Stabilisation of tetrabromo- and tetrachlorosemiquinone (bromanil and chloranil) anion radicals in crystals

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S1 Crystal packings of NaBr$_4$Q$^{\bullet}$ and RbBr$_4$Q$^{\bullet}$

The crystal packing of solvent-free salts, **NaBr$_4$Q$^{\bullet}$** and **RbBr$_4$Q$^{\bullet}$** are more compact than their solvates (Table 4). In **NaBr$_4$Q$^{\bullet}$** π-stacking in the direction [010] resembles stacking of the aromatic rings (centroid-centroid distance is 3.669 Å, offset is > 1.5 Å). The cation-anion layers are parallel to (101) (Fig. S1). Electrostatic interactions between layers are relatively strong, contributing to the stability of the structure. Sodium cation (located on an inversion centre at 1, 0, 0) is in a distorted octahedral coordination. The **Br$_4$Q$^{\bullet -}$** anion is also centrosymmetric; its centroid is located at 1/2, 1/2, 0.

Crystal packing of **RbBr$_4$Q$^{\bullet}$** (Fig. S1) does not reveal π-stacking. Rubidium cation is involved in four short contacts with oxygen atoms and two with bromine atoms; there are also two additional distant bromine neighbours.

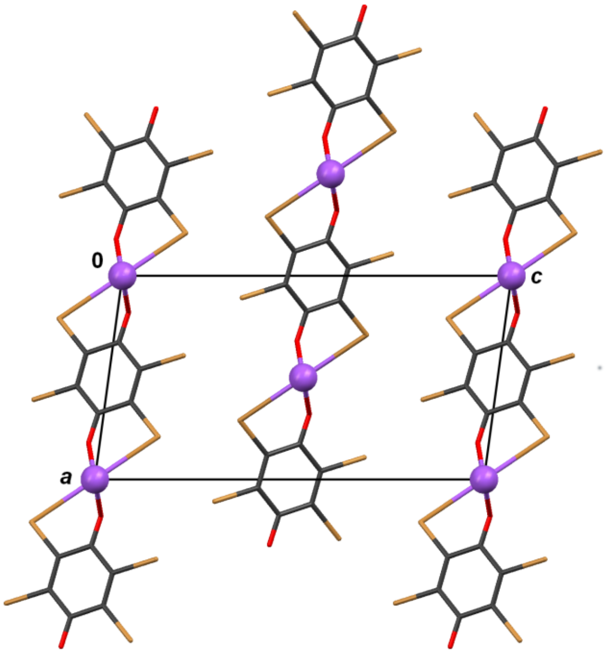

Figure S1 Crystal packing of **NaBr$_4$Q$^{\bullet}$** viewed down the direction [010]. Sodium cations are depicted as spheres of arbitrary radii.

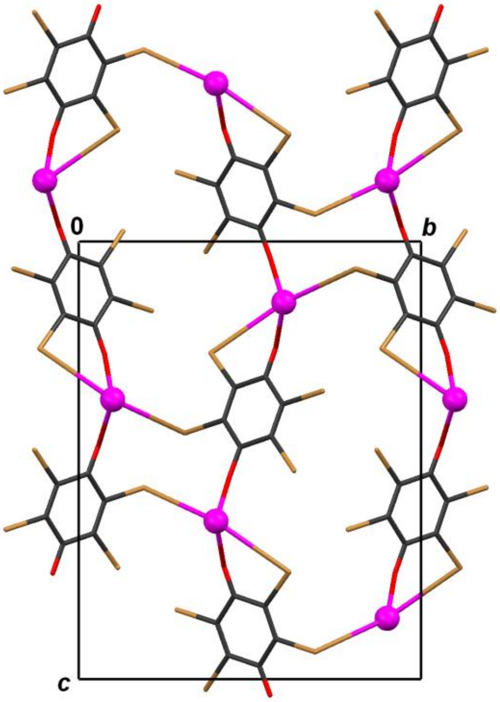

Figure S1 Crystal packing of **RbBr$_4$Q$^\bullet$** viewed down the direction [100]. Rubidium cations are depicted as spheres of arbitrary radii.

S2 Geometries of alkali cation coordination spheres

Table S1 Geometry of rubidium cation coordination sphere in $\mathbf{RbCl_4Q^{\bullet}\cdot Me_2CO}$ (Å, º).

Rb1 – O1^{i}	2.759 (2)
Rb1 – O2^{ii}	2.795 (2)
Rb1 – O1	2.859 (2)
Rb1 – O2^{iii}	2.894 (2)
Rb1 – O3^{i}	2.937 (2)
Rb1 – O3	2.942 (2)
Rb1 – Cl^{iii}	3.4491 (7)
Rb1 – Cl1	3.5730 (7)
O1^{i} – Rb1 – O2^{ii}	70.69 (5)
O1^{i} – Rb1 – O1	130.93 (5)
O1^{i} – Rb1 – O2^{iii}	85.12 (5)
O1^{i} – Rb1 – O3^{i}	74.76 (6)
O1^{i} – Rb1 – O3	136.44 (6)
O1^{i} – Rb1 – Cl2^{iii}	82.48 (4)
O1^{i} – Rb1 – Cl1	149.34 (4)
O2^{ii} – Rb1 – O1	85.14 (5)
O2^{ii} – Rb1 – O2^{iii}	154.64 (5)
O2^{ii} – Rb1 – O3^{i}	103.48 (6)
O2^{ii} – Rb1 – O3	77.76 (6)
O3^{ii} – Rb1 – Cl2^{iii}	113.46 (4)
O2^{ii} – Rb1 – Cl1	133.97 (3)
O1 – Rb1 – O2^{iii}	106.24 (5)
O1 – Rb1 – O3^{i}	154.02 (6)
O1 – Rb1 – O3	73.24 (6)
O1 – Rb1 – Cl2^{iii}	68.69 (4)
O1 – Rb1 – Cl1	52.55 (4)
O2^{iii} – Rb1 – O3^{i}	76.32 (5)
O2^{iii} – Rb1 – O3	126.91 (6)
O2^{iii} – Rb1 – Cl2^{iii}	53.86 (4)
O2^{iii} – Rb1 – Cl1	66.97 (3)
O3^{i} – Rb1 – O3	84.55 (6)
O3^{i} – Rb1 – Cl2^{iii}	126.63 (4)
O3^{i} – Rb1 – Cl1	108.69 (4)

O3 – Rb1 – Cl2^{iii}	138.77 (4)
O3 – Rb1 – Cl1	73.56 (4)
Cl2^{iii} – Rb1 – Cl1	71.08 (1)

Symmetry operators: *i*) *x*,1/2-*y*,-1/2+*z*, *ii*) 2-*x*,1/2+*y*,3/2-*z*, *iii*) 2-*x*,-*y*,1-*z*.

Table S2 Geometry of potassium cation coordination sphere in **$KCl_4Q^{\bullet}\cdot Me_2CO$** (Å, º).

K1 – O1^{i}	2.648 (1)
K1 – O2^{ii}	2.668 (1)
K1 – O1	2.756 (1)
K1 – O2^{iii}	2.756 (1)
K1 – O3	2.800 (1)
K1 – O3^{i}	2.858 (1)
K1 – Cl^{iii}	3.4102 (7)
K1 – Cl1	3.5845 (6)
O1^{i} – K1 – O2^{ii}	73.84 (4)
O1^{i} – K1 – O1	133.19 (5)
O1^{i} – K1 – O2^{iii}	84.60 (4)
O1^{i} – K1 – O3^{i}	72.35 (4)
O1^{i} – K1 – O3	138.47 (5)
O1^{i} – K1 – Cl2^{iii}	82.48 (3)
O1^{i} – K1 – Cl1	150.45 (3)
O2^{ii} – K1 – O1	84.24 (4)
O2^{ii} – K1 – O2^{iii}	157.02 (5)
O2^{ii} – K1 – O3^{i}	104.65 (4)
O2^{ii} – K1 – O3	77.81 (5)
O3^{ii} – K1 – Cl2^{iii}	112.88 (4)
O2^{ii} – K1 – Cl1	131.89 (3)
O1 – K1 – O2^{iii}	105.70 (4)
O1 – K1 – O3^{i}	154.34 (5)
O1 – K1 – O3	71.71 (4)
O1 – K1 – Cl2^{iii}	68.61 (3)
O1 – K1 – Cl1	52.79 (3)
O2^{iii} – K1 – O3^{i}	75.45 (4)
O2^{iii} – K1 – O3	124.79 (5)
O2^{iii} – K1 – Cl2^{iii}	55.09 (3)
O2^{iii} – K1 – Cl1	67.35 (3)

O3^{i} – K1 – O3	86.47 (4)
O3 – K1 – Cl2^{iii}	137.21 (3)
O3 – K1 – Cl1	69.54 (3)
O3^{i} – K1 – Cl2^{iii}	126.21 (3)
O3^{i} – K1 – Cl1	107.46 (3)
Cl2^{iii} – K1 – Cl1	74.07 (1)

Symmetry operators: *i*) *x*,1/2-*y*,-1/2+*z*, *ii*) 2-*x*,1/2+*y*,3/2-*z*, *iii*) 2-*x*,-*y*,1-*z*.

Table S3 Geometry of potassium cation coordination spheres in **KBr$_4$Q$^\bullet$·Me$_2$CO** (Å, º).

K1A – O2B^{i}	2.65 (1)	K1B – O1A	2.669 (9)
K1A – O1B	2.696 (9)	K1B – O2A^{iii}	2.676 (9)
K1A – O1A	2.755 (9)	K1B – O2B^{iv}	2.78 (1)
K1A – O3A	2.79 (1)	K1B – O1B	2.822 (9)
K1A – O2A^{ii}	2.919 (9)	K1B – O3A^{v}	2.83 (1)
K1A – O3B	2.93 (1)	K1B – O3B	2.86 (1)
K1A – Br1A	3.426 (3)	K1B – Br1B	3.487 (3)
K1A – Br2A^{ii}	3.572 (3)		
O2B^{i} – K1A – O1B	74.8 (3)	O1A – K1B – O2A^{iii}	71.8 (3)
O2B^{i} – K1A – O1A	152.6 (3)	O1A – K1B – O2B^{iv}	145.4 (3)
O2B^{i} – K1A – O3A	81.8 (3)	O1A – K1B – O1B	87.6 (3)
O2B^{i} – K1A – O2A^{ii}	77.9 (3)	O1A – K1B – O3A^{v}	110.8 (3)
O2B^{i} – K1A – O3B	113.9 (3)	O1A – K1B – O3B	78.7 (3)
O2B^{i} – K1A – Br1A	103.6 (2)	O1A – K1B – Br1B	90.2 (2)
O2B^{i} – K1A – Br2A^{ii}	128.7 (2)	O2A^{iii} – K1B – O2B^{iv}	79.9 (3)
O1B – K1A – O1A	88.4 (3)	O2A^{iii} – K1B – O1B	140.6 (3)
O1B – K1A – O3A	88.4 (3)	O2A^{iii} – K1B – O3A^{v}	73.6 (3)
O1B – K1A – O2A^{ii}	144.7 (3)	O2A^{iii} – K1B – O3B	138.4 (3)
O1B – K1A – O3B	64.3 (3)	O2A^{iii} – K1B – Br1B	90.7 (2)
O1B – K1A – Br1A	97.8 (2)	O2B^{iv} – K1B – O1B	102.8 (3)
O1B – K1A – Br2A^{ii}	156.4 (2)	O2B^{iv} – K1B – O3A^{v}	78.7 (3)
O1A – K1A – O3A	125.5 (3)	O2B^{iv} – K1B – O3B	135.6 (3)
O1A – K1A – O2A^{ii}	106.8 (3)	O2B^{iv} – K1B – Br1B	70.3 (2)
O1A – K1A – O3B	76.2 (3)	O1B – K1B – O3A^{v}	145.8 (3)
O1A – K1A – Br1A	56.7 (2)	O1B – K1B – O3B	63.8 (3)
O1A – K1A – Br2A^{ii}	69.0 (2)	O1B – K1B – Br1B	55.3 (2)
O3A – K1A – O2A^{ii}	70.7 (3)	O3A^{v} – K1B – O3B	91.0 (3)

O3A – K1A – O3B	82.9 (3)	O3A^{v} – K1B – Br1B	147.3 (2)
O3A – K1A – Br1A	135.3 (2)	O3B – K1B – Br1B	118.4 (2)
O3A – K1A – Br2A^{ii}	67.0 (2)		
O2A^{ii} – K1A – O3B	149.5 (3)		
O2A^{ii} – K1A – Br1A	67.4 (2)		
O2A^{ii} – K1A – Br2A^{ii}	54.2 (2)		
O3B – K1A – Br1A	130.5 (2)		
O3B – K1A – Br2A^{ii}	101.9 (2)		
Br1A – K1A – Br2A^{ii}	76.22 (6)		

Symmetry operators: *i*) 1-*x*,1-*y*,2-*z*; *ii*) 1-*x*,-*y*,2-*z*; *iii*) 1-*x*,-*y*,1-*z*; *iv*) 1-*x*,1-*y*,1-*z*; *v*) *x*,*y*,-1+*z*.

Table S4 Geometry of sodium cation coordination sphere in **NaBr$_4$Q$^{\bullet}$** (Å, °).

Na1 – O1^{i}	2.34 (1)
Na1 – O1	2.34 (1)
Na1 – O1^{ii}	2.37 (1)
Na1 – O1^{iii}	2.37 (1)
Na1 – Br1^{i}	3.122 (1)
Na1 – Br1	3.122 (1)
O1^{i} – Na1 – O1	180.00
O1^{i} – Na1 – O1^{ii}	77.7 (4)
O1^{i} – Na1 – O1^{iii}	102.3 (4)
O1^{i} – Na1 – Br1^{i}	65.0 (3)
O1^{i} – Na1 – Br1	115.0 (3)
O1 – Na1 – O1^{ii}	102.3 (4)
O1 – Na1 – O1^{iii}	77.7 (4)
O1 – Na1 – Br1^{i}	115.0 (3)
O1 – Na1 – Br1	65.0 (3)
O1^{ii} – Na1 – O1^{iii}	180.0 (6)
O1^{ii} – Na1 – Br1^{i}	94.8 (3)
O1^{ii} – Na1 – Br1	85.2 (3)
O1^{iii} – Na1 – Br1^{i}	85.2 (3)
O1^{iii} – Na1 – Br1	94.8 (3)
Br1^{i} – Na1 – Br1	180.00

Symmetry operators: *i*) 2-*x*,-*y*,-*z*; *ii*) *x*,-1+*y*,*z*; *iii*) 2-*x*,1-*y*,-*z*.

Table S5 Geometry of rubidium cation coordination sphere in **RbBr$_4$Q$^{\bullet}$** (Å, º).

Rb1 – O1	2.819 (7)
Rb1 – O1^{i}	2.847 (7)
Rb1 – O2^{ii}	2.851 (7)
Rb1 – O2^{iii}	2.881 (7)
Rb1 – Br1^{i}	3.585 (1)
Rb1 – Br2^{iv}	3.589 (1)
O1 – Rb1 – O1^{i}	99.8 (2)
O1 – Rb1 – O2^{ii}	78.8 (2)
O1 – Rb1 – O2^{iii}	162.6 (2)
O1 – Rb1 – Br1^{i}	71.6 (1)
O1 – Rb1 – Br2^{iv}	133.5 (1)
O1^{i} – Rb1 – O2^{ii}	162.6 (2)
O1^{i} – Rb1 – O2^{iii}	77.8 (2)
O1^{i} – Rb1 – Br1^{i}	54.5 (1)
O1^{i} – Rb1 – Br2^{iv}	87.6 (1)
O2^{ii} – Rb1 – O2^{iii}	98.2 (2)
O2^{ii} – Rb1 – Br1^{i}	109.4 (1)
O2^{ii} – Rb1 – Br2^{iv}	106.1 (1)
O2^{iii} – Rb1 – Br1^{i}	93.7 (1)
O2^{iii} – Rb1 – Br2^{iv}	63.8 (1)
Br1^{i} – Rb1 – Br2^{iv}	140.32 (3)

Symmetry operators: *i*) -1+*x*,*y*,*z*; *ii*) 3/2-*x*,1-*y*,-1/2+z; *iii*) 1/2-*x*,1-*y*,-1/2+z; *iv*) 1-*x*,1/2+*y*,1/2-*z*.

S3 ORTEP drawings of cation coordination spheres

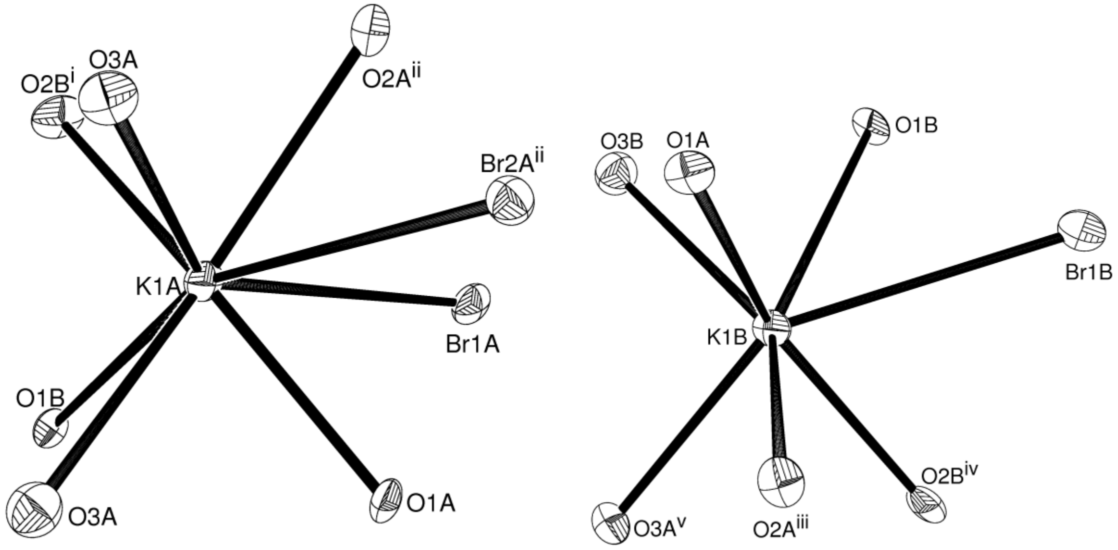

Figure S3 ORTEP-3 drawing of coordination spheres of potassium cations in **$KBr_4Q^{\bullet}\cdot Me_2CO$**. Displacement ellipsoids are drawn for the probability of 50 %. Symmetry operators: *i*) 2-*x*, 1-*y*, 1-*z*; *ii*) 2-*x*, 1-*y*,-*z*; *iii*) 1-*x*, 1-*y*, -*z*; *iv*) 1-*x*, 1-*y*, 1-*z*; *v*) -1+*x*, *y*, *z*.

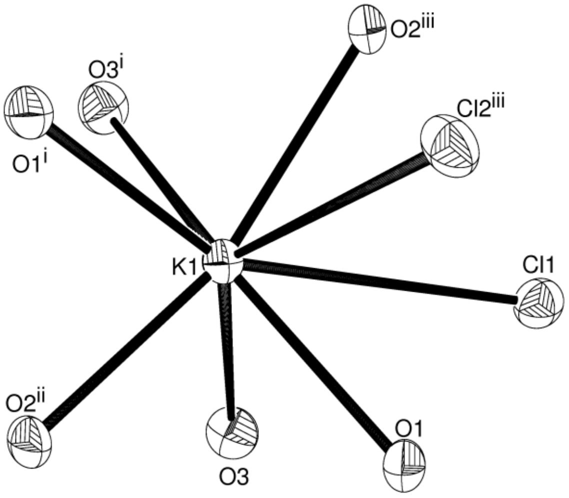

Figure S4 ORTEP-3 drawing of coordination sphere of potassium cation in **$KCl_4Q^{\bullet}\cdot Me_2CO$**. Displacement ellipsoids are drawn for the probability of 50 %. Symmetry operators: *i*) *x*, 1/2-*y*, -1/2+*z*; *ii*) 2-*x*, -*y*, 1-*z*; *iii*) 2-*x*, -*y*, 1-*z*.

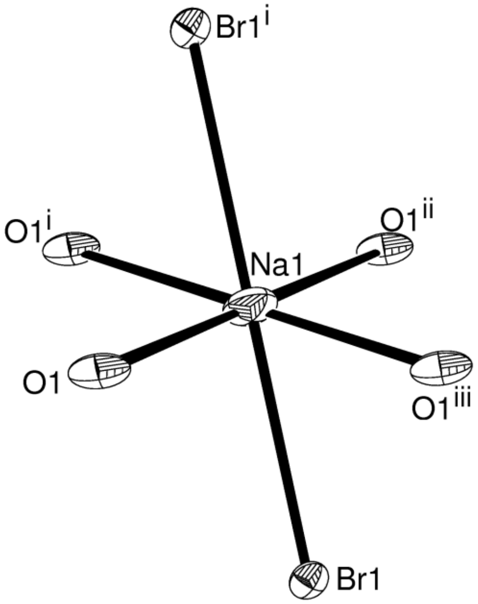

Figure S5 ORTEP-3 drawing of coordination sphere of sodium cation in **NaBr$_4$Q$^{\bullet}$**. Displacement ellipsoids are drawn for the probability of 50 %. Symmetry operators: *i*) 2-*x*, -*y*, -*z*; *ii*) *x*, -1+*y*, *z*; *iii*) 2-*x*, 1-*y*, -*z*.

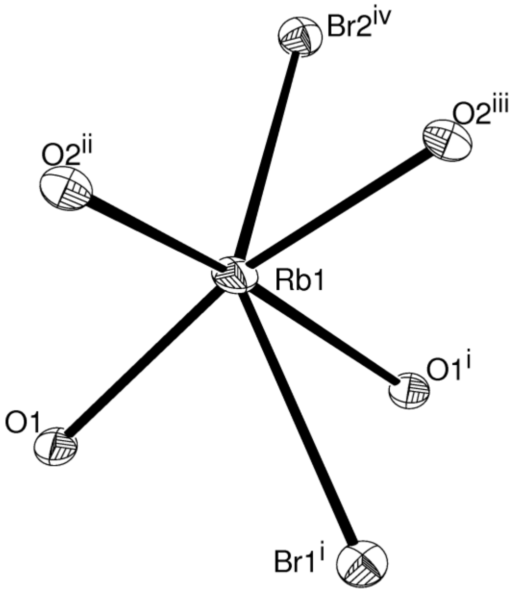

Figure S6 ORTEP-3 drawing of coordination sphere of rubidium cation in **RbBr$_4$Q$^{\bullet}$**. Displacement ellipsoids are drawn for the probability of 50 %. Symmetry operators: *i*) -1+*x*, *y*, *z*; *ii*) 1/2-*x*, 1-*y*, -1/2+*z*; *iii*) 3/2-*x*, 1-*y*, -1/2+*z*; *iv*) 1-*x*, 1/2+*y*, 1/2-*z*.

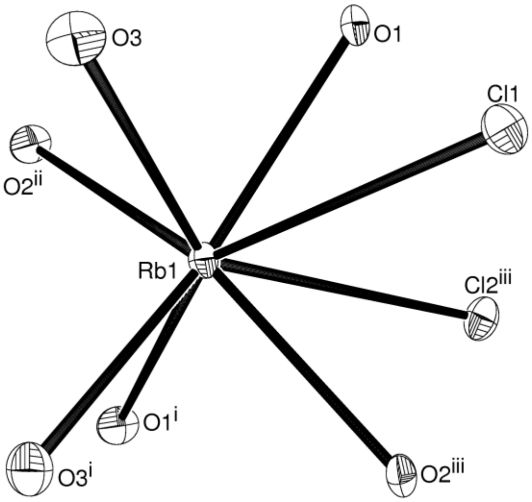

Figure S7 ORTEP-3 drawing of coordination sphere of rubidium cation in **$RbCl_4Q^{\bullet}\cdot Me_2CO$**. Displacement ellipsoids are drawn for the probability of 50 %. Symmetry operators: *i*) *x*, 1/2-*y*, -1/2+*z*; *ii*) 2-*x*, 1/2+*y*, 3/2-*z*; *iii*) 2-*x*, -*y*, 1-*z*.

S4 ORTEP drawings of semiquinone radical anions and Br_4Q

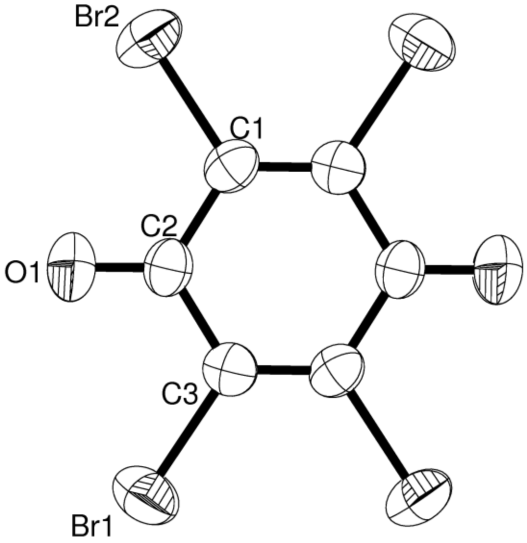

Figure S9 ORTEP-3 drawing of a molecule of tetrabromoquinone (bromanil). Displacement ellipsoids are drawn for the probability of 50 %.

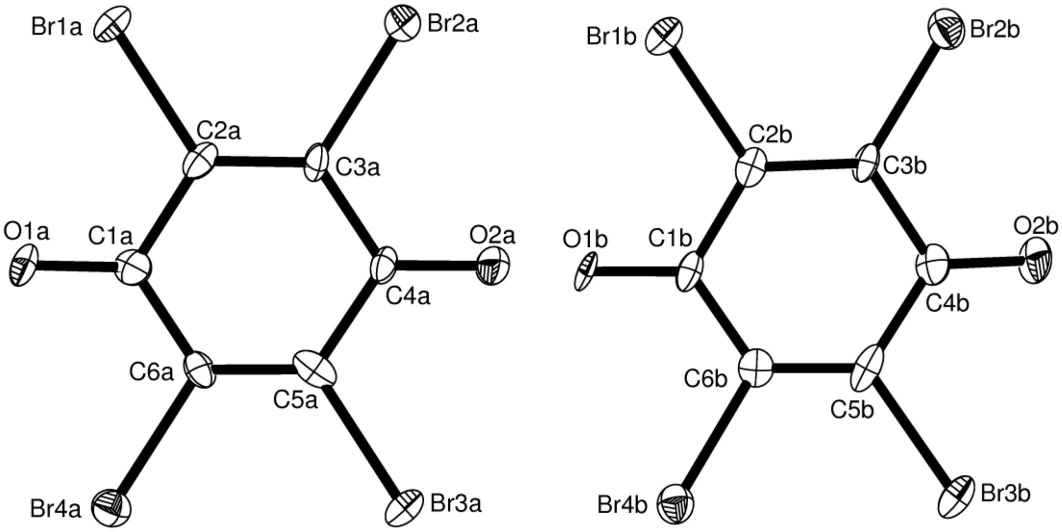

Figure S10 ORTEP-3 drawings of two symmetry-independent tetrabromosemiquinone radical anions from $\mathbf{KBr_4Q^{\bullet}\cdot Me_2CO}$. Displacement ellipsoids are drawn for the probability of 50 %.

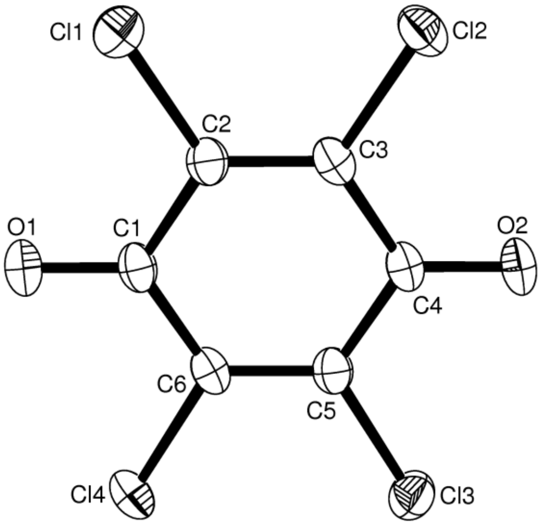

Figure S11 ORTEP-3 drawing of tetrachlorosemiquinone radical anion from **$KCl_4Q^{\bullet}\cdot Me_2CO$**. Displacement ellipsoids are drawn for the probability of 50 %.

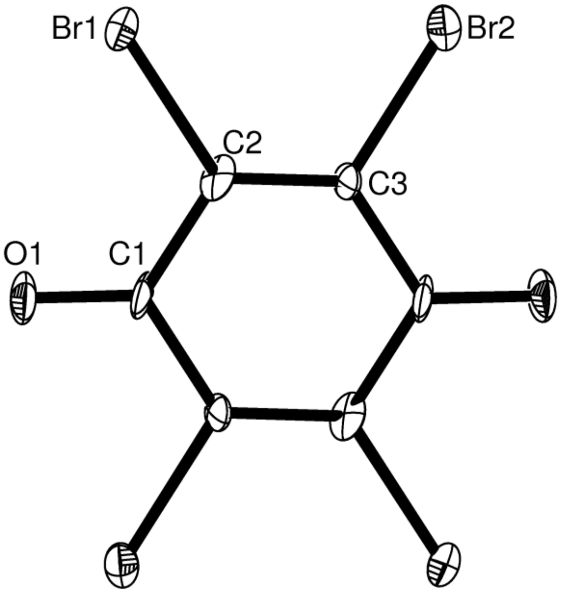

Figure S12 ORTEP-3 drawing of tetrabromosemiquinone radical anion from **$NaBr_4Q^{\bullet}$**. Displacement ellipsoids are drawn for the probability of 50 %.

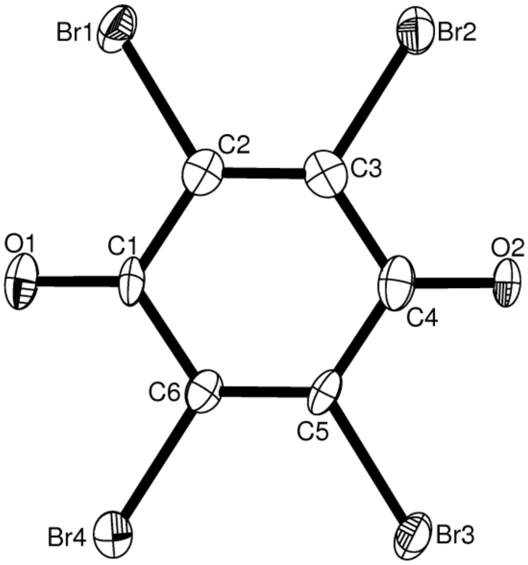

Figure S13 ORTEP-3 drawing of tetrabromosemiquinone radical anion from **$RbBr_4Q^{\bullet}$** measured at 100 K. Displacement ellipsoids are drawn for the probability of 50 %.

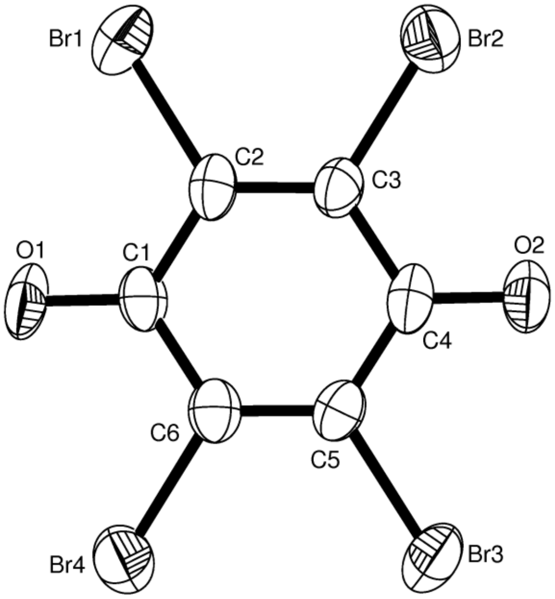

Figure S14 ORTEP-3 drawing of tetrabromosemiquinone radical anion from **$RbBr_4Q^{\bullet}$** measured at room temperature. Displacement ellipsoids are drawn for the probability of 50 %.

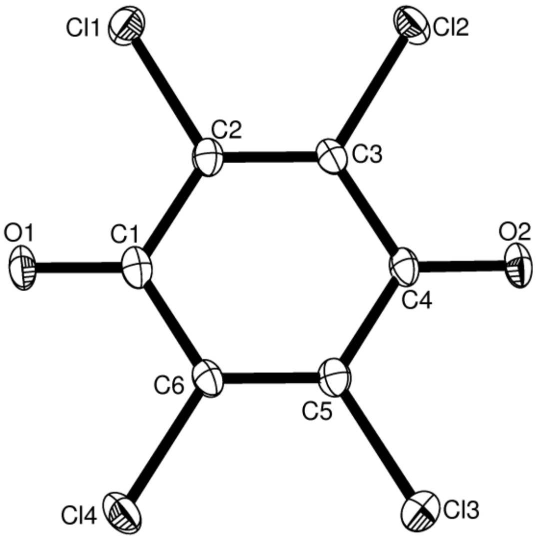

Figure S15 ORTEP-3 drawing of tetrachlorosemiquinone radical anion from **$RbCl_4Q^{\bullet}{\cdot}Me_2CO$**. Displacement ellipsoids are drawn for the probability of 50 %.

S5 Geometry of **RbBr$_4$Q$^\bullet$** measured at room temperature

Table S7 Bond lengths in **RbBr$_4$Q$^\bullet$** measured at RT.

C1 – C2	1.434 (12)
C2 – C3	1.365 (10)
C3 – C4	1.438 (11)
C4 – C5	1.440 (12)
C5 – C6	1.349 (10)
C6 – C1	1.444 (11)
C1 – O1	1.262 (9)
C4 – O2	1.261 (9)
C2 – Br1	1.885 (8)
C3 – Br2	1.892 (8)
C5 – Br3	1.898 (8)
C6 – Br4	1.893 (8)

S6 Experimental details on the structures of Br_4Q and room-temperature $RbBr_4Q^{\bullet}$

Two crystal structures of tetrabromoquinone have been deposited in the CSD with REFCODE: TBENQ [1] and TBENQ01 [2]. However, in the first one the geometric parameters are unrealistic, while no atomic coordinates are given for the second one. Therefore, we redetermined the crystal structure of tetrabromoquinone to obtain reliable geometric data for comparison with the structures of semiquinone radicals presented in this paper. The molecule is centrosymmetric, its centroid being located on a crystallographic inversion centre. The ORTEP drawing of the tetrabromosemiquinone molecule is shown in Fig. S9, and its geometry is discussed in the main text (also listed in Table 3).

Crystallographic measurements were performed at room temperature since lengths of the covalent bonds are almost temperature-independent (at least in the range 100 – 293 K) and tetrabromoquinone is stable in air and at room temperature. A structure of **$RbBr_4Q^{\bullet}$** measured at RT (Fig. S13, Table S7) confirms this finding. Dark-yellow crystals were grown from acetone solution at room temperature. According to the unit cell our structure is isostructural with the one studied by Ueda [1]. Crystallographic, data collection and structure refinement data are given in the Table S8.

Table S8 Crystallographic, data collection and structure refinement data of tetrabromoquinone and **$RbBr_4Q^{\bullet}$** measured at room temperature.

Compound	**$RbBr_4Q^{\bullet}$**	**Br_4Q**
Empirical formula	$C_6Br_4O_2Rb$	$C_6Br_4O_2$
Formula wt. / g mol^{-1}	509.17	423.68
Colour	red	dark yellow
Crystal dimensions / mm	0.10 x 0.08 x 0.04	0.15 x 0.08 x 0.04
Space group	$P\ 2_1\ 2_1\ 2_1$	$P\ 2_1/c$
a / Å	4.3382 (1)	9.0589 (3)
b / Å	13.8640 (2)	6.1970 (2)
c / Å	17.4665 (2)	8.6426 (3)
α / °	90	90
β / °	90	105.932 (3)
γ / °	90	90
Z	4	2

V / Å^3	1050.52 (3)	466.54 (3)
D_{calc} / g cm^{-3}	3.219	3.016
μ / mm^{-1}	24.044	20.726
Θ range / °	4.07 – 75.84	5.08 – 75.00
T / K	293 (2)	293 (2)
Diffractometer type	Xcalibur Nova	Xcalibur Nova
Range of h, k, l	$-5 < h < 4$; $-17 < k < 14$; $-20 < l < 21$	$-11 < h < 10$; $-7 < k < 7$; $-10 < l < 10$
Reflections collected	3488	2308
Independent reflections	1920	954
Observed reflections ($I \geq 2\sigma$)	1771	867
Absorption correction	Multi-scan	Multi-scan
T_{min}, T_{max}	1.000; 0.18836	0.4360; 0.1670
R_{int}	0.0278	0.0179
$R (F)$	0.0450	0.0353
$R_w (F^2)$	0.1241	0.0949
Goodness of fit	1.032	1.090
No. of parameters, restraints	118, 0	55, 0
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (eÅ^{-3})	1.378; -0.600	0.606; -0.475

S7 IR spectrum of $\mathbf{RbBr_4Q^{\bullet}}$

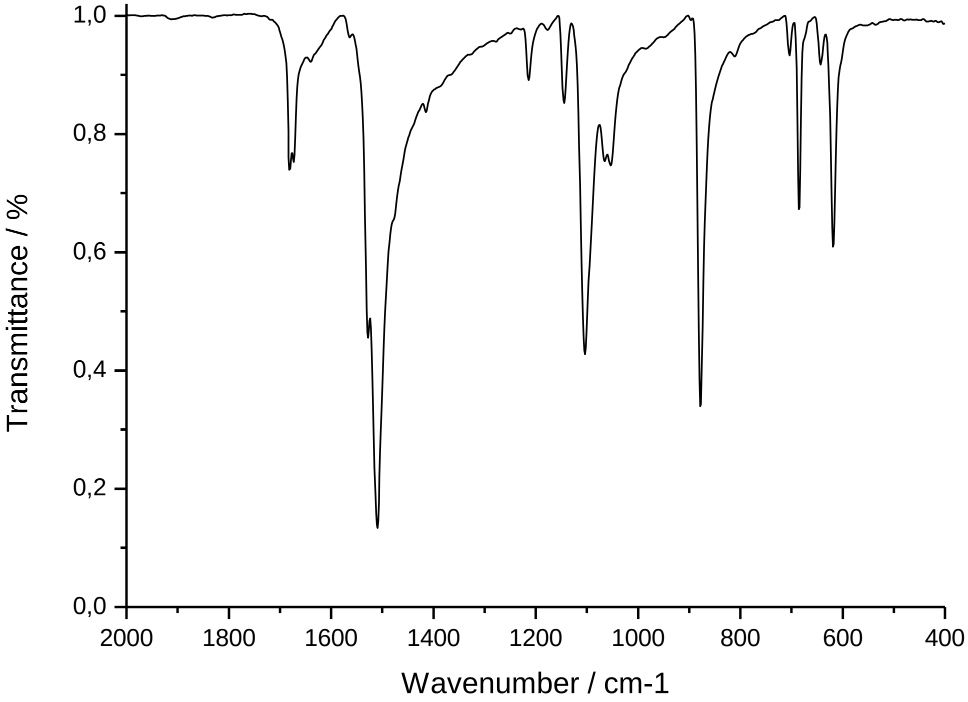

Figure S16 IR spectrum of $\mathbf{RbBr_4Q^{\bullet}}$.

Infrared spectra were recorded by using KBr pellets with a Bruker Alpha-T spectrometer, in the 4000–350 cm–1 region. At wavelengths greater than 2000 cm^{-1} there are only a few weak bands which are attributed to impurities. The spectrum can be assigned in analogy to a detailed study of similar quinones and hydroquinones [3]; it can be noted that frequencies of double bonds (C=O and C=C) are significantly red-shifted, while single bonds (C-C) are blue-shifted. This is in accord with bond lengths and quantum chemical calculations which indicate that the structure of the radical is between aromatic and quinoid (see Results and Discussion).

S8 References

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