Electronic Supplementary Information for Dalton Transactions

Supporting Information

Halide binding in laterally non-symmetric aza-oxa cryptands through N/O/C─H···halide interactions with characterization of small water clusters

Madhab C. Das, Sujit K. Ghosh and Parimal K. Bharadwaj*

Department of Chemistry, Indian Institute of Technology Kanpur 208016, India
Email: pkb@iitk.ac.in

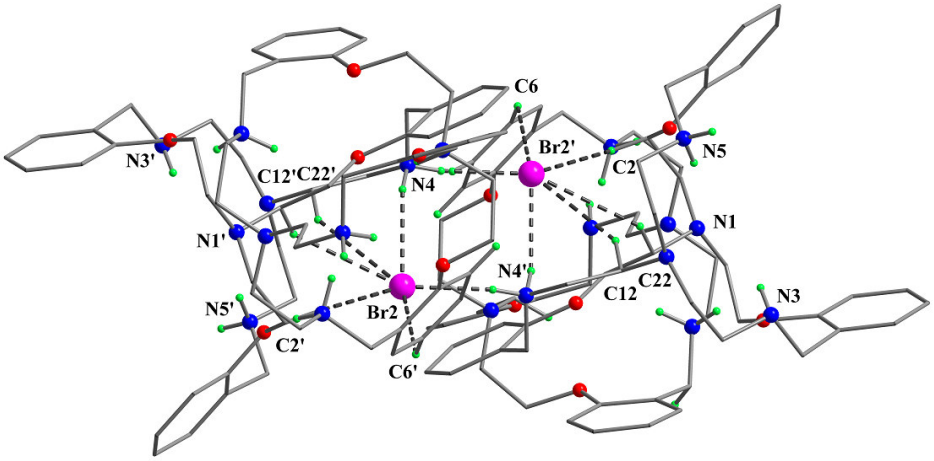

Figure S1: A diagram representing the sandwiched dimeric bromide unit within the opposite-side directed arms of two cryptand ($\mathbf{L_o}$) moieties along with its immediate H-bonding coordination environment in complex **2**.

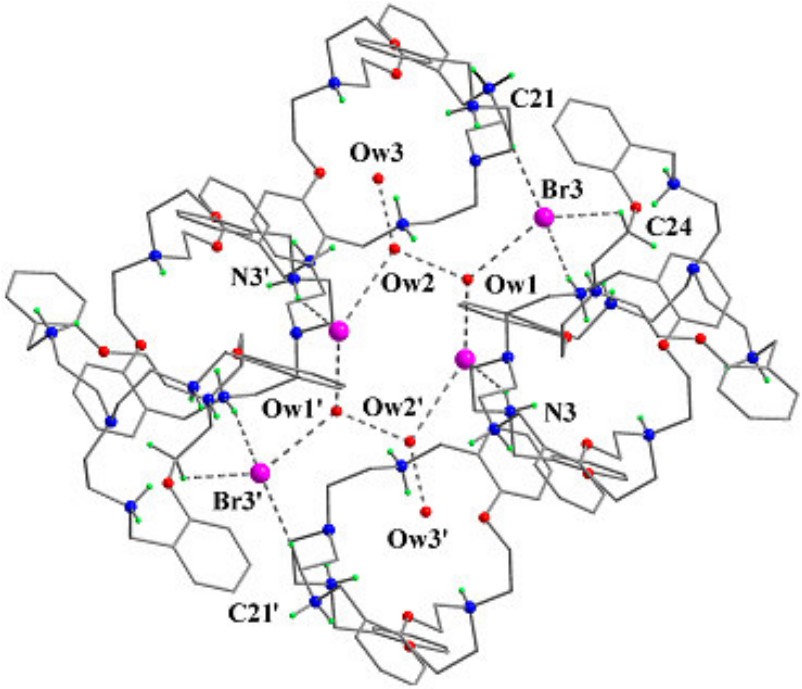

Figure S2: A diamond representation of the discrete water trimer forming a planar water-bromide hexameric unit along with its immediate H-bonding interactions in complex **2**. Only the H atoms involved in H-bonding interactions are shown for clarity).

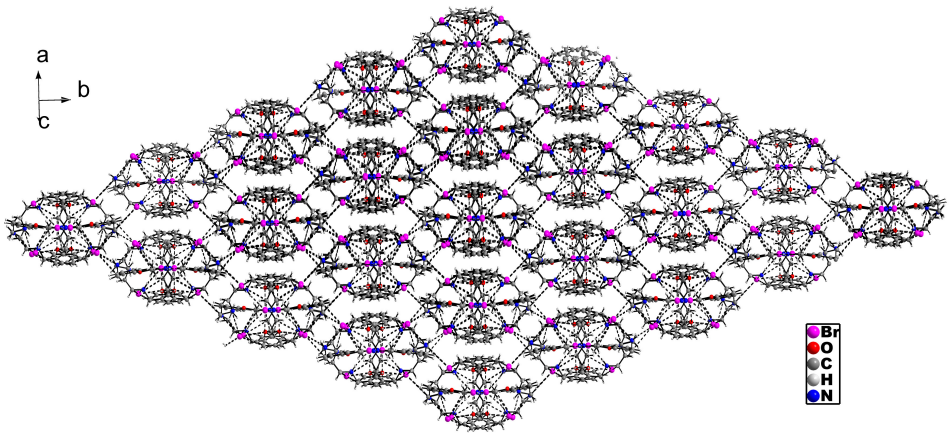

Figure S3: A packing diagram of complex **2** depicting three-dimensional H-bonded supramolecular array involving the protonated cryptand moieties, the bromide anions, and trimeric water clusters, along with several of their molecular interactions.

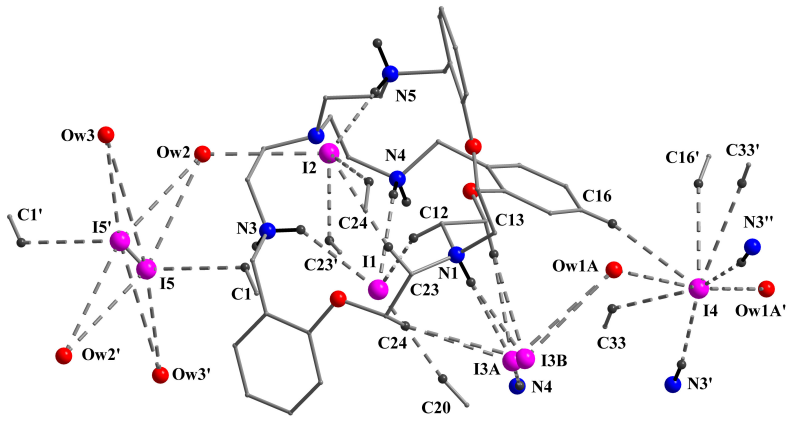

Figure S4: The H-bonding coordination environment of all of the iodides present in complex **3**. H atoms of $\mathbf{L_o}$ that are not involved in H-bonding interactions are omitted for clarity; all the disordered positions of I5 and I3 are shown.

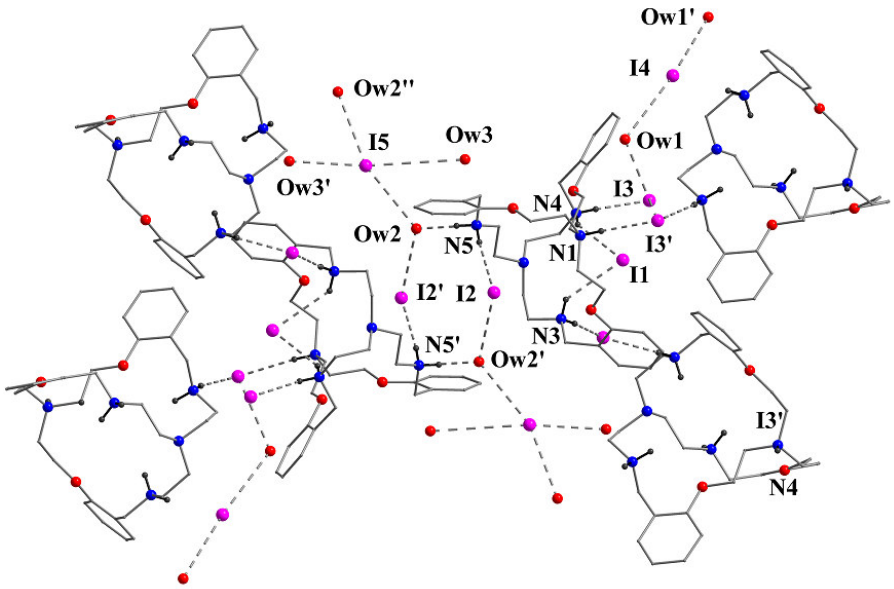

Figure S5: Representation of the puckered-boat hexagon with its H-bonding coordination environment with the surrounding cryptand moieties in complex **3** (only the H atoms involved in H-bonding interactions are shown for clarity).

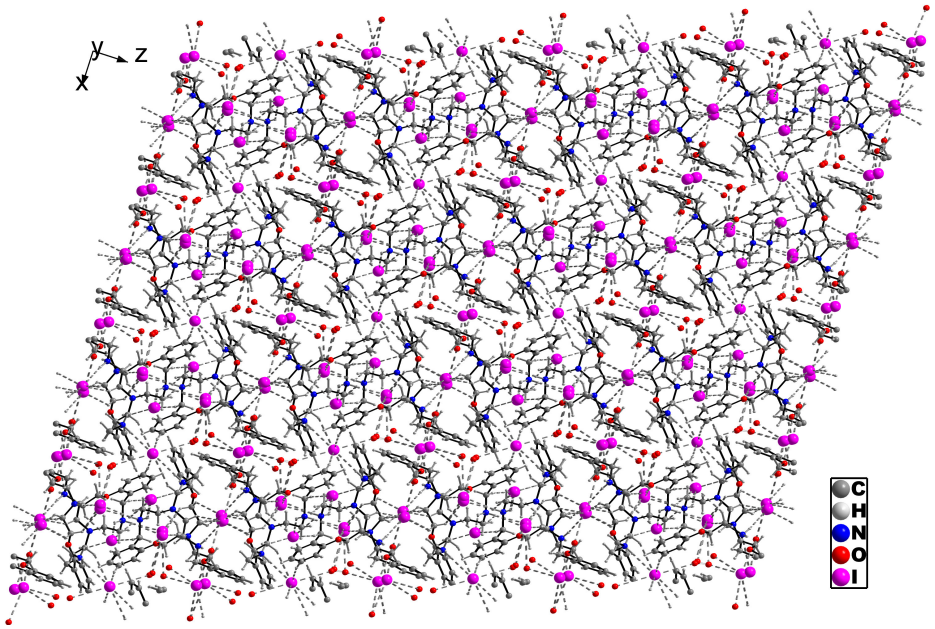

Figure S6: Packing diagram of complex **3** viewed down the *y* axis with various H-bonding interactions showing the 3D architecture along the *xz* plane.

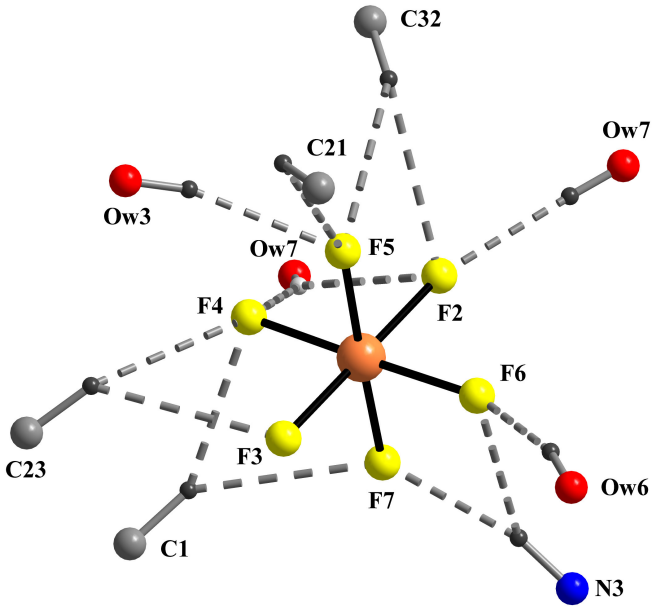

Figure S7: The H-bonding geometry of the multi-atomic anionic species hexafluorosilicate in complex **4** having a 14-point contacts on it, out of which there are five bifurcated H-bonding interactions.

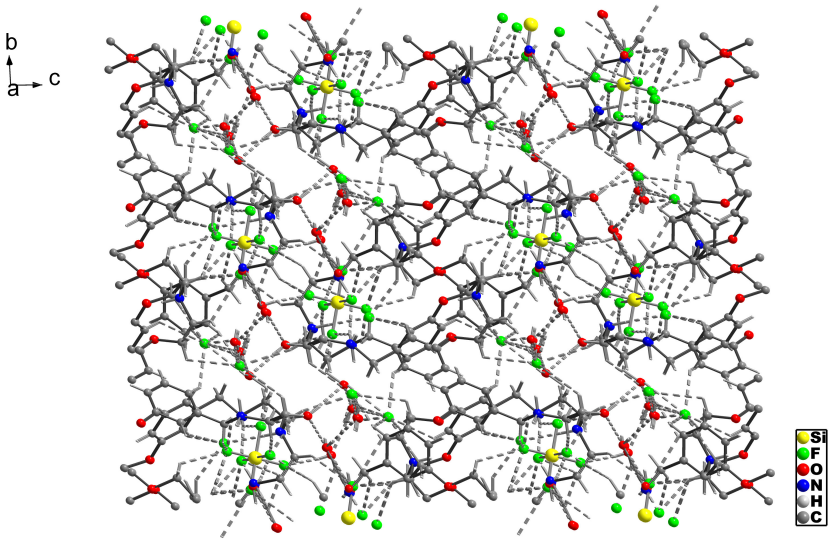

Figure S8: Packing diagram with various H-bonding interactions in **4** viewed down the *a* axis.

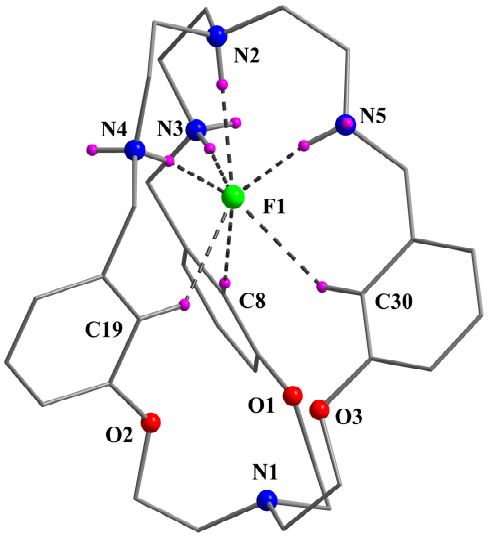

Figure S9: The encapsulated fluoride bound by seven H-bonding contacts within the receptor cavity of $\mathbf{L_m}$ in complex **5**.

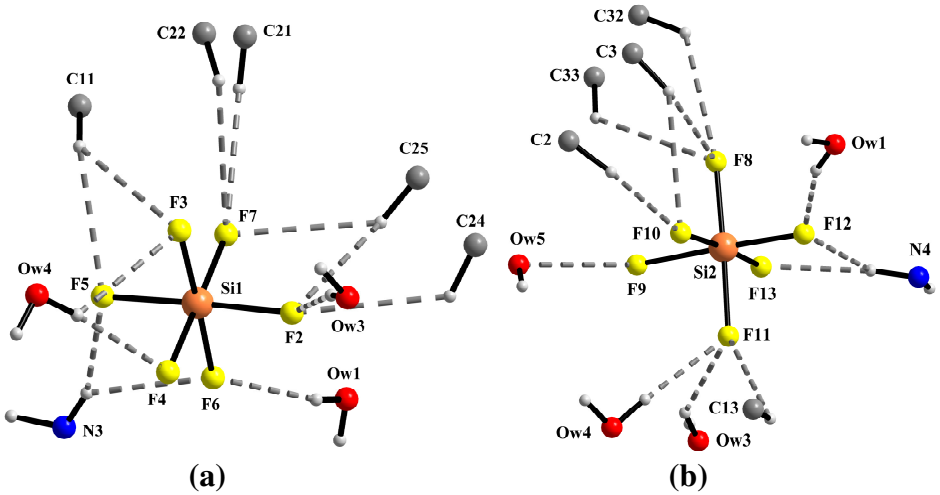

Figure S10: Interactions of hexafluorosilicate anions with the surrounding cryptand moieties and crystallized water molecules in **5**.

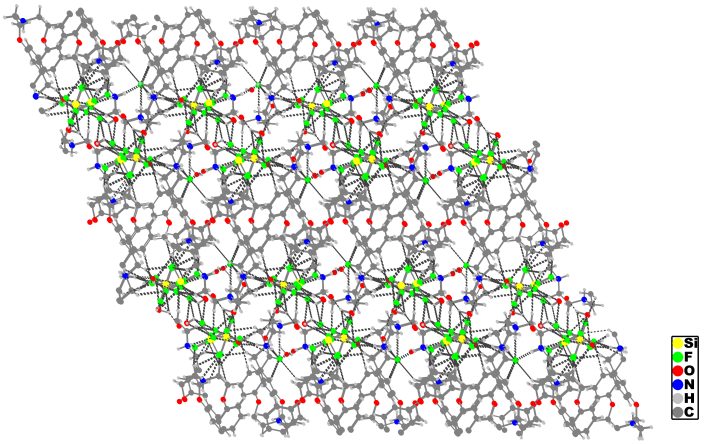

Figure S11: Packing diagram of complex **5** viewed down the C_3 axis joining the two bridgehead N atoms with various H-bonding interactions showing the 3D framework.

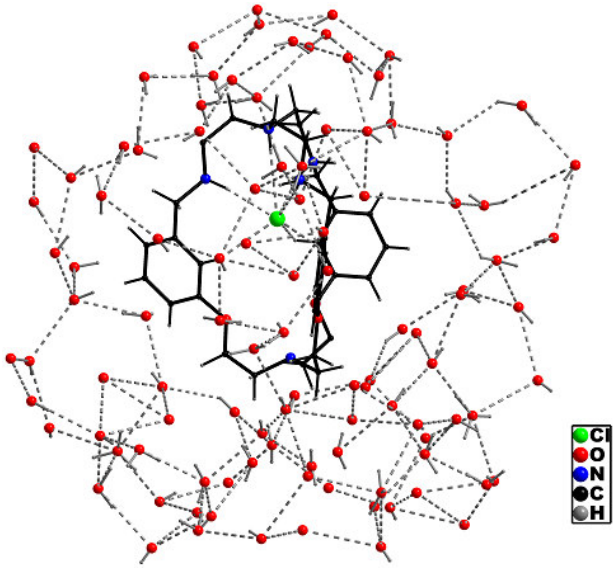

Figure 12: A representation of the host-within-a-host-like structure resembling the Russian nesting doll in complex **6**.

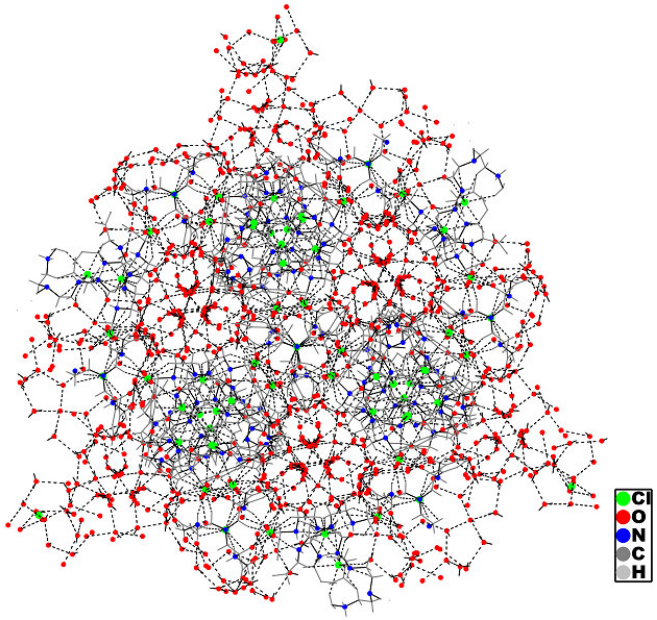

Figure S13: Packing diagram of **6** showing various molecular interactions involving the protonated cryptand moieties, the chloride anions, and water clusters.

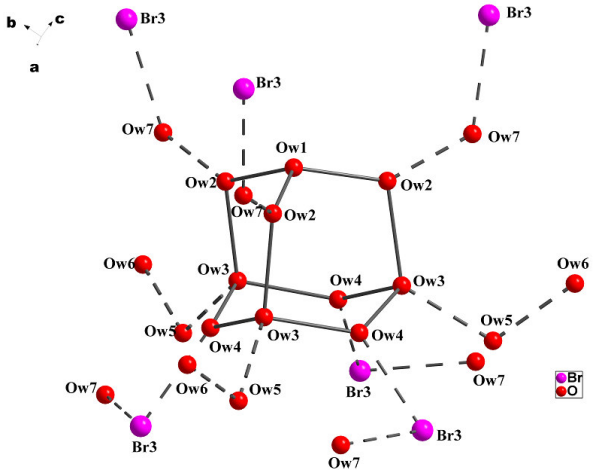

Figure S14: Adamantanoid water cluster along with its immediate H-bonding coordination environment in **7**.

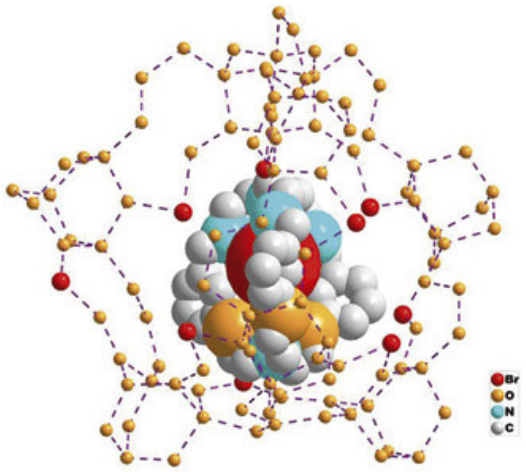

Figure S15: View of the host-within-a-host-like structure showing the encapsulated bromide within the cryptand cavity is surrounded by a water-bromide H-bonded cage resembling Russian nesting doll in complex **7**.

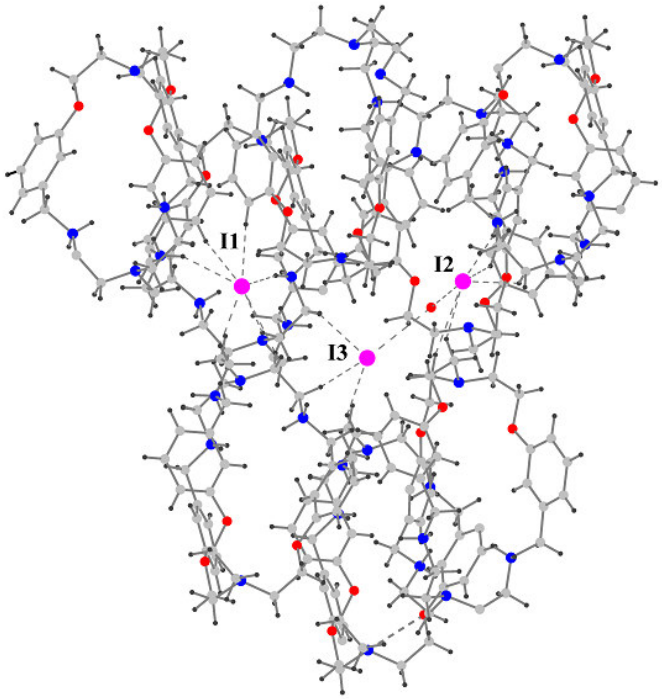

Figure S16: The H-bonding coordination environment of all of the iodides in complex **8**.

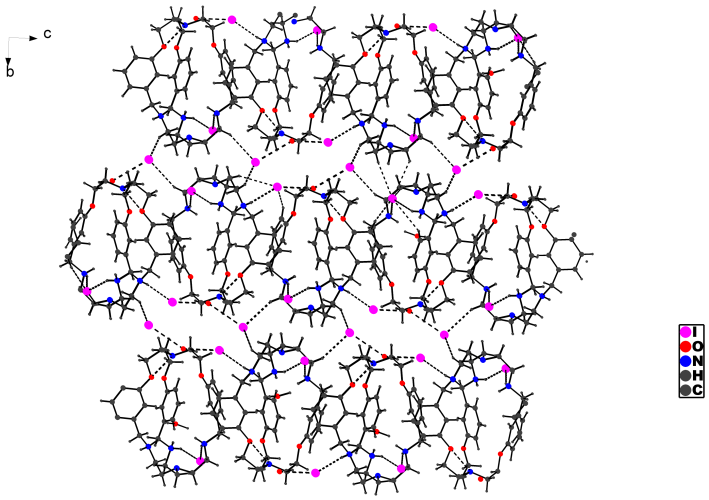

Figure S17: Packing diagram of complex **8** vied down *a* axis showing the iodides (I1, I2) connect the cryptand moieties of each layer, while iodide (I3) communicates within these layers through C─H···I interactions.

Table S1:

H-bonding Interactions Among Different Species of Complex **1-6** and complex **8**.

Complex	D–H···A[a]	*d*(H···A) (Å)	*d*(D···A) (Å)	∠DHA (deg)
Complex **1**	N8–H8A···F2	1.880(3)	2.707(4)	151.73(2)
	N9–H9B···F2	1.920(5)	2.802(5)	165.84(2)
	N10–H10B···F2	1.750(5)	2.645(4)	173.04(3)
	N6–H1N6···F2	1.881(4)	2.734(6)	170.64(4)
	C13–H13A···F6	2.612(5)	3.543(7)	160.79(6)
$B(1)F_4$	OW7–H1W9···F7	2.120(4)	2.900(8)	150.21(5)
	C50–H50···F7	2.722(6)	3.537(9)	146.76(3)
	C17–H17···F7	2.475(5)	3.244(8)	140.11(4)
	OW4–H2W4···F8	2.126(5)	2.932(7)	172.40(4)
	C13–H13A···F8	2.660(3)	3.460(5)	139.99(3)
	C15–H15···F8	2.717(5)	3.482(8)	140.12(6)
	C35–H35B···F8	2.445(5)	3.376(7)	160.96(3)
	C56–H56B···F5	2.310(4)	3.240(7)	160.40(3)
$B(2)F_4$	OW8–H1W8···F22	2.084(4)	2.885(10)	177.78(4)
	C42–H42B···F21	2.374(4)	3.307(6)	161.04(3)
	C1–H1A···F23	2.437(5)	3.397(7)	163.71(3)
	C10–H10D···F23	2.496(4)	3.306(5)	140.86(2)
	C9–H9C···F24	2.421(4)	3.348(7)	159.89(3)
	C11–H11A···F24	2.621(4)	3.242(6)	122.02(3)
	C10–H10D···F24	2.747(6)	3.349(7)	120.76(3)
$Si(1)F_6^{2-}$	OW6–H2W6···F15	1.977(4)	2.737(7)	156.63(4)
	C12–H12A···F15	2.483(3)	3.439(6)	168.76(3)
	C64–H64B···F15	2.499(6)	3.233(8)	132.36(3)
	OW3–H1W3···F16	1.903(3)	2.692(6)	164.02(6)
	OW5–H2W5···F16	2.249(4)	2.995(5)	153.42(4)
	C10–H10C···F16	2.641(4)	3.505(8)	148.65(3)
	N4–H4A···F17	1.922(3)	2.726(5)	147.73(4)
	C1–H1B···F18	2.578(3)	3.487(5)	155.89(3)
	C64–H64B···F19	2.522(4)	3.397(6)	149.89(3)
	C65–H65A···F19	2.361(4)	3.273(6)	156.48(3)
	OW8–H2W8···F20	2.228(3)	2.956(5)	155.52(3)
	OW5–H2W5···F20	2.324(6)	2.994(8)	140.32(4)
	C65–H65A···F20	2.558(6)	3.352(8)	139.25(3)
$Si(2)F_6^{2-}$	C35–H35A···F9	2.541(4)	3.205(7)	125.63(3)
	C18–H18···F9	2.834(6)	3.712(10)	157.79(4)

	C21–H21B···F9	2.312(3)	3.253(5)	162.84(3)
	C34–H34A···F9	2.602(3)	3.241(7)	123.69(3)
	N9–H9A···F10	1.980(4)	2.787(6)	148.33(3)
	N8–H8B···F11	1.930(3)	2.778(4)	156.52(2)
	C46–H46B···F11	2.535(4)	3.174(6)	123.45(3)
	C45–H45A···F11	2.437(3)	3.109(5)	126.14(2)
	OW3–H2W3···F12	1.934(4)	2.736(5)	172.82(4)
	C45–H45A···F12	2.549(3)	3.500(5)	166.61(2)
	C43–H43B···F12	2.494(4)	3.345(7)	146.33(3)
	OW1–H2W1···F13	2.066(6)	2.818(7)	155.56(5)
	C20–H20A···F13	2.345(5)	3.190(8)	145.35(3)
	C57–H57B···F13	2.313(3)	3.263(5)	166.07(2)
	OW5–H1W5···F14	1.990(4)	2.752(7)	155.60(4)
Complex **2**	N4–H4A··· Br2	2.322(1)	3.212(8)	170.30(5)
	N4–H4B··· Br2	2.525(3)	3.338(9)	150.19(5)
	C12–H12A···Br2	3.082(4)	3.866(11)	138.90(5)
	C22–H22B··· Br2	2.939(3)	3.763(10)	143.47(4)
	C2–H2B··· Br2	3.000(1)	3.777(8)	137.95(5)
	C6–H6··· Br2	3.260(1)	3.85(1)	123.37(6)
	N5–H5A··· Br3	2.417(7)	3.254(13)	154.81(5)
	C21–H21A···Br3	2.874(3)	3.841(11)	175.20(5)
	C24–H24B···Br3	3.133(1)	3.811(8)	128.39(4)
	Ow1··· Br3		3.066(6)	
	Ow1··· Ow2		2.846(3)	
	Ow2··· Ow3		2.861(2)	
	Ow1···Ow2···Ow3			121.79(9)
	Br3···Ow1···Ow2			101.58(11)
	Ow1··· Br4		2.998(6)	
	Ow2··· Br4		3.143(2)	
	Ow2···Ow1···Br4			106.30(11)
	Br3···Ow1···Br4			152.12(12)
	Ow1···Br4···Ow2			123.78(10)
	N3–H3B··· Br4	2.495(11)	3.326(2)	153.63(5)
Complex **3**	N3–H3A···I1^{i}	2.947(3)	3.643(9)	135.36(4)
	N4–H4A···I1	2.730(1)	3.441(7)	136.75(4)
	C12–H12B···I1	2.950(12)	3.789(17)	145.34(15)
	C20–H20A···I1	3.032(1)	3.996(9)	172.10(5)

	N5–H5A···I2	2.591(3)	3.485(9)	172.74(4)
	Ow2···I2		3.452(7)	
	C24–H24B···I2	3.247(5)	3.895(9)	135.14(5)
	C23–H23A···I2^{ii}	2.997(1)	3.957(9)	170.55(5)
	C23´–H23A···I2^{ii}	3.058(2)	3.895(9)	145.34(5)
	Ow1A···I3A		3.722	
	Ow1A···I3B		3.458	
	N1–H1··· I3A	2.484(8)	3.385(10)	171.22(4)
	N1–H1··· I3B	2.579(7)	3.468	166.19(4)
	N4–H4B··· I3A	2.630(1)	3.504(12)	163.75(4)
	N4–H4B··· I3B	2.749(11)	3.628(13)	165.44(4)
	C24–H24A··· I3A	3.064(8)	3.774(14)	131.07(5)
	C24–H24A··· I3B	3.358(7)	4.034(14)	128.42(6)
	N3'–H3B···I4^{i}	2.70(1)	3.583(15)	167.10(4)
	Ow1A···I4		3.704	
	C16–H16··· I4	3.076(1)	3.961(9)	159.53(5)
	C33–H33A··· I4	3.264(1)	4.080(17)	142.87(5)
	Ow2···I5^{iii}		3.550(7)	
	Ow2···I5'^{iii}		3.424(8)	
	Ow3···I5		4.24(2)	
	Ow3···I5'		3.304(2)	
	C1–H1B···I5	3.147(7)	3.801(10)	126.10(5)
	C1–H1B···I5'	3.723(4)	4.422(9)	131.11(5)
	Symmetry codes: (i) 0.5-x, 0.5+y, 0.5-z, (ii) 0.5-x, -0.5-y, -z, (iii) -x, 1-y, -z			
Complex **4**	N4–H2N4•••F9	1.770(4)	2.663(7)	170.90(3)
	Ow1–H2w1•••F9	1.837(9)	2.652(9)	174.33(9)
	Ow2–H2w2•••F9	1.478(9)	2.271(5)	162.48(8)
	C22–H30A···F9	2.799(9)	3.482(13)	128.02(4)
	C2–H31B···F8	2.197(12)	3.166(15)	176.60(4)
	C12–H25B···F8	2.568(12)	3.496(15)	159.97(5)
$(H_2O)_7$ of	Ow3–H2w3···Ow4	2.239(7)	2.786(7)	121.56(8)
Complex **4**	Ow4–H2w4···Ow2	2.360(7)	3.069(2)	151.26(6)
	Ow4–H1w4···Ow5	1.884(6)	2.559(7)	156.94(7)
	Ow5–H1w5···Ow6	1.902(11)	2.734(14)	175.47(9)
	Ow6–H2w6···Ow1	1.957(3)	2.748(12)	155.73(18)
	Ow1–H1w1···Ow7	1.862(10)	2.639(11)	164.45(8)
	Ow3–H1w3···F5	2.036(9)	2.823(12)	164.72(8)
	N5–H2N5···Ow3	2.144(7)	2.980(9)	154.21(4)

	N5–H2N5···Ow4	2.370(13)	3.023(16)	129.55(4)
	Ow2–H2w2···F9	1.478(9)	2.270(15)	162.48(9)
	Ow6–H1w6···F6	1.852(3)	2.730(9)	166.51(2)
	Ow1–H2w1···F9	1.837(9)	2.652(9)	174.33(9)
	Ow7–H1w7···F4	1.917(9)	2.775(9)	157.88(8)
	Ow7–H2w7···F2	1.944(7)	2.697(8)	173.32(8)
	∠Ow3···Ow4···Ow2			81.42(3)
	∠Ow3···Ow4···Ow5			168.97(6)
	∠Ow4···Ow5···Ow6			113.20(4)
	∠Ow2···Ow4···Ow5			106.84(6)
	∠Ow5···Ow6···Ow1			102.62(3)
	∠Ow6···Ow1···Ow7			107.02(3)
$Si(1)F_6^{2-}$of	OW7–H2W7···F2	1.944(7)	2.697(8)	173.32(8)
Complex **4**	C32–H42B···F2	2.505(8)	3.188(12)	127.24(7)
	OW7–H1W7···F2	2.237(8)	3.106(8)	136.62(7)
	C23–H28A···F3	2.473(10)	3.169(13)	128.58(4)
	C23–H28A···F4	2.457(6)	3.273(10)	141.75(4)
	C1–H46A···F4	2.302(5)	3.136(8)	143.39(4)
	OW7–H1W7···F4	1.917(9)	2.775(9)	157.88(8)
	C21–H37A···F5	2.769(6)	3.369(11)	120.74(4)
	C32–H42B···F5	2.659(8)	3.557(12)	154.12(4)
	OW3–H1W3···F5	2.036(9)	2.823(12)	164.72(8)
	OW6–H1W6···F6	1.852(3)	2.730(9)	166.51(2)
	N3–H2N3···F6	2.229(6)	2.978(8)	140.37(3)
	N3–H2N3···F7	1.980(8)	2.799(11)	155.57(3)
	C1–H46A···F7	2.409(9)	3.226(13)	141.53(4)
Complex **5**	Ow6–H1w6···Ow7	1.946(18)	2.788(13)	165.17(15)
$(H_2O)_7$	Ow7···Ow5		2.771(11)	
	Ow5···Ow4		2.980(13)	
	Ow4···Ow6		2.839(11)	
	Ow6···Ow2		2.795(15)	
	Ow3···Ow5		3.011(13)	
	Ow2–H2w2···Ow1	1.914(9)	2.700(11)	159.02(6)
	Ow1–H2w1···F6	1.993(5)	2.744(12)	155.04(7)
	Ow1–H1w1···F12	2.025(8)	2.797(10)	160.09(9)
	N5–H5B···Ow2	2.278(10)	2.963(12)	132.86(5)
	N5–H5B···Ow7	2.229(10)	2.963(13)	138.57(4)
	Ow5···F9		2.595(13)	
	Ow5–H2w5···F4	1.912(7)	2.712(11)	173.06(6)
	Ow4–H2w4···F11	2.041(12)	2.873(14)	177.21(11)
	Ow3–H1w3···F11	2.063(10)	2.747(10)	138.86(9)
	Ow3–H2w3···F2	1.904(7)	2.711(11)	167.59(6)

	∠Ow6···Ow7···Ow5			82.26(3)
	∠Ow7···Ow5···Ow4			94.66(3)
	∠Ow5···Ow4···Ow6			81.51(3)
	∠Ow4···Ow6···Ow7			97.52(4)
	∠Ow7···Ow5···Ow3			96.26(3)
	∠Ow5···Ow3···Ow2			85.17(2)
	∠Ow3···Ow2···Ow6			102.04(3)
	∠Ow2···Ow6···Ow7			68.18(3)
	∠Ow3···Ow2···Ow1			116.88(3)
	∠Ow1···Ow2···Ow6			111.37(2)
$Si(1)F_6^{2-}$ of	OW3–H2W3···F2	1.904(7)	2.711(11)	167.59(6)
Complex **5**	C24–H24B···F2	2.645(6)	3.272(10)	122.63(4)
	C25–H25A···F2	2.726(13)	3.511(16)	138.44(4)
	OW4–H1W4···F3	2.506(10)	3.025(15)	121.62(9)
	C11–H11A···F3	2.592(6)	3.389(8)	139.72(3)
	OW4–H1W4···F4	2.130(10)	2.954(12)	171.89(10)
	N3–H3B···F5	2.033(5)	2.897(8)	160.67(5)
	C11–H11A···F5	2.538(6)	3.224(9)	127.83(3)
	OW1–H2W1···F6	1.993(5)	2.744(12)	155.04(6)
	N3–H3B···F6	2.210(5)	2.884(8)	131.40(3)
	C25–H25A···F7	2.579(6)	3.325(9)	133.84(4)
	C21–H21B···F7	2.629(7)	3.372(10)	133.58(4)
	C22–H22A···F7	2.862(6)	3.457(10)	120.46(4)
$Si(2)F_6^{2-}$ of	C3–H3C···F8	2.685(8)	3.405(12)	131.38(4)
Complex **5**	C32–H32B···F8	2.760(7)	3.444(11)	128.15(4)
	C33–H33A···F8	2.832(8)	3.489(12)	125.74(3)
	Ow5···F9		2.595(13)	
	C2–H2B···F10	2.618(9)	3.289(12)	126.47(4)
	C3–H3C···F10	2.654(7)	3.466(11)	141.47(4)
	Ow4–H2w4···F11	2.041(12)	2.873(14)	177.21(11)
	Ow3–H1w3···F11	2.063(11)	2.747(10)	138.86(9)
	C13–H13B···F11	2.812(8)	3.438(12)	122.99(4)
	Ow1–H1w1···F12	2.025(7)	2.797(10)	160.09(7)
	N4–H4A···F12	2.233(9)	2.885(12)	129.00(3)
	N4–H4A···F13	2.076(4)	2.952(7)	164.16(3)
Complex **6**	N3–HN3···Cl1	2.598(7)	3.417(3)	180.00
	N2–H2B···Cl1	2.212(1)	3.080(4)	161.87(2)
	C8–H8···Cl1	2.694(1)	3.332(4)	126.50(2)
	N2–H2A···Cl2	2.329(2)	3.196(4)	161.49(2)
	Ow1–H1W1···Cl2	2.436(9)	3.263(5)	153.60(8)
	C9–H9A···Cl2	2.872(1)	3.704(5)	144.36(2)

	C10–H10B···Cl2	2.789(1)	3.636(4)	146.44(2)
	C11–H11B···Cl2	2.873(2)	3.670(5)	140.06(2)
	Ow1–H2w1···Ow3	1.872(8)	2.719(7)	171.03(7)
	Ow2···Ow3		2.976(8)	
	Ow2–H2w2···Ow4	2.352(11)	2.803(3)	114.92(6)
	Ow2–H1w2···Ow5	2.079(5)	2.871(9)	162.77(4)
	Ow5–H1w5···Ow1	2.073(4)	2.870(7)	173.93(4)
	Ow5···Ow6		2.929(11)	
	Ow7···Ow7′[a]		2.886(9)	
	Ow5–H2w5···Ow7	2.312(6)	3.052(2)	158.57(5)

Ow7 is related to Ow7′ with the symmetry code -1.25+y, 1.25+x, 3.25-z

Complex **8**	N3–H3B···I1	2.710(9)	3.532(11)	152.44(6)
	N4–H4A···I1	2.678(1)	3.544(9)	161.62(5)
	C5–H5···I1	3.324(1)	3.955(10)	127.09(6)
	C29–H29···I1	2.944(5)	3.818(13)	157.03(6)
	C12′–H12A···I1	3.283(1)	4.022(11)	134.47(4)
	C23–H23A···I1	3.178(3)	3.981(11)	141.42(6)
	C12–H12B···I1	3.072(5)	3.913(13)	145.94(7)
	N5–H5A···I2	2.630(4)	3.468(11)	155.43(5)
	C11–H11B···I2	3.215(6)	4.014(6)	140.81(2)
	C18–H18···I2	3.296(3)	4.005(12)	134.69(7)
	C22–H22B···I2	3.176(1)	4.031(13)	147.70(8)
	C23–H23B···I2	3.194(1)	3.988(12)	140.24(6)
	Ow2···I2		3.530(1)	
	C2–H2B···I3	3.234(7)	4.049(15)	142.75(7)
	C13–H13A···I3	2.995(4)	3.85(1)	147.48(6)
	C24–H22A···I3	2.937(4)	3.822(13)	152.27(6)
	Ow2···I3		3.35(2)	

C12 is related to C12′ with the symmetry code 1-x, -y, 1-z.