Spin-coupling in dimer of 2,3-dicyano-5,6-dichlorosemiquinone radical anions characterised by ring separation distance of 2.81 Å

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Supplementary Material

S1 ORTEP PLOTS

S2 IR SPECTRA

S3 GEOMETRIES OF CRYSTAL STRUCTURE EXCERPTS USED FOR CALCULATION OF VIBRATIONS

S4 DETAILS OF REFINEMENT OF ACENTRIC/TWINNED STRUCTURES

S1 ORTEP PLOTS

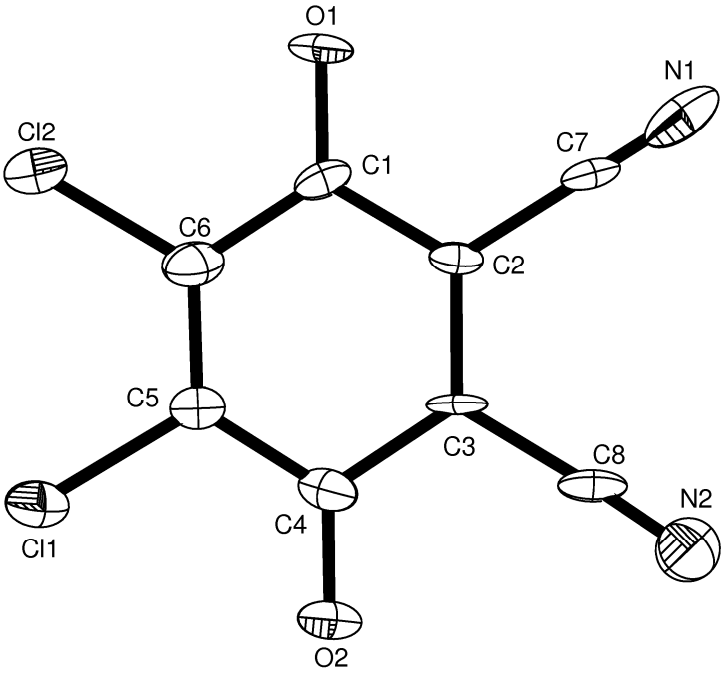

Figure S1 ORTEP-3 drawing of a DDQ anion in CsDDQ·2H_2O measured at 120 K. Displacement ellipsoids are drawn for the probability of 50 %.

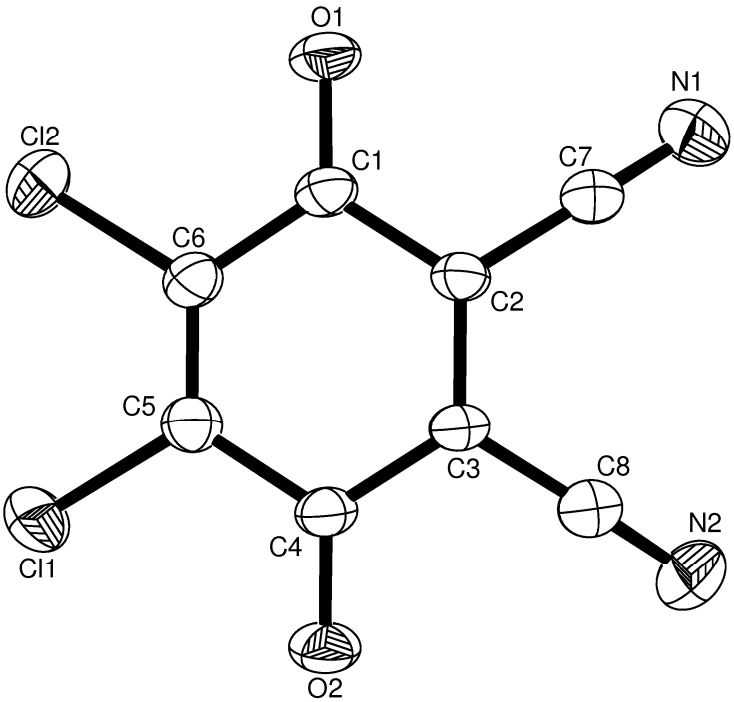

Figure S2 ORTEP-3 drawing of a DDQ anion in CsDDQ·2H_2O measured at RT. Displacement ellipsoids are drawn for the probability of 50 %.

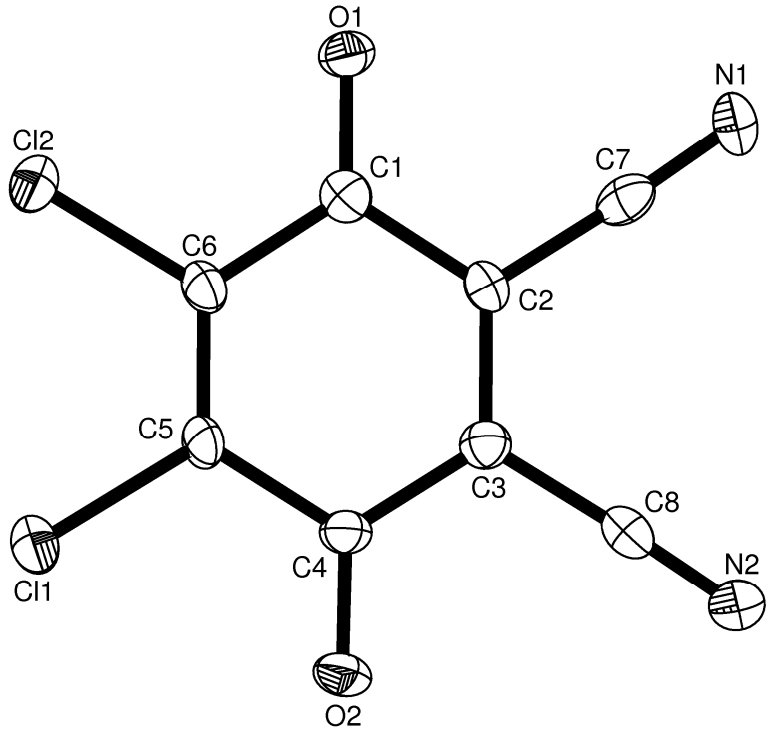

Figure S3 ORTEP-3 drawing of a DDQ anion in RbDDQ·2H_2O measured at 120 K. Displacement ellipsoids are drawn for the probability of 50 %.

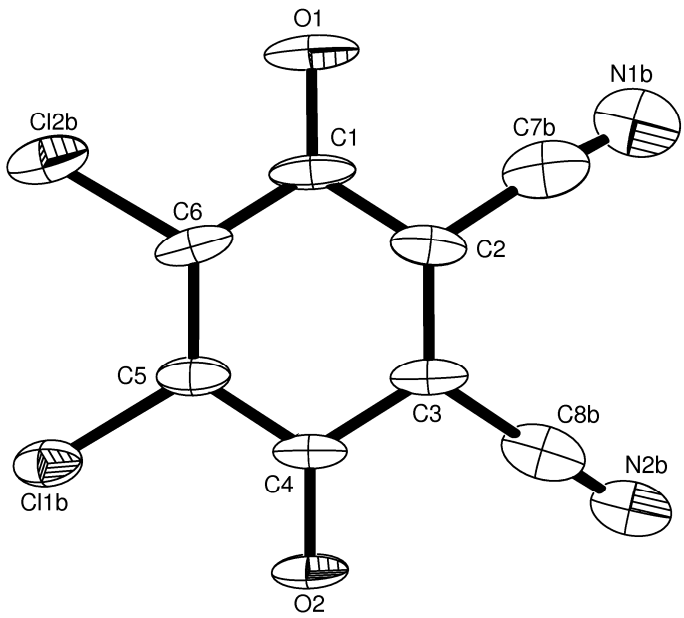

Figure S4 ORTEP-3 drawing of a DDQ anion in LiDDQ·2H_2O·Me_2CO measured at 120 K. Only the major component of the disorder is shown. Displacement ellipsoids are drawn for the probability of 50 %.

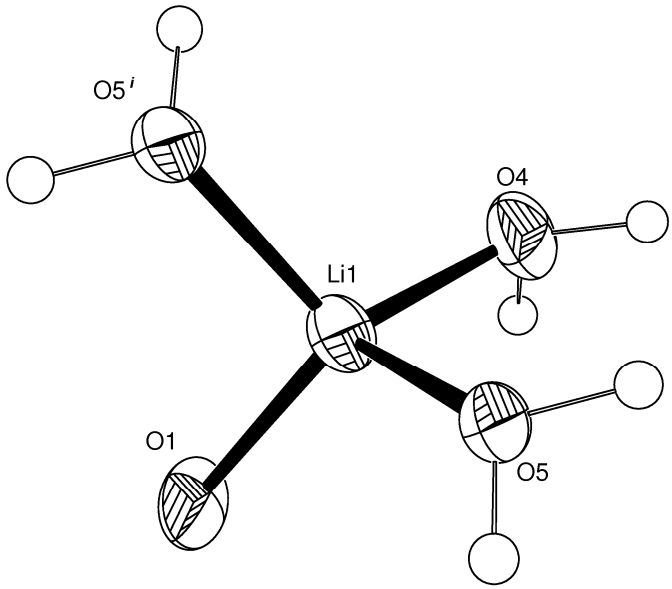

Figure S5 ORTEP-3 drawing of the Li coordination sphere from LiDDQ·2H_2O·Me_2CO measured at120 K. Displacement ellipsoids are drawn for the probability of 50 %. Symmetry operator: *i*) 1–*x*, 1–*y*, –*z*.

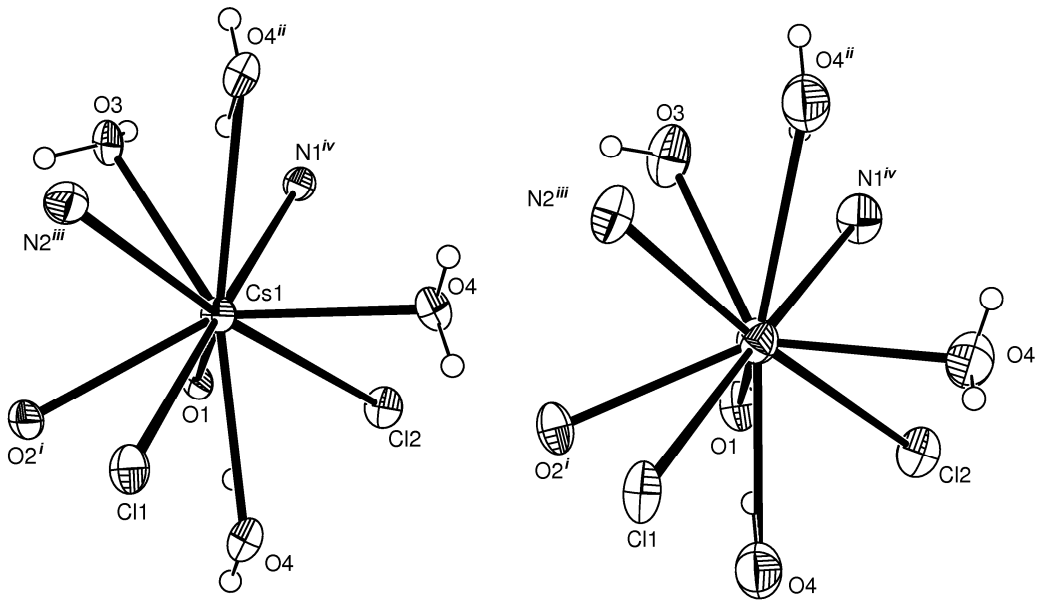

Figure S6 ORTEP-3 drawing of the Cs coordination sphere in CsDDQ·2H_2O measured at a) 120 K and b) RT. Displacement ellipsoids are drawn for the probability of 50 %. Symmetry operators: *i*) *x*, *y*, –1+*z*; *ii*) 1/2+*x*, 1/2–*y*, 1–*z*; *iii*) –*x*, 1–*y*, –1+*z*; *iv*) –*x*, 1–*y*, *z*.

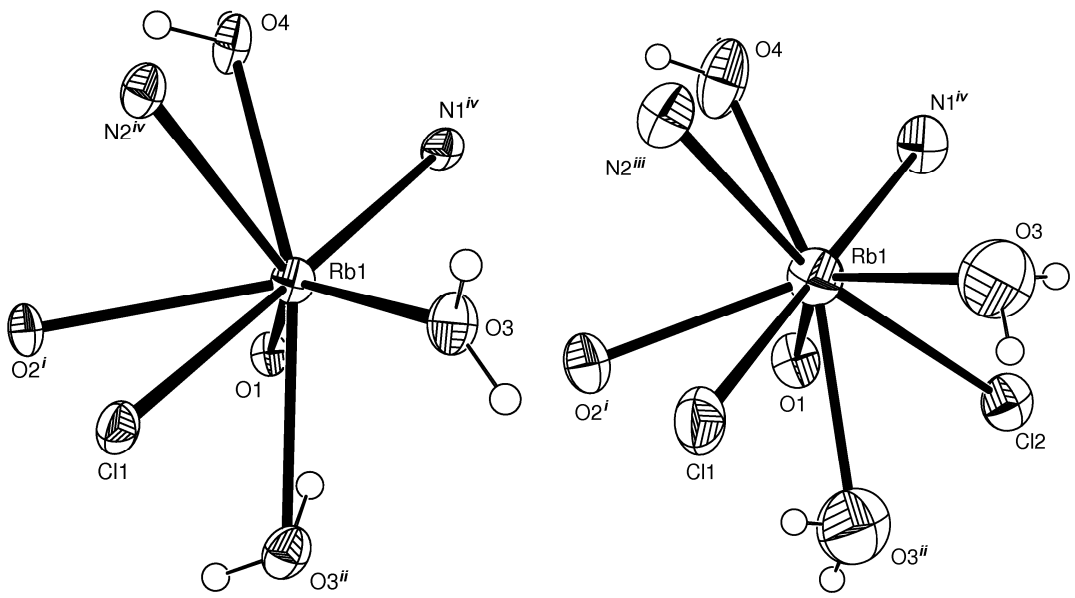

Figure S7 ORTEP-3 drawing of the Cs coordination sphere in RbDDQ·$2H_2O$ measured at a) 120 K and b) RT. Displacement ellipsoids are drawn for the probability of 50 %. Symmetry operators: *i*) *x*, *y*, 1+*z*; *ii*) 1/2+*x*, 3/2–*y*, 2–*z*; *iii*) –*x*, 1–*y*, *z*; *iv*) –1/2+*x*, 3/2–*y*, 2–*z*.

S2 IR SPECTRA

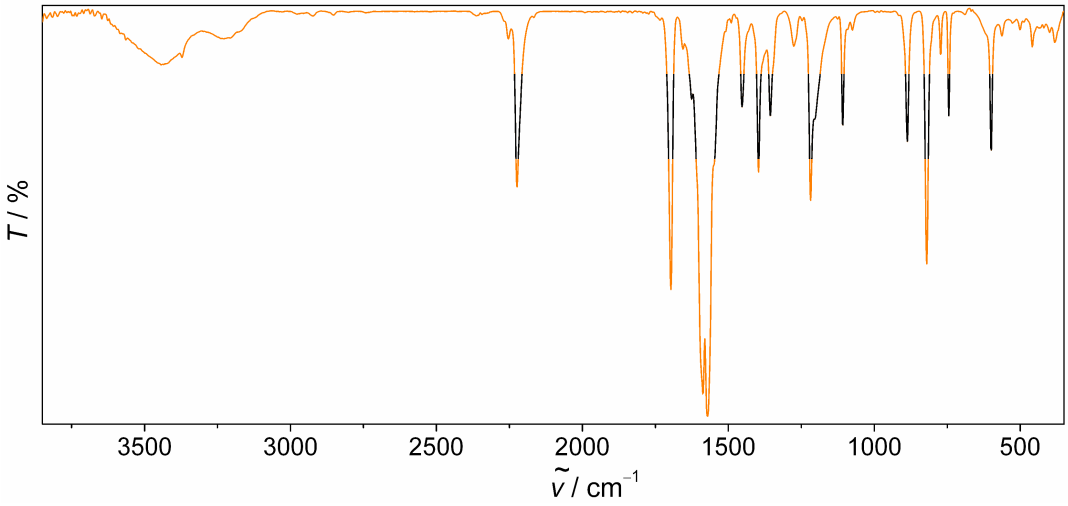

Figure S8 IR spectrum of RbDDQ·2H_2O**.**

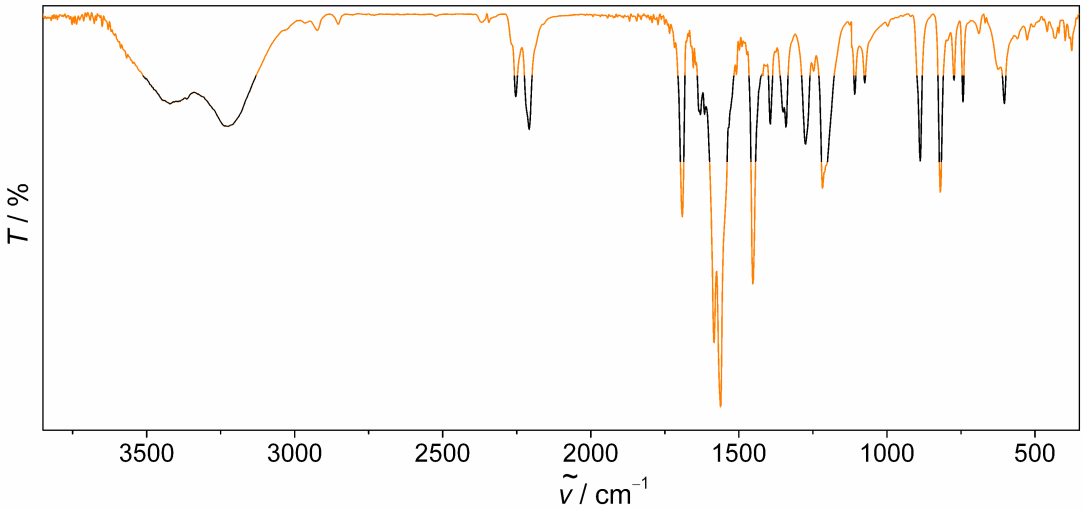

Figure S9 IR spectrum of CsDDQ·2H_2O**.**

S3 GEOMETRIES OF CRYSTAL STRUCTURE EXCERPTS USED FOR CALCULATION OF VIBRATIONS

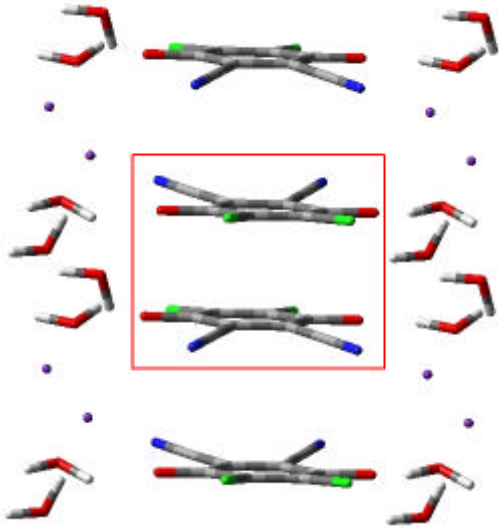

Figure S10 Excerpt taken from the crystal structure of RbDDQ·2H_2O (RT); atoms whose positions were optimized are within the central frame

Table S1 Atomic coordinates of the excerpt from the crystal structure of RbDDQ·2H2O (RT) used for calculation of vibrations.

atom(fragment)	x/Å	y/Å	z/Å
O(Fragment=1)	11.08708992	8.15500968	21.15787030
C(Fragment=1)	11.08513728	8.15864544	22.39588708
C(Fragment=1)	11.28040128	9.36208200	23.18756370
C(Fragment=1)	10.94519808	6.91339764	23.18275400
C(Fragment=1)	11.28495744	9.33663168	24.56698566
C(Fragment=1)	11.61495360	10.56006492	22.44206020
Cl(Fragment=1)	10.81892736	5.46927377	22.27891518
C(Fragment=1)	10.93738752	6.89703672	24.52177448
C(Fragment=1)	11.07732672	8.12228784	25.34230930
C(Fragment=1)	11.59933248	10.51643580	25.34230930
N(Fragment=1)	11.90264256	11.44900824	21.82064696
Cl(Fragment=1)	10.83910464	5.43182544	25.39338831
O(Fragment=1)	11.06691264	8.10774480	26.56301116
N(Fragment=1)	11.88506880	11.39992548	25.99161880
O(Fragment=2)	14.94811008	10.02379032	21.15787030
C(Fragment=2)	14.95006272	10.02015456	22.39588708
C(Fragment=2)	14.75479872	8.81671800	23.18756370
C(Fragment=2)	15.09000192	11.26540236	23.18275400
C(Fragment=2)	14.75024256	8.84216832	24.56698566
C(Fragment=2)	14.42024640	7.61873508	22.44206020
Cl(Fragment=2)	15.21627264	12.70952623	22.27891518
C(Fragment=2)	15.09781248	11.28176328	24.52177448
C(Fragment=2)	14.95787328	10.05651216	25.34230930
C(Fragment=2)	14.43586752	7.66236420	25.34230930
N(Fragment=2)	14.13255744	6.72979176	21.82064696
Cl(Fragment=2)	15.19609536	12.74697456	25.39338831
O(Fragment=2)	14.96828736	10.07105520	26.56301116
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C(Fragment=3)	17.45399808	6.91339764	23.18275400
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O(Fragment=5)	11.32270848	10.05287640	28.69947990
H(Fragment=5)	11.14306560	9.65294280	29.53155800
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H(Fragment=5)	10.07562240	12.36158400	19.83520280
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Rb(Fragment=6)	13.67271072	11.78168028	19.06767087
Rb(Fragment=7)	13.67271072	11.78168028	28.68707087
Rb(Fragment=8)	12.36248928	6.39711972	19.06767087
Rb(Fragment=9)	12.36248928	6.39711972	28.68707087
H(Fragment=10)	15.11343360	6.01718280	18.62315840
O(Fragment=10)	15.88472640	5.56453068	18.93001726
H(Fragment=10)	15.95957760	5.81721600	19.83520280
O(Fragment=10)	14.71249152	8.12592360	19.08007990
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H(Fragment=10)	15.12645120	8.65310880	28.04055100
O(Fragment=10)	14.71249152	8.12592360	28.69947990
H(Fragment=10)	14.89213440	8.52585720	29.53155800
H(Fragment=10)	15.11343360	6.01718280	28.24255840
O(Fragment=10)	15.88472640	5.56453068	28.54941726
H(Fragment=10)	15.95957760	5.81721600	29.45460280
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H(Fragment=10)	17.43056640	12.16161720	18.62315840
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Rb(Fragment=12)	20.18151072	11.78168028	19.06767087
Rb(Fragment=13)	18.87128928	6.39711972	19.06767087
Rb(Fragment=14)	18.87128928	6.39711972	28.68707087
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O(Fragment=15)	21.22129152	8.12592360	28.69947990
H(Fragment=15)	21.40093440	8.52585720	29.53155800
H(Fragment=15)	21.62223360	6.01718280	28.24255840
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H(Fragment=15)	22.46837760	5.81721600	29.45460280

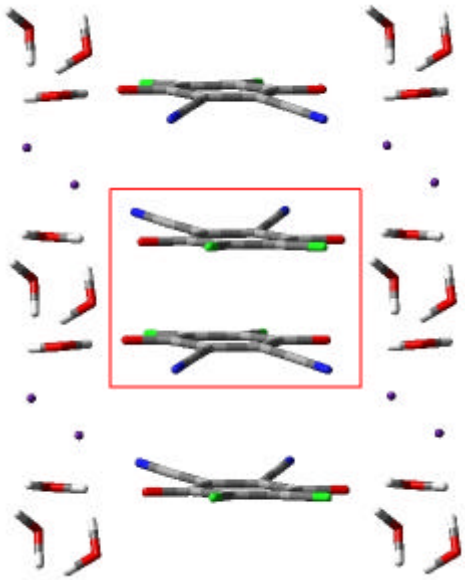

Figure S9 Excerpt taken from the crystal structure of CsDDQ·2H_2O (RT); ; atoms whose positions were optimized are within the central frame

Table S2 Atomic coordinates of the excerpt from the crystal structure of CsDDQ·2H_2O (RT) used for calculation of vibrations.

atom(fragment)	x/Å	y/Å	z/Å
O(Fragment=1)	4.57989642	10.15467476	7.48728522
C(Fragment=1)	4.60315812	10.12369872	8.72881182
C(Fragment=1)	4.85637834	8.91198892	9.48057084
C(Fragment=1)	4.43080000	11.34269700	9.54997902
C(Fragment=1)	5.20929156	7.76405332	8.70926022
C(Fragment=1)	4.86036606	8.87554652	10.87068960
Cl(Fragment=1)	4.29477444	12.81697429	8.69205481
C(Fragment=1)	4.42238148	11.30443248	10.88633088
N(Fragment=1)	5.53429074	6.87485876	8.06699016
C(Fragment=1)	4.61711514	10.07267936	11.67230520
C(Fragment=1)	5.23720560	7.69663488	11.59116606
Cl(Fragment=1)	4.28746362	12.74099189	11.81239241
O(Fragment=1)	4.61046894	10.05810240	12.90992148
N(Fragment=1)	5.56419864	6.77464216	12.17478132
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C(Fragment=2)	8.08310844	10.45714668	8.70926022
C(Fragment=2)	8.43203394	9.34565348	10.87068960
Cl(Fragment=2)	8.99762556	5.40422571	8.69205481
C(Fragment=2)	8.87001852	6.91676752	10.88633088
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C(Fragment=2)	8.05519440	10.52456512	11.59116606
Cl(Fragment=2)	9.00493638	5.48020811	11.81239241
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C(Fragment=3)	11.50656606	8.87554652	10.87068960
Cl(Fragment=3)	10.94097444	12.81697429	8.69205481
C(Fragment=3)	11.06858148	11.30443248	10.88633088
N(Fragment=3)	12.18049074	6.87485876	8.06699016
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C(Fragment=3)	11.88340560	7.69663488	11.59116606
Cl(Fragment=3)	10.93366362	12.74099189	11.81239241
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N(Fragment=3)	12.21039864	6.77464216	12.17478132
N(Fragment=4)	14.37440136	11.44655784	12.17478132
O(Fragment=4)	15.32813106	8.16309760	12.90992148
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Cl(Fragment=4)	15.64382556	5.40422571	8.69205481
C(Fragment=4)	15.07823394	9.34565348	10.87068960
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Cs(Fragment=5)	6.01022512	11.89971908	5.28958762
Cs(Fragment=6)	12.65642512	11.89971908	5.28958762
Cs(Fragment=7)	12.65642512	11.89971908	15.06538762
Cs(Fragment=8)	7.28217488	6.32148092	15.06538762
Cs(Fragment=9)	7.28217488	6.32148092	5.28958762
Cs(Fragment=10)	13.92837488	6.32148092	5.28958762
Cs(Fragment=11)	13.92837488	6.32148092	15.06538762
Cs(Fragment=12)	6.01022512	11.89971908	15.06538762
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H(Fragment=13)	2.41257060	11.98954960	4.89767580
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H(Fragment=13)	4.75203300	8.69151240	6.11965080
O(Fragment=13)	4.82979354	8.27789116	5.28870780
H(Fragment=13)	4.85837220	8.83728200	4.62395340
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O(Fragment=13)	3.82289424	5.69594712	15.33627504
H(Fragment=13)	2.91103560	5.95833240	15.28935120
H(Fragment=13)	4.23362940	6.23165040	4.89767580
O(Fragment=13)	3.82289424	5.69594712	5.56047504
H(Fragment=13)	2.91103560	5.95833240	5.51355120
H(Fragment=13)	9.05877060	11.98954960	4.89767580
O(Fragment=13)	9.46950576	12.52525288	5.56047504
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O(Fragment=13)	8.46260646	9.94330884	5.28870780
H(Fragment=13)	8.54036700	9.52968760	6.11965080
H(Fragment=13)	8.43402780	9.38391800	4.62395340
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O(Fragment=13)	8.46260646	9.94330884	15.06450780
H(Fragment=13)	8.54036700	9.52968760	15.89545080
H(Fragment=13)	9.05877060	11.98954960	14.67347580
O(Fragment=13)	9.46950576	12.52525288	15.33627504
H(Fragment=13)	10.38136440	12.26286760	15.28935120

H(Fragment=13)	11.39823300	8.69151240	6.11965080
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H(Fragment=13)	11.50457220	8.83728200	14.39975340
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H(Fragment=13)	11.39823300	8.69151240	15.89545080
H(Fragment=13)	10.87982940	6.23165040	14.67347580
O(Fragment=13)	10.46909424	5.69594712	15.33627504
H(Fragment=13)	9.55723560	5.95833240	15.28935120
H(Fragment=13)	10.87982940	6.23165040	4.89767580
O(Fragment=13)	10.46909424	5.69594712	5.56047504
H(Fragment=13)	9.55723560	5.95833240	5.51355120
H(Fragment=13)	15.70497060	11.98954960	4.89767580
O(Fragment=13)	16.11570576	12.52525288	5.56047504
H(Fragment=13)	17.02756440	12.26286760	5.51355120
O(Fragment=13)	15.10880646	9.94330884	5.28870780
H(Fragment=13)	15.18656700	9.52968760	6.11965080
H(Fragment=13)	15.08022780	9.38391800	4.62395340
H(Fragment=13)	15.08022780	9.38391800	14.39975340
O(Fragment=13)	15.10880646	9.94330884	15.06450780
H(Fragment=13)	15.18656700	9.52968760	15.89545080
H(Fragment=13)	15.70497060	11.98954960	14.67347580
O(Fragment=13)	16.11570576	12.52525288	15.33627504
H(Fragment=13)	17.02756440	12.26286760	15.28935120
H(Fragment=13)	16.20343560	5.95833240	5.51355120
O(Fragment=13)	17.11529424	5.69594712	5.56047504
H(Fragment=13)	17.52602940	6.23165040	4.89767580
H(Fragment=13)	16.20343560	5.95833240	15.28935120
O(Fragment=13)	17.11529424	5.69594712	15.33627504
H(Fragment=13)	17.52602940	6.23165040	14.67347580
H(Fragment=13)	3.73516440	12.26286760	15.28935120
O(Fragment=13)	2.82330576	12.52525288	15.33627504
H(Fragment=13)	2.41257060	11.98954960	14.67347580

S4 DETAILS OF REFINEMENT OF ACENTRIC/TWINNED STRUCTURES

	CsDDQ·2H$_2$O, 120 K		
	non-twinned	inverted	twinned
*R*1	0.0778	0.0628	0.0591
*R*1 (all data)	0.0804	0.0649	0.0611
w*R*2	0.2222	0.1716	0.1600
GooF	1.457	1.119	1.040
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (eÅ^{-3})	2.11; -1.56	1.62; -1.25	1.59; -1.32
Flack parameter	0.70(2)	0.26(2)	
BASF			0.71879

	CsDDQ·2H$_2$O, RT		
	non-twinned	inverted	twinned
*R*1	0.0369	0.0804	0.0369
*R*1 (all data)	0.0377	0.0817	0.0377
w*R*2	0.0940	0.2304	0.0936
GooF	1.050	2.670	1.070
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (eÅ^{-3})	0.83; -0.93	2.43; -1.21	0.83; -0.93
Flack parameter	-0.014(8)	1.02(3)	
BASF			0.00001

	RbDDQ·2H$_2$O, 120 K		
	non-twinned	inverted	twinned
*R*1	0.0441	0.0425	0.0414
*R*1 (all data)	0.0455	0.0439	0.0611
w*R*2	0.1270	0.1218	0.1193
GooF	1.202	1.152	1.128
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (eÅ^{-3})	0.69; -0.73	0.71; -0.76	0.70; -0.75
Flack parameter	0.61(4)	0.34(4)	
BASF			0.64085

	RbDDQ·2H$_2$O, RT		
	non-twinned	inverted	twinned
*R*1	0.0434	0.0438	0.0421
*R*1 (all data)	0.0456	0.0460	0.0443
w*R*2	0.1229	0.1236	0.1194
GooF	1.060	1.067	1.040
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (eÅ^{-3})	0.62; -0.82	0.62; -0.82	0.62; -0.81
Flack parameter	0.44(4)	0.50(4)	
BASF			0.47409