	-46.6	-134.3	110.4	-97.1