

Spin pairing, electrostatic and dipolar interactions shape stacking of radical anions in alkali salts of 4,5-dichloro-3,6-dioxocyclohexa-1,4-diene-1,2-dicarbonitrile (DDQ)

Supplementary Data

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S1 ORTEP drawings of DDQ anions

S2 Details on metal coordinations

S3 Crystal packing of compounds 1-5

S1 ORTEP drawings of DDQ anions

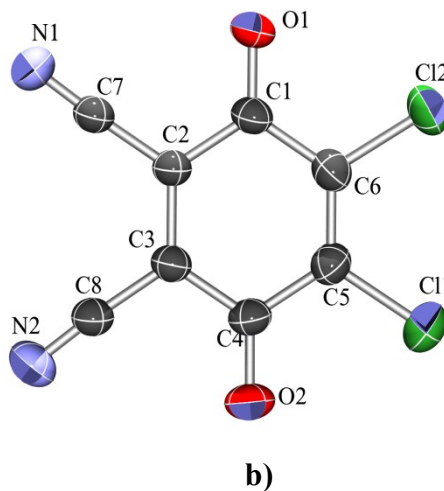
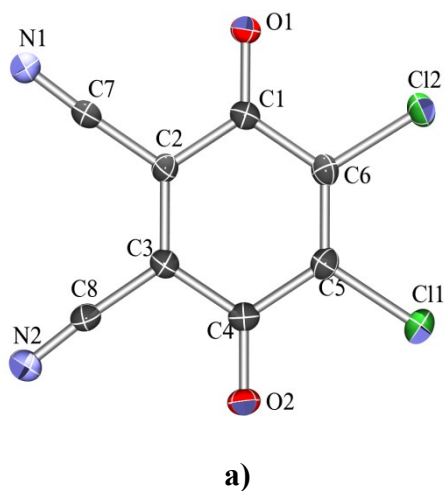


Figure S1 ORTEP-3 drawings of DDQ anion in **1** at a) 120 K and b) room temperature. Displacement ellipsoids are drawn for the probability of 50 %.

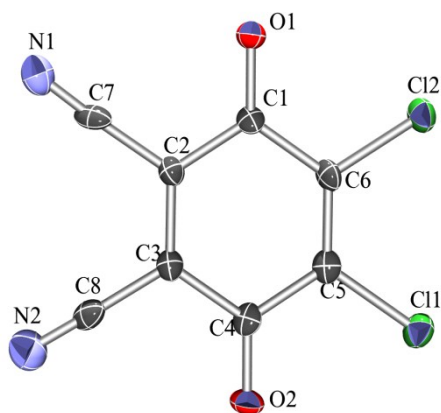


Figure S2 ORTEP-3 drawing of DDQ anion in **4**. Displacement ellipsoids are drawn for the probability of 50 %.

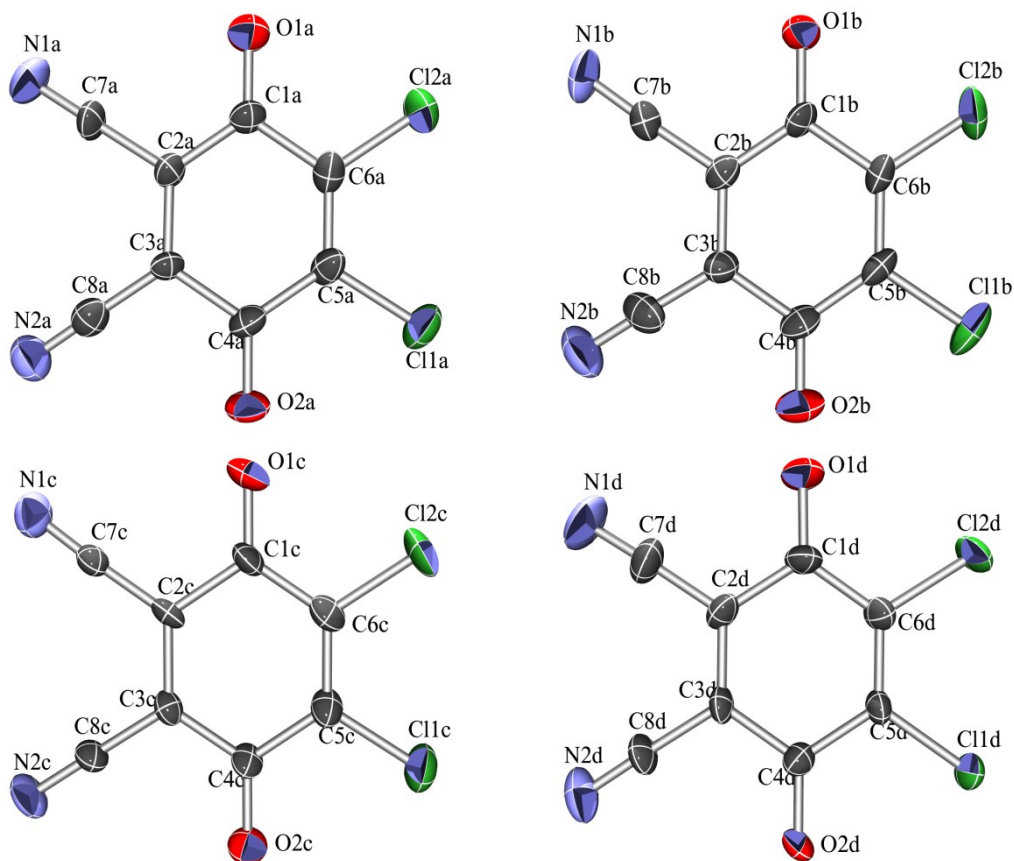


Figure S3 ORTEP-3 drawings of four symmetry-independent DDQ anions in **5** (labelled as a, b, c and d). Displacement ellipsoids are drawn for the probability of 50 %.

S2 Details on metal coordinations

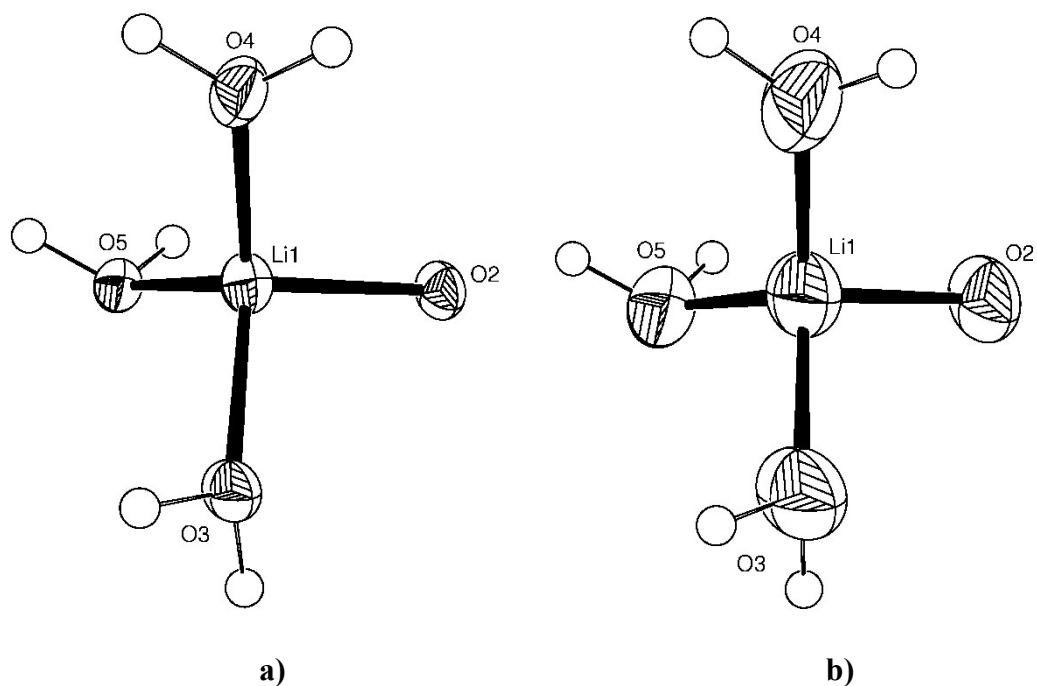


Figure S4 ORTEP-3 drawings of Li coordination spheres in **1** at a) 120 K and b) room temperature. Displacement ellipsoids are drawn for the probability of 50 % and hydrogen atoms are shown as spheres of arbitrary radii.

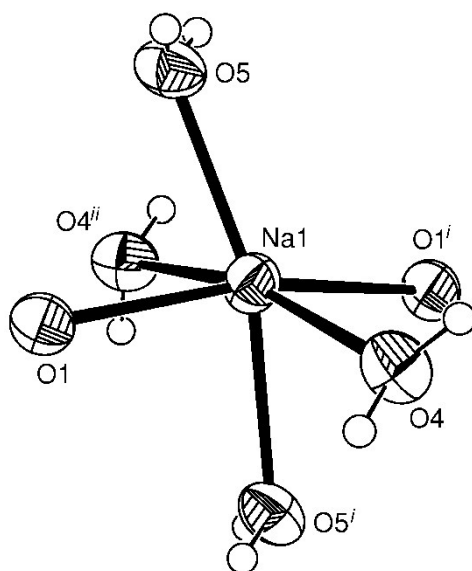


Figure S5 ORTEP-3 drawing of Na coordination sphere in **2**. Displacement ellipsoids are drawn for the probability of 50 % and hydrogen atoms are shown as spheres of arbitrary radii. Symmetry operators *i*) $3/2-x, 1/2+y, 1/2-z$; *ii*) $3/2-x, -1/2+y, 1/2-z$.

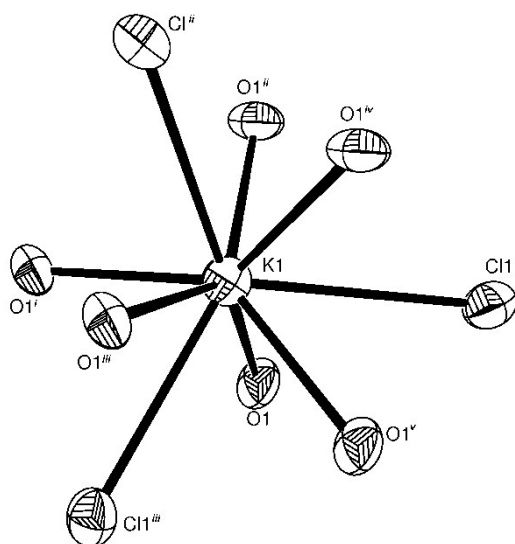


Figure S6 ORTEP-3 drawing of K1 coordination sphere in **3**. Displacement ellipsoids are drawn for the probability of 50 %. Symmetry operators: *i*) $1-x+y, 1-x, z$; *ii*) $1-y, x-y, z$; *iii*) $1-x+y, 1-x, 1+z$; *iv*) $1-y, x-y, 1+z$; *v*) $x, y, 1+z$.

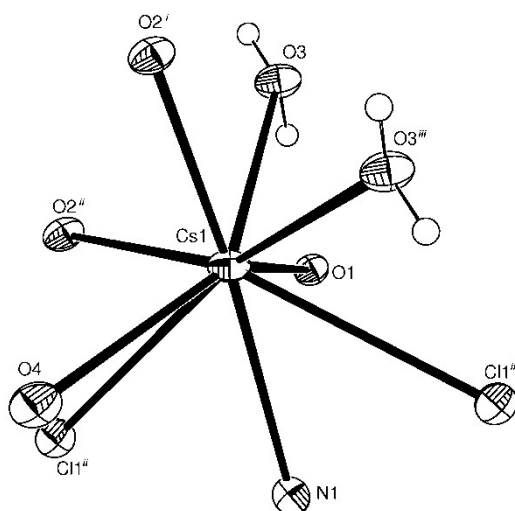


Figure S7 ORTEP-3 drawing of Cs1 coordination sphere in **4**. Displacement ellipsoids are drawn for the probability of 50 % and hydrogen atoms are shown as spheres of arbitrary radii. Symmetry operators: *i*) $x, -1+y, z$; *ii*) $1-x, 1-y, 2-z$; *iii*) $-x, 2-y, 2-z$.

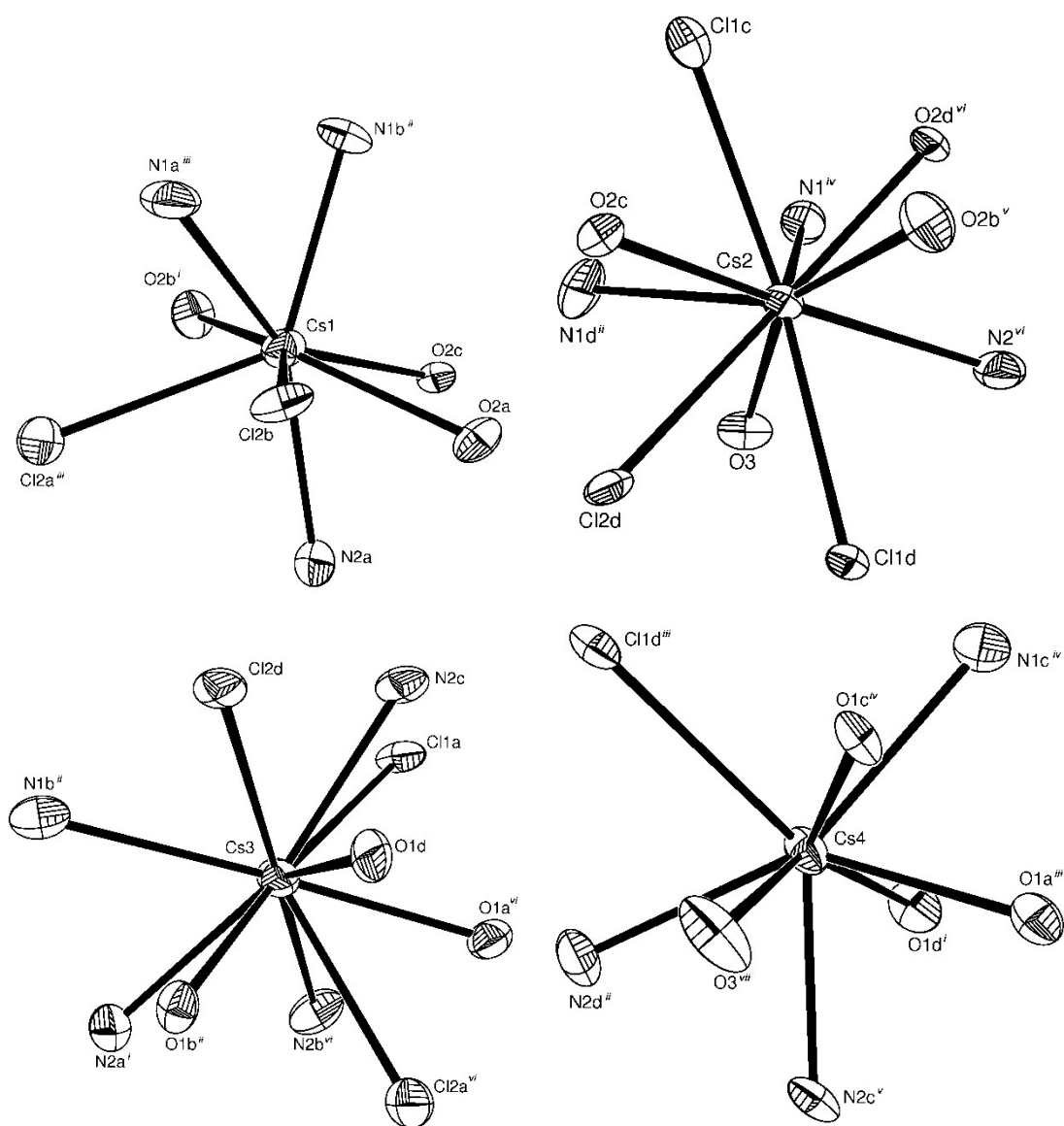


Figure S8 ORTEP-3 drawings of coordination spheres of four symmetry-independent Cs ions in **5**. Displacement ellipsoids are drawn for the probability of 50. Symmetry operators: *i*) $1-x, 1/2+y, z$; *ii*) $1-x, -1/2+y, z$; *iii*) $1-x, -y, -1/2+z$; *iv*) $-x, 1/2+y, z$; *v*) $1-x, 1/2+y, z$; *vi*) $x, -y+1/2, z+1/2$; *vii*) $-x, 1/2+y, z$.

S3 Crystal packing of compounds 1-5

In **1** stacks of radical anions extend in the direction [100]. Lithium cation is in tetrahedral coordination, by O2 of DDQ and three water molecules (Fig. S4). These water molecules are donors of 7 symmetry-independent hydrogen bonds and acceptors of two; DDQ accepts five hydrogen bonds (Table S1). Overall, a 3D hydrogen bonding network is formed (Fig. S9).

Sodium cation in **2** has a distorted octahedral coordination (Fig. S5) by O1 of DDQ and two water molecules; two symmetry-equivalent halves of the coordination sphere are related by a 2_1 axis. Ligands bridge the sodium ions forming chains parallel to [010]; DDQ anions from neighbouring chains form π -interaction, so the stacks are also parallel to [010] (Fig. S10). There are four symmetry-inequivalent hydrogen bonds (Table S1): donors are water molecules and acceptors are O2 from DDQ, O3 from MeCOEt (both accepting two hydrogen bonds), forming layers parallel to $(10\bar{1})$.

DDQ anion in **3** has a crystallographic symmetry C_s , so two symmetry-independent K cations are located in special positions: K1 on a C_3 axis (p.p. 0.33) and K2 in an intersection of three m planes (p.p. 0.17), therefore asymmetric unit comprises a half of a DDQ anion, a half of a K cation and a half of a water molecule. K1 is coordinated by 6 O1 atoms and 3 Cl1 atoms of DDQ (Fig. S6); O1 acts as a bridging ligand, forming a 3D motive (Fig. S11). K2 occupies a cavity, so its only close contacts are 4 water molecules (O4, distance 3.56 Å) and 2 symmetry-equivalent K2 (distance 3.55 Å). A single symmetry-inequivalent hydrogen bond links the water molecule and N1 of DDQ (Table S1), forming a cyclic motive $R_2^2(27)$ around the K2. Anions form stacks parallel to [001].

Asymmetric unit of **4** comprises a Cs cation, a DDQ anion, a water molecule and a molecule of MeCOEt. The cation is octacoordinated, by O1 and N1 from DDQ, three O2 atoms from three symmetry-equivalent DDQs, two symmetry equivalent water molecules (O3) and a MeCOEt (O4) (Fig. S7). O2 and O3 act as bridging ligands. Two symmetry-independent hydrogen bonds are present (Table S1): the water molecule is a donor, while the acceptors are O1 (DDQ) and O4 (MeCOEt). Anions and cations form layers parallel to [001]; between them are MeCOEt molecules, so the layers are held together by dispersion interactions (Fig. S12). Stacks also extend in the direction [001].

5 crystallises with $Z' = 4$, that is four formula units per asymmetric unit, i.e. $Cs_4DDQ_4 \cdot H_2O$. The cations and anions form a 3D network (Fig. S13) with stacks of DDQ

anions extending in the direction [100]. The water molecule (O3) probably acts as a proton donor, but since hydrogen atoms could not be reliably located, existence of hydrogen bonds can not be determined.

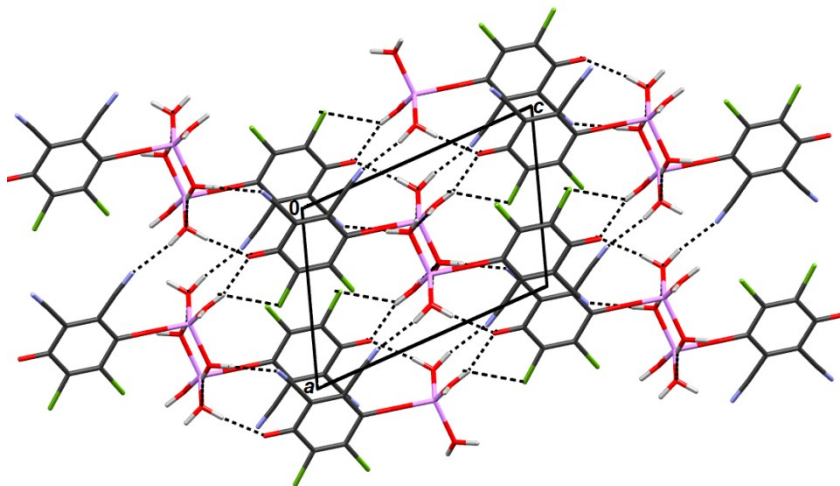


Figure S9 Crystal packing of **1** viewed in the direction [100].

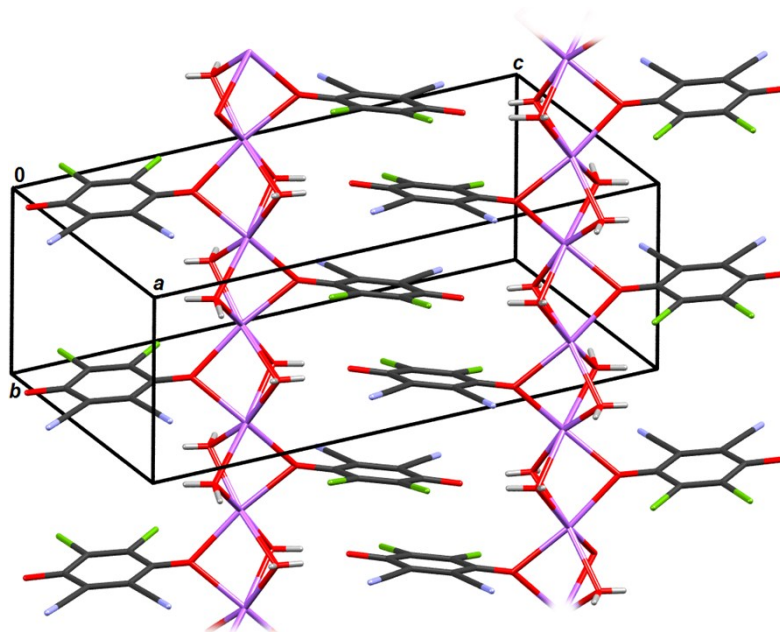


Figure S10 Sodium-ligand chains and π -stacks in **2** parallel to [010]. This motive also forms layers parallel to (10-1).

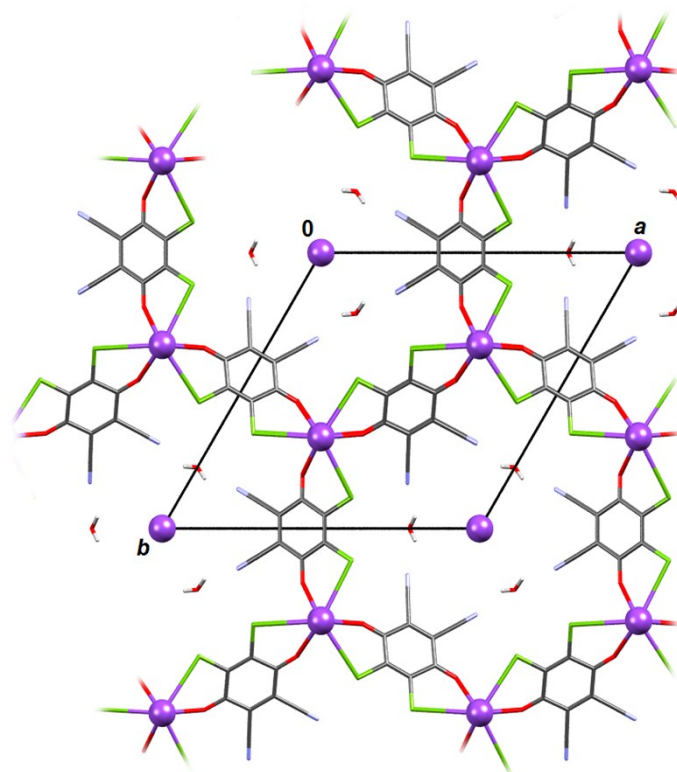


Figure S11 3D packing of **3**. There are two symmetry independent potassium cations with the two distinctive structural roles: connecting three radical anions (K1) forming a hexameric units with bridged radical anions generating a cavity occupied by K2. K atoms are shown as spheres of arbitrary radii.

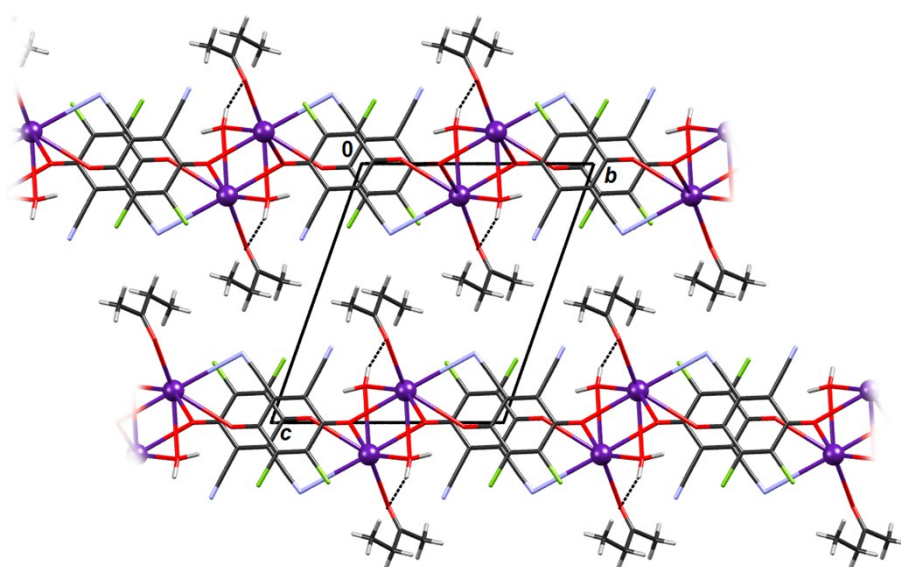


Figure S12 Layered structure of **4**: cation and anions form layers parallel to [001], and in between there are only dispersion interactions.

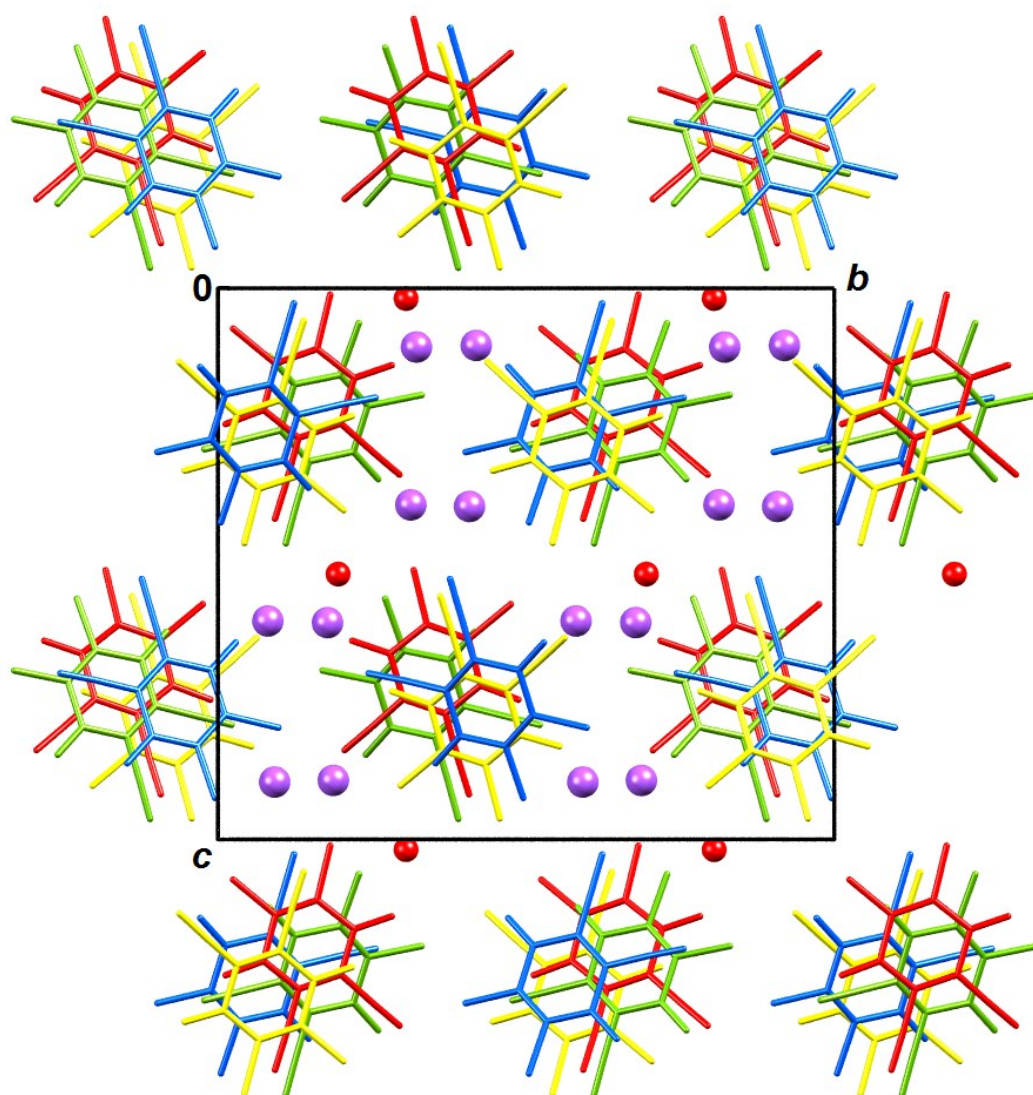


Figure S13 Crystal packing of **5** comprising four molecules in an asymmetric unit (colour-coded: A is red, B is blue, C is yellow and D is green) viewed in the direction [100]. Cs cations and water molecules are shown as purple and red spheres of arbitrary radii.

Table S1 Geometric parameters of hydrogen bonds.

	$D-H / \text{\AA}$	$H \cdots A / \text{\AA}$	$D \cdots A / \text{\AA}$	$D-H \cdots A / ^\circ$	Symm. op. on A
1, 120 K					
O3–H3A \cdots O5	0.92(2)	1.98(2)	2.874(2)	163(3)	1– x , 1– y , 1– z
O3–H3B \cdots N1	0.92(2)	2.02(2)	2.902(2)	162(3)	–1+ x , –1+ y , –1+ z
O4–H4A \cdots Cl2	0.90(3)	2.75(2)	3.313(2)	122(3)	x , y , –1+ z
O4–H4A \cdots O1	0.90(3)	1.97(3)	2.832(2)	162(3)	x , y , –1+ z
O4–H4B \cdots O3	0.94(3)	1.98(4)	2.905(2)	172(3)	1– x , 2– y , 1– z
O5–H5A \cdots O1	0.92(2)	2.00(2)	2.910(2)	170(2)	2– x , 2– y , 2– z
O5–H5B \cdots N2	0.92(3)	2.01(2)	2.924(2)	170(3)	2– x , 2– y , 2– z
1, RT					
O3–H3A \cdots O5	0.95(3)	2.02(4)	2.915(3)	158(5)	1– x , 1– y , 1– z
O3–H3B \cdots N1	0.94(2)	2.00(2)	2.925(3)	170(4)	–1+ x , –1+ y , –1+ z
O4–H4A \cdots Cl2	0.93(4)	2.79(4)	3.342(2)	119(3)	x , y , –1+ z
O4–H4A \cdots O1	0.93(4)	1.94(5)	2.841(4)	164(4)	x , y , –1+ z
O4–H4B \cdots O3	0.94(6)	2.04(5)	2.955(4)	166(5)	1– x , 2– y , 1– z
O5–H5A \cdots O1	0.94(4)	2.01(3)	2.947(3)	173(4)	2– x , 2– y , 2– z
O5–H5B \cdots N2	0.94(4)	2.03(4)	2.954(4)	174(4)	2– x , 2– y , 2– z
2					
O4–H4A \cdots O3	0.95(3)	1.95(3)	2.830(5)	154(3)	x , 1+ y , z
O4–H4B \cdots O2	0.94(3)	2.10(5)	2.870(4)	138(4)	1– x , 2– y , – z
O5–H5A \cdots O3	0.71(5)	2.22(6)	2.885(5)	157(6)	x , y , z
O5–H5B \cdots O2	0.81(6)	2.17(6)	2.888(4)	148(6)	1/2+ x , 3/2– y , 1/2+ z
3					
O4–H4 \cdots N1	0.95(11)	2.04(11)	2.857(14)	144(7)	x , y , z
4					
O3–H3A \cdots O1	0.95(7)	2.01(8)	2.897(6)	155(7)	x , y , z
O3–H3B \cdots O4	0.94(7)	1.95(8)	2.852(6)	161(9)	– x , 1– y , 2– z
C11–H11B \cdots N1	0.97	2.61	3.515(9)	155	– x , 1– y , 1– z