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Bistriazole-*p*-benzoquinone and its alkali salts: electrochemical behaviour in aqueous alkaline solutions

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Content:

1) Thermogravimetric analysis of H_2-btbq·$2H_2O$

The TG analysis of H_2-btbq·$2H_2O$ revealed two steps (Fig. S1). The first step corresponds to the removal of two water molecules (measured: 16.21 %; calculated: 15.92 %). At the second step around 300 °C, the material decomposes (with explosive violence).

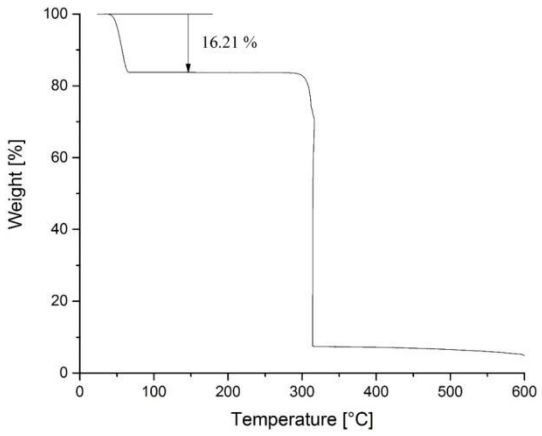


Fig. S1 Thermal stability of H_2-btbq·$2H_2O$ studied by TG analysis under a nitrogen atmosphere.

2) ^{13}C NMR spectrum of H_2-btbq·$2H_2O$

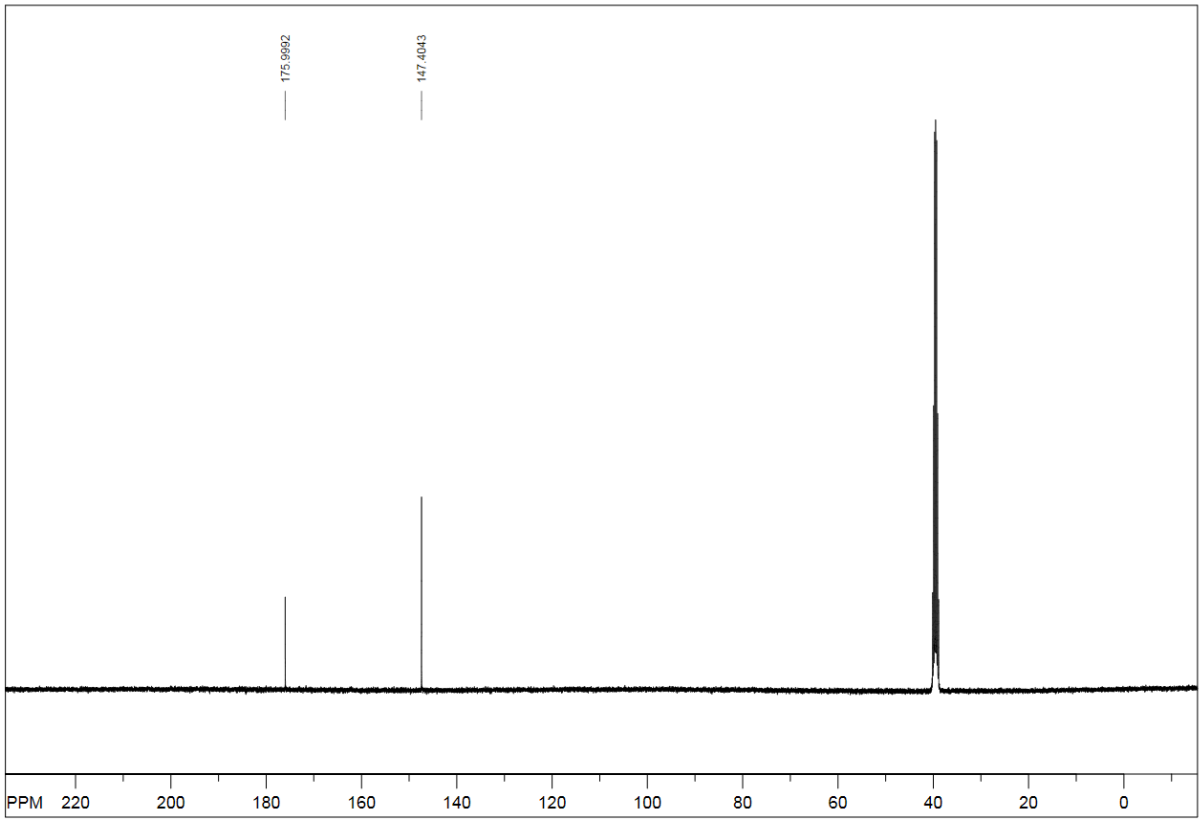


Fig. S2 ^{13}C NMR spectrum of H_2-btbq·$2H_2O$ in d_6-DMSO.

3) IR spectra of H_2-btbq·$2H_2O$ and its alkali salts

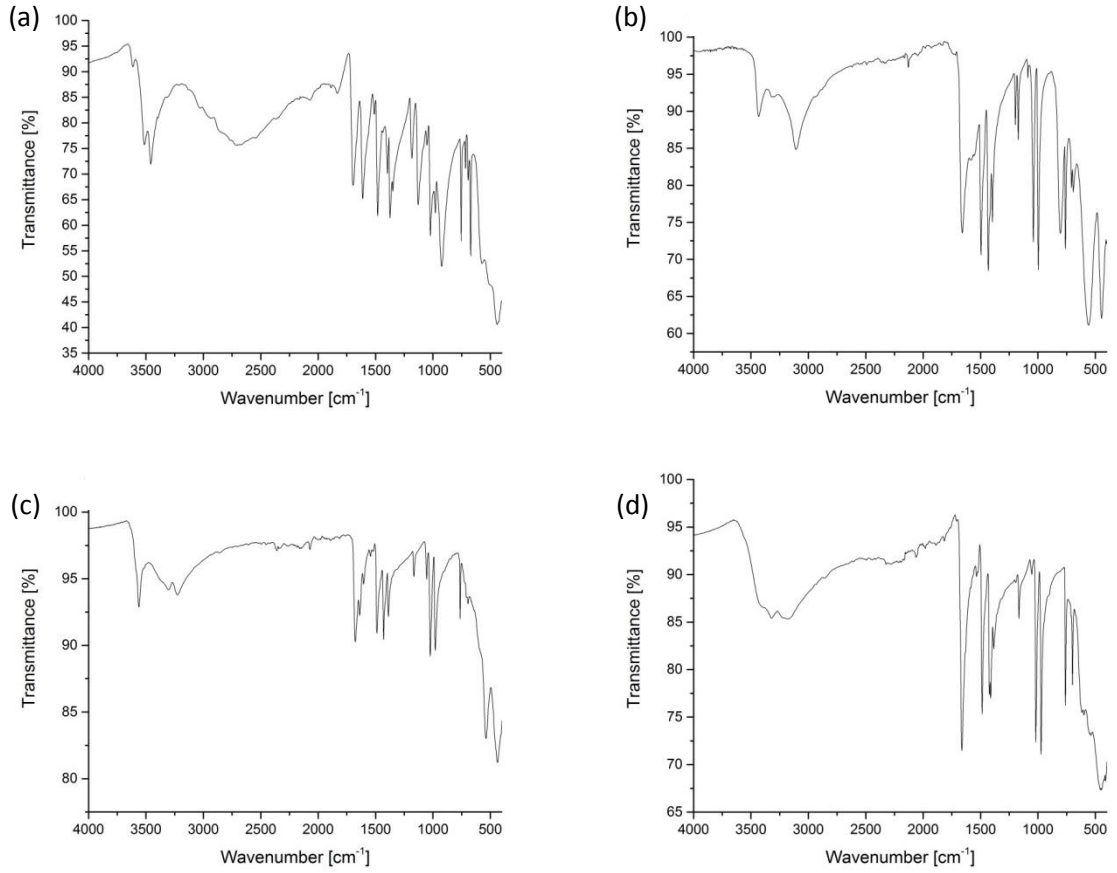


Fig. S3 IR spectra of (a) H_2-btbq·$2H_2O$, (b) Li_2-btbq·$2H_2O$, (c) Na_2-btbq·$4H_2O$ and (d) K_2-btbq·$2H_2O$.

a) *ν*bar = 3513, 3457, **1699 (C=O)**, 1612, 1510, 1482, 1396, 1374, 1349, 1182, 1130, 1052, 1022, 978, 925, 754, 716, 694, 672 and 447 cm^{-1}.

b) *ν*bar = 3432, 3105, **1663 (C=O)**, 1584, 1552, 1496, 1433, 1397, 1197, 1172, 1088, 1040, 997, 806, 760, 707, 691, 572 and 440 cm^{-1}.

c) *ν*bar = 3560, 3300, 3224, **1673 (C=O)**, 1638, 1603, 1487, 1429, 1388, 1165, 1054, 1022, 979, 763, 695, 536 and 430 cm^{-1}.

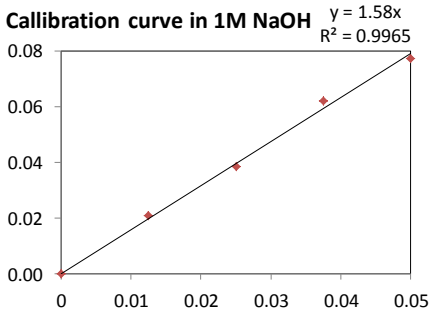
d) *ν*bar = 3320, 3172, **1664 (C=O)**, 1534, 1486, 1422, 1412, 1385, 1165, 1053, 1018, 973, 760, 699, 599 and 449 cm^{-1}.

4) Solubility of H_2-btbq·$2H_2O$ in alkaline aqueous solutions

The room temperature solubility of H_2-btbq·$2H_2O$ in a 1M solution of NaOH and KOH was determined by measuring the absorbance maximum in the visible range at 380 nm and comparing to an absorbance-vs.-concentration calibration curve determined by preparing known concentrations of H_2-btbq·$2H_2O$ in the alkaline solutions. UV-Vis spectroscopy measurements were performed using an Agilent Cary 60 spectrophotometer. A stock solution of H_2-btbq·$2H_2O$ was prepared by dissolving a known amount of the compound in a known volume of a 1M NaOH or KOH solution. Appropriate aliquots of the H_2-btbq stock solution were added to 1M NaOH or KOH blank solutions and their UV-Vis absorbance spectra were measured to prepare the calibration curves. Then, saturated solutions of H_2-btbq·$2H_2O$ in a 1M NaOH or KOH solution were prepared by adding H_2-btbq·$2H_2O$ into the corresponding alkaline solution until a thin layer of precipitate formed. The obtained solutions were filtered through a pad of cotton and a known volume was diluted by known proportions of a 1M NaOH or KOH solution, and the absorbance of the resulting solutions was compared to the calibration curves.

Solubility in 1M NaOH:

Conc. (mg/mL)	Absorbance at 380 nm
0.0000	0.0000
0.0125	0.0209
0.0250	0.0384
0.0375	0.0620
0.0500	0.0772



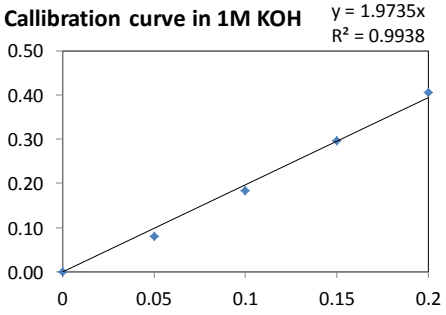
Saturated solution:

1 mg of H_2-btbq·$2H_2O$ was dispersed in 5 mL of 1M NaOH and the mixture was filtrated through a pad of cotton. 1 mL of the filtrate was mixed with 1 mL of 1M NaOH and the absorption of the solution was measured and re-calculated to the concentration of the saturated solution.

A = 0.0797 → c = 0.0504 mg/mL →→ $c_{saturated\ solution}$ = **0.10 mg/mL**

Solubility in 1M KOH:

Conc. (mg/mL)	Absorbance at 380 nm
0.00	0.0000
0.05	0.0804
0.10	0.1830
0.15	0.2973
0.20	0.4055



Saturated solution:

5 mg of H_2-btbq·$2H_2O$ was dispersed in 500 µL of 1M KOH and the mixture was filtrated through a pad of cotton. 100 µL of the filtrate was mixed with 1.9 mL of 1M KOH and the absorption of the solution was measured and re-calculated to the concentration of the saturated solution.

A = 0.783 → c = 0.397 mg/mL →→ $c_{saturated\ solution}$ = **7.94 mg/mL**

Solubility in 1M LiOH:

H_2-btbq·$2H_2O$ is very well soluble in a 1M LiOH solution. More than 100 mg could be dissolved in 1 mL, and therefore, the precise value was not determined by the UV-Vis method.

$c_{saturated\ solution}$ = > **100 mg/mL**

5) VT-XRPD measurements of Li_2-btbq·$2H_2O$, Na_2-btbq·$4H_2O$ and K_2-btbq·$2H_2O$

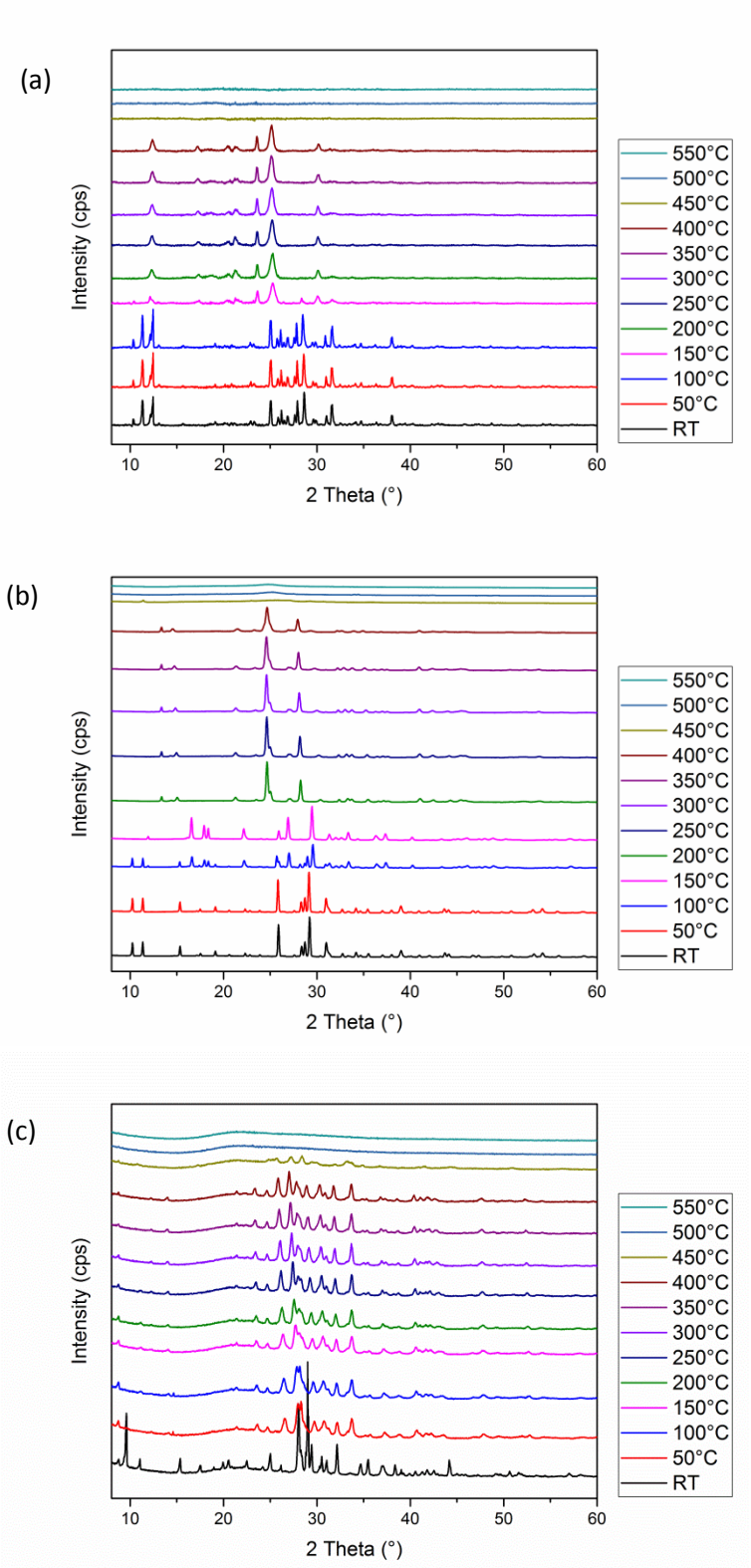


Fig. S4 Variable temperature XRPD measurements of (a) Li_2-btbq·$4H_2O$, (b) Na_2-btbq·$4H_2O$ and (c) K_2-btbq·$2H_2O$ exposed to a nitrogen atmosphere.

6) CV measurements of H_2-btbq·$2H_2O$ in basic aqueous solutions

The CV measurements were carried out on a biologic SP-300 potentiostat using a conventional three-electrode system. The electrochemical cell was equipped with a glassy carbon working electrode (3 mm in a diameter), a saturated calomel electrode (SCE) as a reference electrode and a platinum wire counter-electrode. The experiments were carried out at room temperature at different scan rates from 1000 to 10 mV s^{-1} in a 1M, oxygen free, aqueous solution of LiOH, NaOH, KOH and Bu_4NOH. In the case of using a solution of LiOH and KOH, 2 mg of H_2-btbq·$2H_2O$ (0.009 mmol) in 10 mL were used. In the case of using a solution of NaOH and Bu_4NOH, only 1 mg of H_2-btbq·$2H_2O$ (0.004 mmol) in 10 mL was used (higher amount was not possible to use due to the limited solubility of H_2-btbq in the solutions).

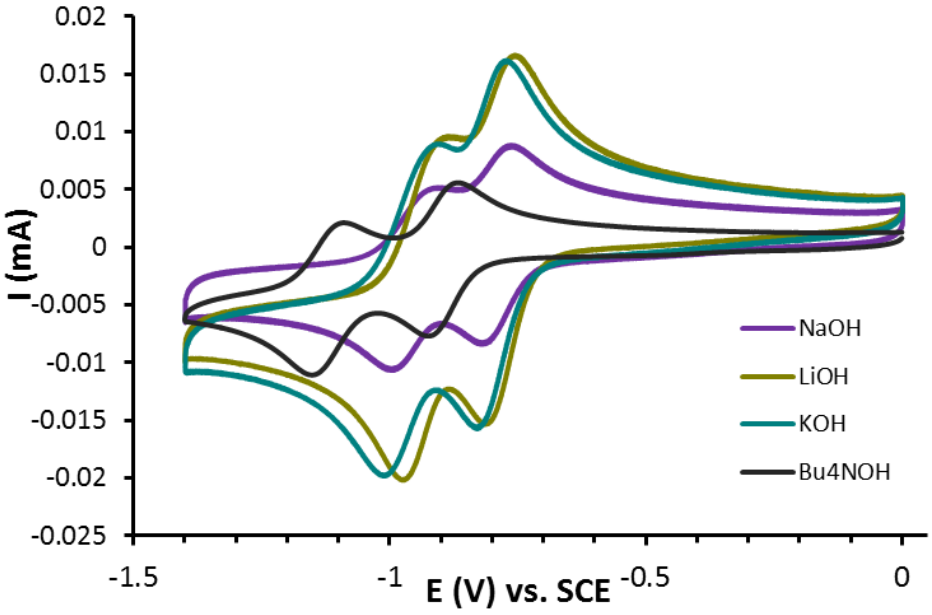


Fig. S5 Cyclic voltammograms of H_2-btbq·$2H_2O$ in a 1M aqueous solution of LiOH, NaOH, KOH and Bu_4NOH measured at room temperature at the rate of 100 mV·s^{-1}.

Table S1 Redox potentials (E_1^0 and E_2^0), corresponding anodic and cathodic peak potential differences (ΔE) and differences between the redox potentials in different aqueous basic electrolytes.

Base	E_1^0 (mV) vs. SCE	ΔE (mV)	E_2^0 (mV) vs. SCE	ΔE (mV)	$E^o_{1,metal} - E^o_{1,Bu_4NOH}$ (mV)	$E^o_{2,metal} - E^o_{2,Bu_4NOH}$ (mV)
LiOH	-782	57	-928	86	86	138
NaOH	-790	57	-953	88	78	113
KOH	-799	57	-958	106	69	108
Bu_4NOH	-868	58	-1066	86	-	-

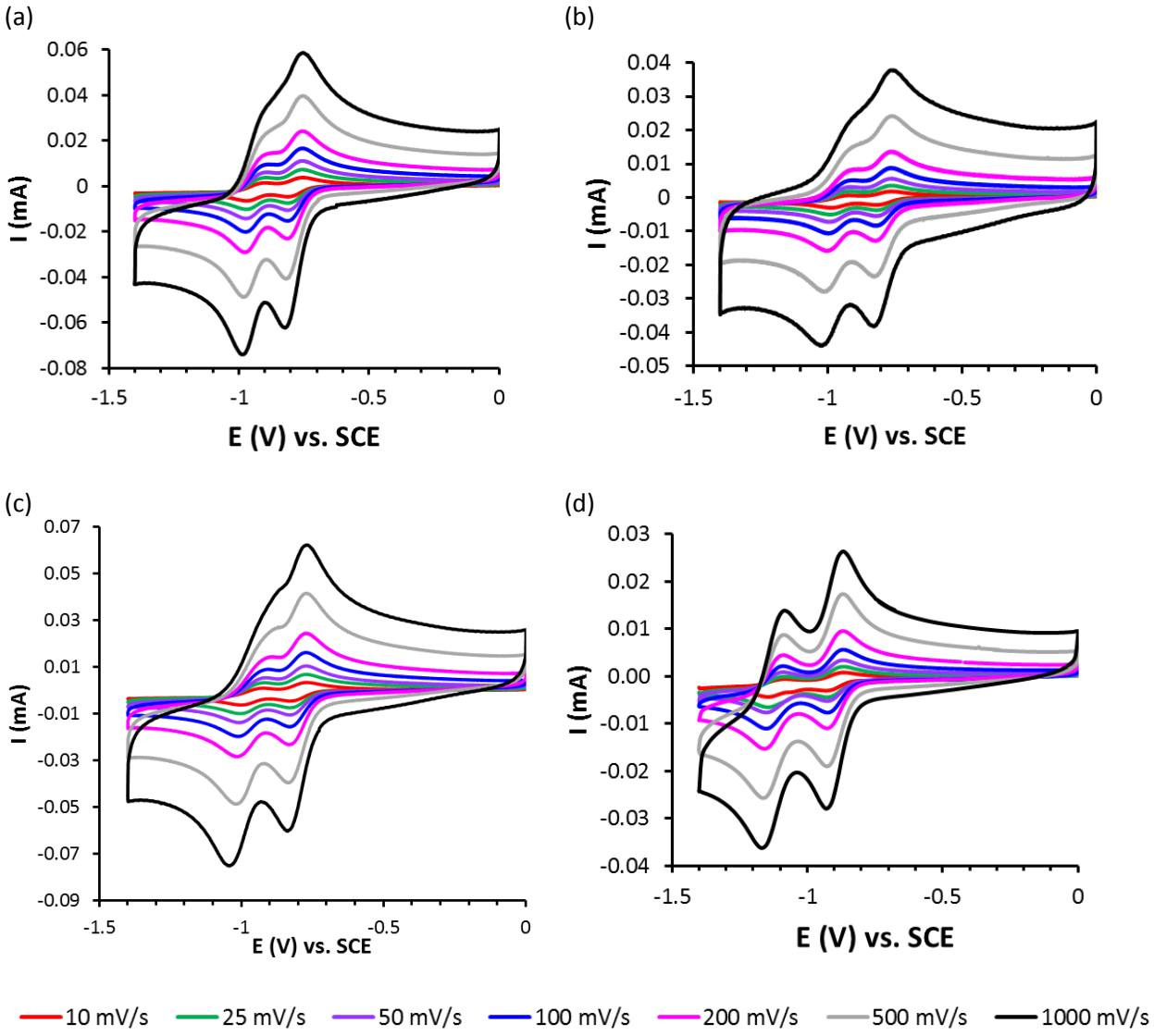


Fig. S6 CV measurements of H_2-btbq·$2H_2O$ in 1M (a) LiOH, (b) NaOH, (c) KOH and (d) Bu_4NOH at the scan rate of 10, 25, 50, 100, 200, 500 and 1000 $mV \cdot s^{-1}$.

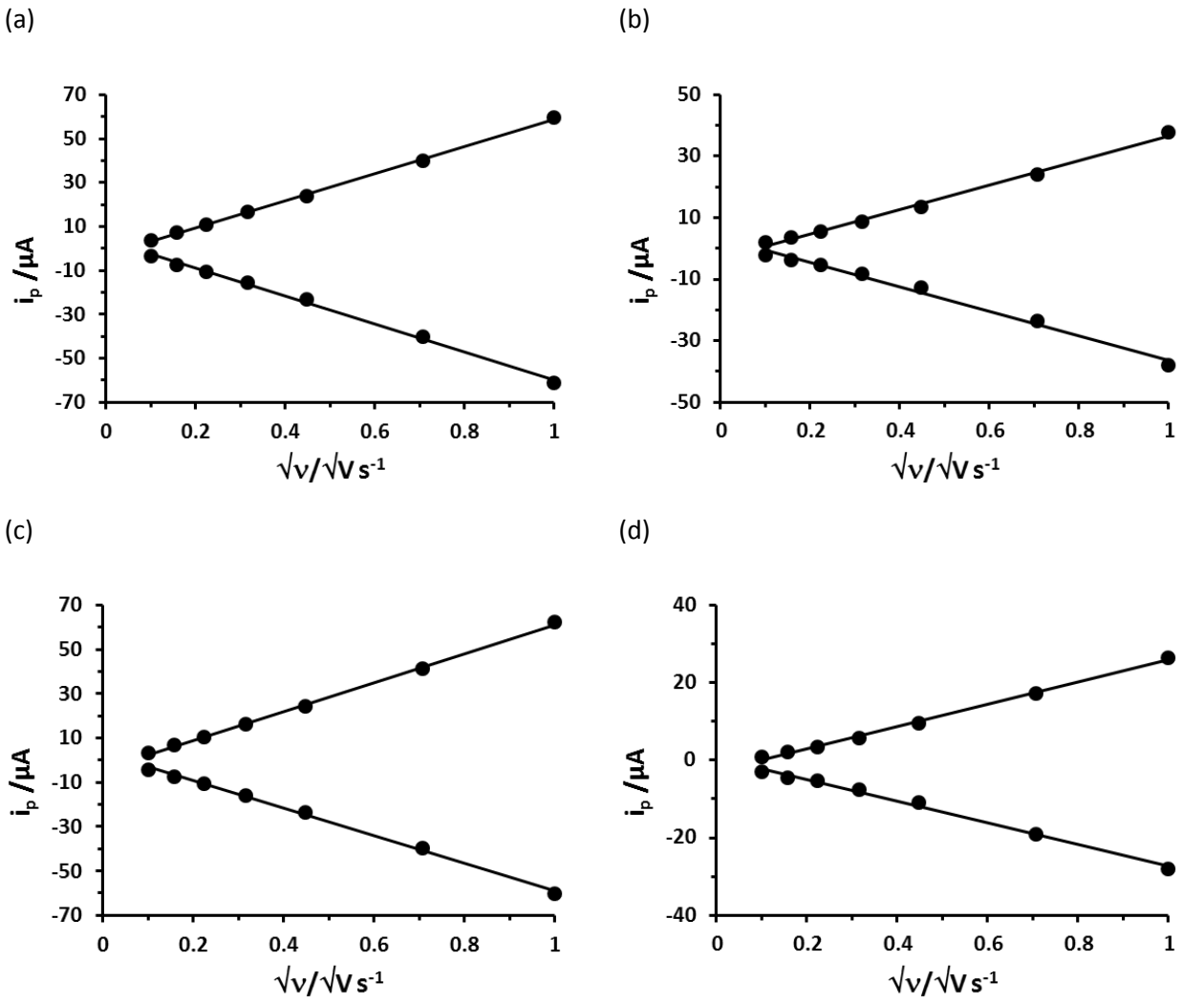


Fig. S7 Randles-Sevčik plots of i_p against $\sqrt{\nu}$ of H_2-btbq·$2H_2O$ in 1M (a) LiOH, (b) NaOH, (c) KOH and (d) Bu_4NOH. Data refer to the first reduction and the corresponding oxidation wave and indicate a diffusion controlled electrode reaction.

7) X-ray single crystal analysis

Optical microscopy images of H_2-btbq·$2H_2O$ and its alkali salts

Images of crystals were taken using an Olympus IX70 microscope equipped with a camera.

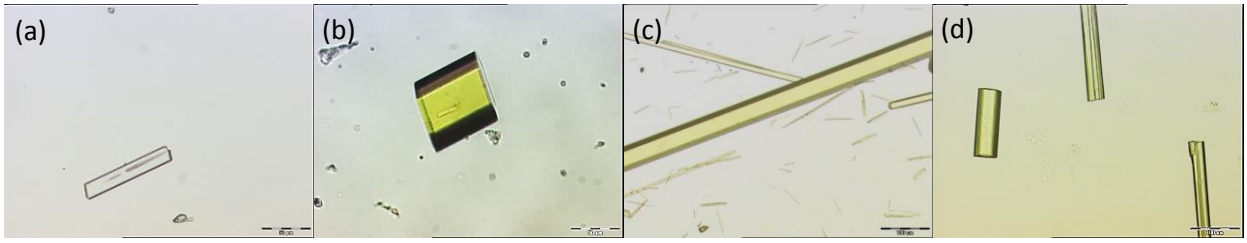


Fig. S8 Optical microscopy images of crystals of (a) H_2-btbq·$2H_2O$, (b) Li_2-btbq·$2H_2O$, (c) Na_2-btbq·$4H_2O$ and (d) K_2-btbq·$2H_2O$; scale bar: 50 µm (a, b) and 100 µm (c, d).

Measured and simulated XRPD patterns of Li_2-btbq·$2H_2O$, Na_2-btbq·$4H_2O$ and K_2-btbq·$2H_2O$

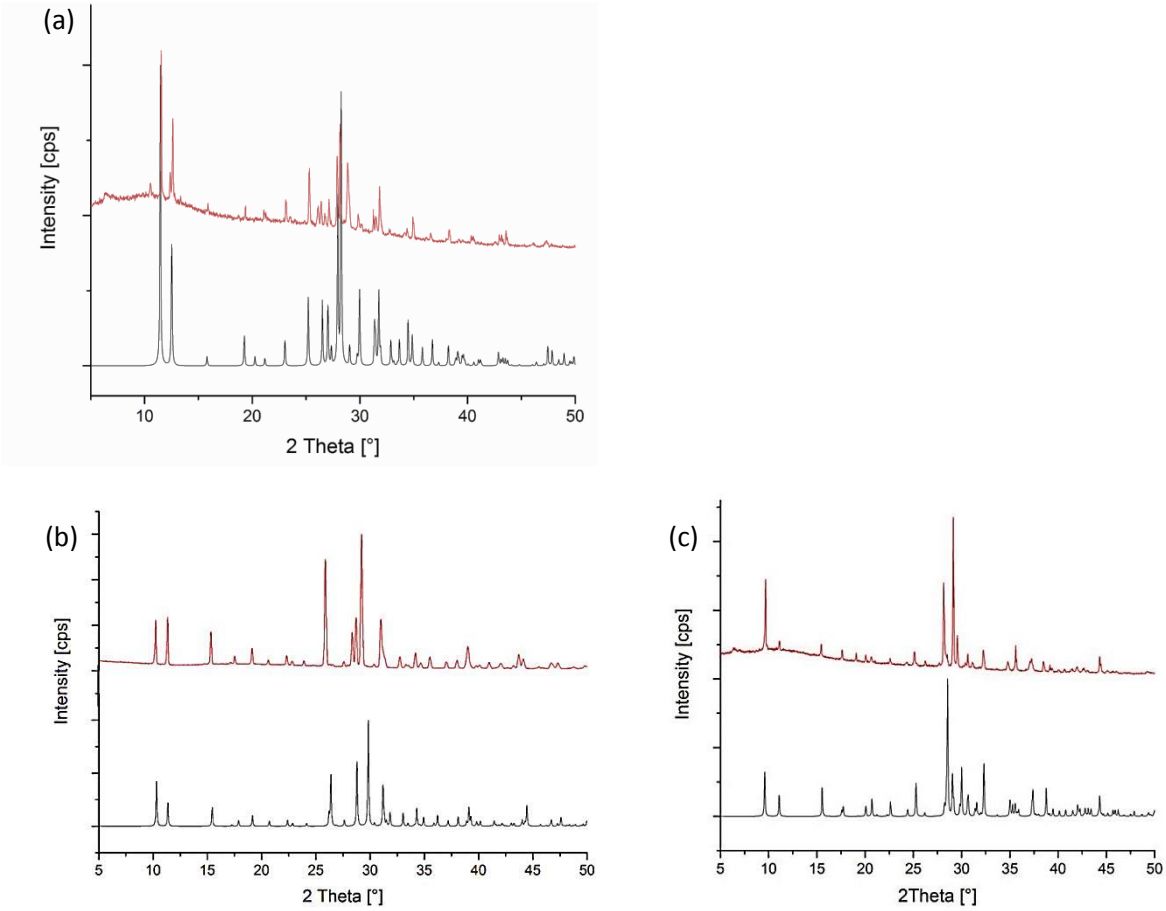


Fig. S9 Simulated (black) and measured (red) XRPD patterns of (a) Li_2-btbq·$2H_2O$, (b) Na_2-btbq·$4H_2O$ and (c) K_2-btbq·$2H_2O$ (bulk samples).

X-ray single crystal analysis of Li_2-btbq·$2H_2O$

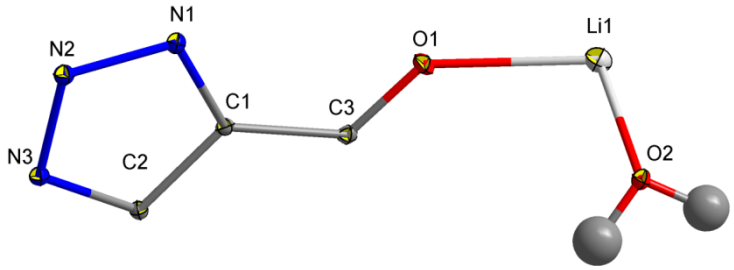


Fig. S10 ORTEP-style plot of the asymmetric units of Li_2-btbq·$2H_2O$. Thermal ellipsoids probability: 50 %.

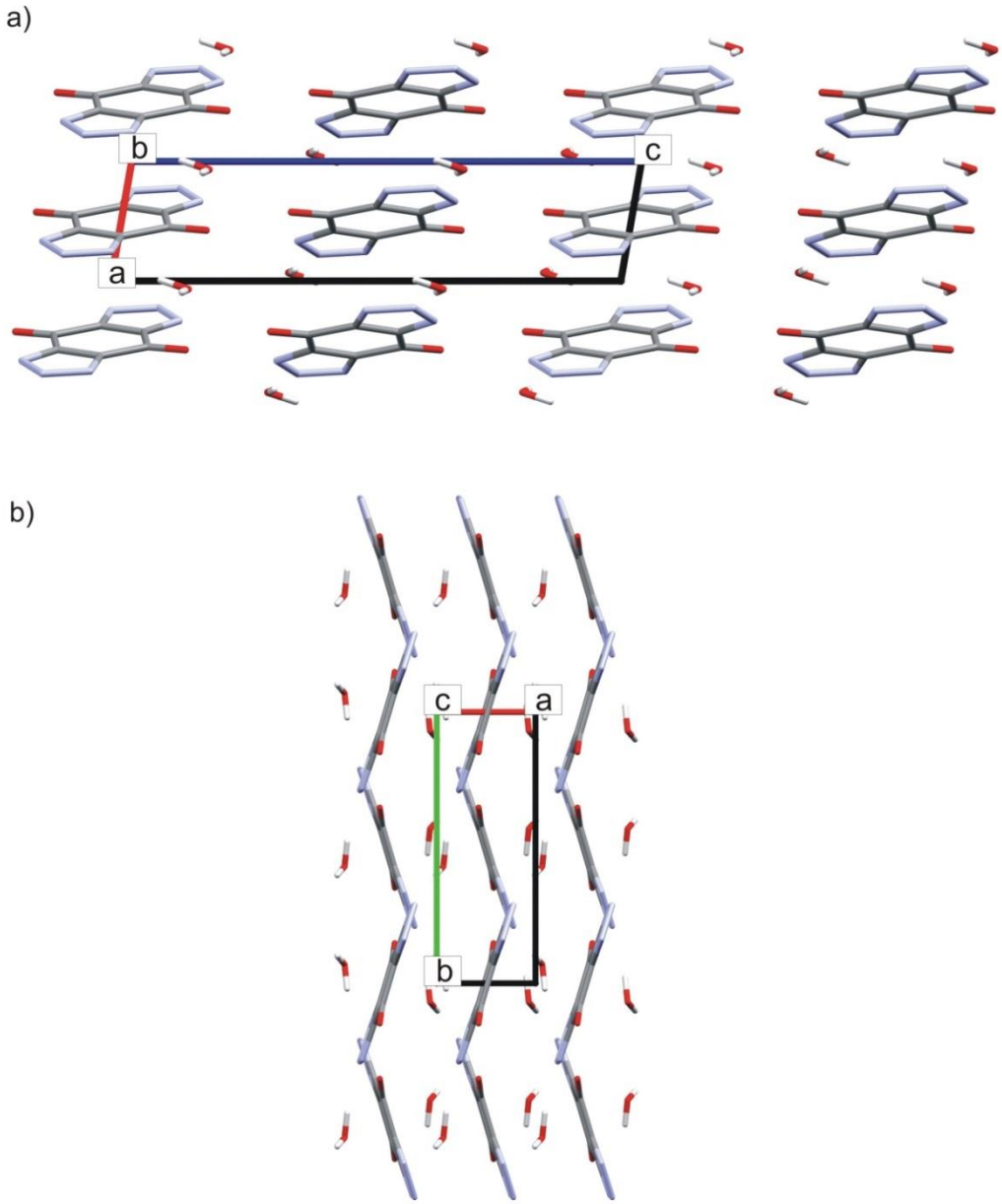


Fig. S11 Packing diagram of the structure of Li_2-btbq·$2H_2O$, view in *b*- (a) and *c*-direction (b). Li-cations are omitted for clarity.

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) of Li_2-btbq·$2H_2O$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Li(1)	-6099(6)	-8552(2)	-7101(2)	11(1)
O(1)	-5759(2)	-6478(1)	-6695(1)	8(1)
O(2)	-681(2)	-9307(1)	-6544(1)	7(1)
N(1)	-3330(3)	-3372(1)	-6472(1)	6(1)
N(2)	-2243(3)	-2117(1)	-6024(1)	7(1)
N(3)	-2464(3)	-2203(1)	-5101(1)	6(1)
C(1)	-4270(3)	-4292(1)	-5816(1)	5(1)
C(2)	-3738(3)	-3557(1)	-4952(1)	5(1)
C(3)	-5500(3)	-5819(1)	-5944(1)	5(1)

Table S3. Bond lengths [Å] and angles [°]of Li_2-btbq·$2H_2O$.

Li(1)-O(1)	1.995(2)
Li(1)-O(2)#1	1.998(2)
Li(1)-O(2)	2.007(2)
Li(1)-N(1)#2	2.027(2)
Li(1)-Li(1)#3	3.40910(11)
Li(1)-Li(1)#1	3.40910(11)
O(1)-C(3)	1.2260(13)
O(2)-Li(1)#3	1.998(2)
O(2)-H(1)	0.86(2)
O(2)-H(2)	0.85(2)
N(1)-N(2)	1.3432(14)
N(1)-C(1)	1.3459(14)
N(1)-Li(1)#4	2.027(2)
N(2)-N(3)	1.3411(13)
N(3)-C(2)	1.3491(15)
C(1)-C(2)	1.3951(15)
C(1)-C(3)	1.4700(16)
C(2)-C(3)#5	1.4705(15)
C(3)-C(2)#5	1.4705(15)
O(1)-Li(1)-O(2)#1	103.11(10)

O(1)-Li(1)-O(2)	102.26(10)
O(2)#1-Li(1)-O(2)	116.70(11)
O(1)-Li(1)-N(1)#2	101.96(10)
O(2)#1-Li(1)-N(1)#2	119.04(11)
O(2)-Li(1)-N(1)#2	110.64(10)
O(1)-Li(1)-Li(1)#3	89.54(7)
O(2)#1-Li(1)-Li(1)#3	148.27(7)
O(2)-Li(1)-Li(1)#3	31.57(7)
N(1)#2-Li(1)-Li(1)#3	85.59(7)
O(1)-Li(1)-Li(1)#1	90.46(7)
O(2)#1-Li(1)-Li(1)#1	31.73(7)
O(2)-Li(1)-Li(1)#1	148.43(7)
N(1)#2-Li(1)-Li(1)#1	94.41(7)
Li(1)#3-Li(1)-Li(1)#1	179.999(2)
C(3)-O(1)-Li(1)	136.29(10)
Li(1)#3-O(2)-Li(1)	116.70(11)
Li(1)#3-O(2)-H(1)	97.5(14)
Li(1)-O(2)-H(1)	111.2(14)
Li(1)#3-O(2)-H(2)	121.8(14)
Li(1)-O(2)-H(2)	107.2(14)
H(1)-O(2)-H(2)	100(2)
N(2)-N(1)-C(1)	106.65(9)
N(2)-N(1)-Li(1)#4	121.58(10)
C(1)-N(1)-Li(1)#4	131.37(10)
N(3)-N(2)-N(1)	111.35(9)
N(2)-N(3)-C(2)	106.50(9)
N(1)-C(1)-C(2)	107.71(10)
N(1)-C(1)-C(3)	127.75(10)
C(2)-C(1)-C(3)	124.51(10)
N(3)-C(2)-C(1)	107.80(10)
N(3)-C(2)-C(3)#5	127.52(10)
C(1)-C(2)-C(3)#5	124.68(10)
O(1)-C(3)-C(1)	124.03(10)
O(1)-C(3)-C(2)#5	125.19(10)
C(1)-C(3)-C(2)#5	110.76(9)

Symmetry transformations used to generate equivalent atoms:

#1 x-1,y,z #2 -x-1,y-1/2,-z-3/2 #3 x+1,y,z

#4 -x-1,y+1/2,-z-3/2 #5 -x-1,-y-1,-z-1

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) of Li_2-btbq·$2H_2O$.

The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Li(1)	13(1)	10(1)	9(1)	0(1)	2(1)	0(1)
O(1)	12(1)	7(1)	5(1)	-2(1)	2(1)	-1(1)
O(2)	11(1)	5(1)	6(1)	0(1)	1(1)	-2(1)
N(1)	6(1)	5(1)	6(1)	0(1)	1(1)	0(1)
N(2)	8(1)	6(1)	6(1)	0(1)	1(1)	-1(1)
N(3)	8(1)	5(1)	5(1)	0(1)	1(1)	0(1)
C(1)	6(1)	5(1)	4(1)	1(1)	1(1)	1(1)
C(2)	6(1)	5(1)	5(1)	0(1)	1(1)	0(1)
C(3)	5(1)	5(1)	6(1)	0(1)	0(1)	0(1)

Table S5. Hydrogen Bonds.

Donor---Hydrogen...Acceptor	Don--Hyd [Å]	Hyd--Acc [Å]	Don--Acc [Å]	D--H-----A
O2»3---H2»3...N2»2	0.85	1.93	2.770	168.6°
O2»4---H2»4...N2»5	0.85	1.93	2.770	168.6°

X-ray single crystal analysis of Na_2-btbq·$4H_2O$

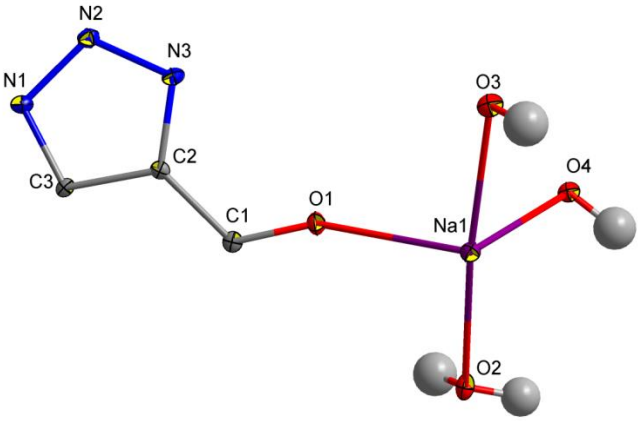
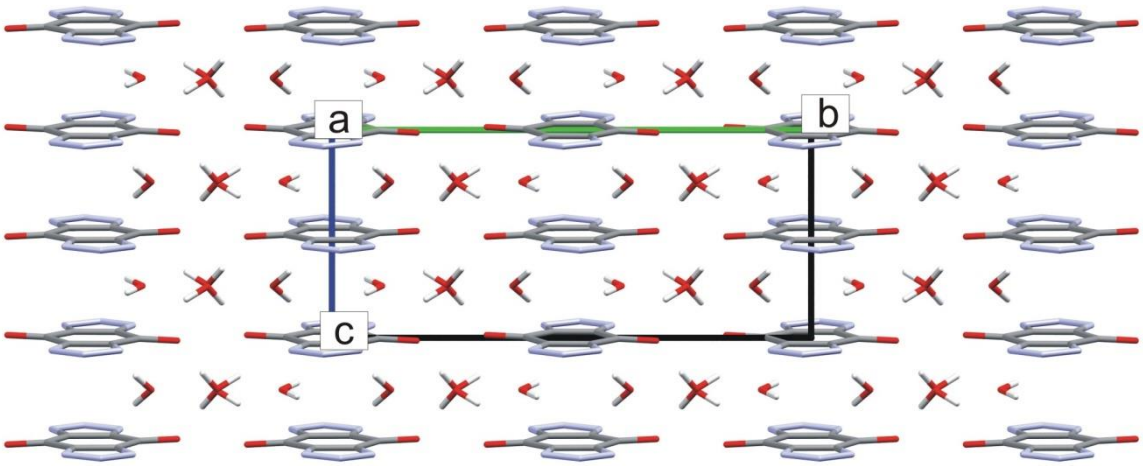


Fig. S12 ORTEP-style plot of the asymmetric units Na_2-btbq·$4H_2O$. Thermal ellipsoids probability: 50 %.

a)



b)

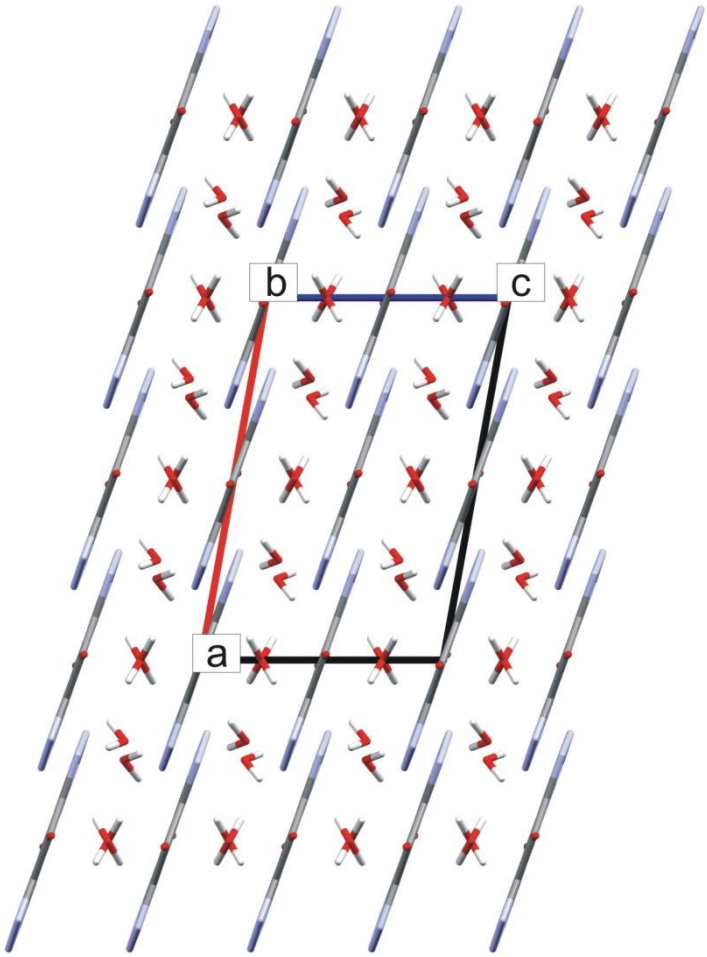


Fig. S13 Packing diagram of the structure of Na_2-btbq·$4H_2O$, view in *a*- (a) and *b*-direction (b). Na-cations are omitted for clarity.

Table S6. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) of Na_2-btbq·$4H_2O$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Na(1)	6227(1)	8116(1)	5160(1)	10(1)
O(1)	5156(1)	6768(1)	4867(2)	10(1)
O(2)	7757(1)	7402(1)	7533(2)	11(1)
O(3)	5000	8767(1)	7500	13(1)
O(4)	5000	8954(1)	2500	10(1)
N(1)	2623(1)	4420(1)	5611(2)	8(1)
N(2)	2031(1)	5176(1)	5797(2)	9(1)
N(3)	2826(1)	5844(1)	5611(2)	8(1)
C(1)	5112(2)	5981(1)	4958(2)	7(1)
C(2)	3952(1)	5503(1)	5286(2)	7(1)
C(3)	3829(1)	4611(1)	5295(2)	6(1)

Table S7. Bond lengths [Å] and angles [°]of Na_2-btbq·$4H_2O$.

Na(1)-O(2)	2.3458(13)
Na(1)-O(1)	2.3668(12)
Na(1)-O(4)	2.4165(11)
Na(1)-O(2)#1	2.4241(13)
Na(1)-O(3)	2.4433(9)
Na(1)-N(1)#2	2.4838(14)
Na(1)-Na(1)#1	3.3126(12)
Na(1)-Na(1)#3	4.0690(12)
O(1)-C(1)	1.2265(18)
O(2)-Na(1)#1	2.4241(13)
O(2)-H(1)	0.837(16)
O(2)-H(2)	0.816(16)
O(3)-Na(1)#4	2.4433(9)
O(3)-H(3)	0.85(2)
O(4)-Na(1)#3	2.4165(11)
O(4)-H(4)	0.83(2)
N(1)-N(2)	1.3431(18)

N(1)-C(3)	1.3480(18)
N(1)-Na(1)#5	2.4838(14)
N(2)-N(3)	1.3498(18)
N(3)-C(2)	1.3437(19)
C(1)-C(2)	1.471(2)
C(1)-C(3)#6	1.471(2)
C(2)-C(3)	1.394(2)
C(3)-C(1)#6	1.471(2)
O(2)-Na(1)-O(1)	83.84(4)
O(2)-Na(1)-O(4)	169.42(4)
O(1)-Na(1)-O(4)	103.57(5)
O(2)-Na(1)-O(2)#1	92.04(4)
O(1)-Na(1)-O(2)#1	84.56(4)
O(4)-Na(1)-O(2)#1	81.29(4)
O(2)-Na(1)-O(3)	96.44(4)
O(1)-Na(1)-O(3)	97.38(5)
O(4)-Na(1)-O(3)	90.15(3)
O(2)#1-Na(1)-O(3)	171.44(4)
O(2)-Na(1)-N(1)#2	89.36(4)
O(1)-Na(1)-N(1)#2	172.39(5)
O(4)-Na(1)-N(1)#2	82.73(4)
O(2)#1-Na(1)-N(1)#2	92.29(4)
O(3)-Na(1)-N(1)#2	86.75(5)
O(2)-Na(1)-Na(1)#1	47.00(3)
O(1)-Na(1)-Na(1)#1	81.64(4)
O(4)-Na(1)-Na(1)#1	125.83(3)
O(2)#1-Na(1)-Na(1)#1	45.05(3)
O(3)-Na(1)-Na(1)#1	143.43(4)
N(1)#2-Na(1)-Na(1)#1	91.22(4)
O(2)-Na(1)-Na(1)#3	149.79(3)
O(1)-Na(1)-Na(1)#3	73.21(3)
O(4)-Na(1)-Na(1)#3	32.66(4)
O(2)#1-Na(1)-Na(1)#3	66.89(3)
O(3)-Na(1)-Na(1)#3	105.61(2)
N(1)#2-Na(1)-Na(1)#3	111.91(3)
Na(1)#1-Na(1)-Na(1)#3	108.95(3)

C(1)-O(1)-Na(1)	154.22(10)
Na(1)-O(2)-Na(1)#1	87.96(4)
Na(1)-O(2)-H(1)	123.8(17)
Na(1)#1-O(2)-H(1)	106.2(16)
Na(1)-O(2)-H(2)	117.5(17)
Na(1)#1-O(2)-H(2)	110.5(18)
H(1)-O(2)-H(2)	108(2)
Na(1)#4-O(3)-Na(1)	130.98(8)
Na(1)#4-O(3)-H(3)	107.9(17)
Na(1)-O(3)-H(3)	100.7(17)
Na(1)#3-O(4)-Na(1)	114.69(7)
Na(1)#3-O(4)-H(4)	114.7(17)
Na(1)-O(4)-H(4)	102.4(17)
N(2)-N(1)-C(3)	106.31(12)
N(2)-N(1)-Na(1)#5	117.21(9)
C(3)-N(1)-Na(1)#5	134.66(10)
N(1)-N(2)-N(3)	111.40(12)
C(2)-N(3)-N(2)	106.33(12)
O(1)-C(1)-C(2)	123.45(14)
O(1)-C(1)-C(3)#6	125.59(14)
C(2)-C(1)-C(3)#6	110.94(12)
N(3)-C(2)-C(3)	107.97(13)
N(3)-C(2)-C(1)	126.41(14)
C(3)-C(2)-C(1)	125.62(13)
N(1)-C(3)-C(2)	107.97(13)
N(1)-C(3)-C(1)#6	128.60(14)
C(2)-C(3)-C(1)#6	123.41(13)

Symmetry transformations used to generate equivalent atoms:

#1 -x+3/2,-y+3/2,-z+1 #2 x+1/2,y+1/2,z #3 -x+1,y,-z+1/2

#4 -x+1,y,-z+3/2 #5 x-1/2,y-1/2,z #6 -x+1,-y+1,-z+1

Table S8. Anisotropic displacement parameters ($Å^2 x\ 10^3$) of Na_2-btbq·$4H_2O$.

The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}

Na(1)	9(1)	9(1)	11(1)	1(1)	2(1)	-1(1)
O(1)	12(1)	7(1)	12(1)	0(1)	2(1)	-1(1)
O(2)	12(1)	9(1)	11(1)	1(1)	1(1)	-3(1)
O(3)	11(1)	15(1)	13(1)	0	2(1)	0
O(4)	9(1)	10(1)	12(1)	0	2(1)	0
N(1)	7(1)	10(1)	8(1)	-1(1)	2(1)	1(1)
N(2)	8(1)	10(1)	10(1)	-1(1)	2(1)	-1(1)
N(3)	7(1)	11(1)	7(1)	-1(1)	1(1)	-1(1)
C(1)	8(1)	8(1)	4(1)	0(1)	-1(1)	0(1)
C(2)	7(1)	7(1)	6(1)	0(1)	0(1)	0(1)
C(3)	6(1)	8(1)	5(1)	0(1)	1(1)	-1(1)

Table S9. Hydrogen Bonds

Donor---Hydrogen...Acceptor	Don--Hyd [Å]	Hyd--Acc [Å]	Don--Acc [Å]	D--H-----A
O2---H1...N3»2	0.84	2.02	2.851	174.2°
O2---H2...O1»12	0.82	2.23	3.012	159.5°
O3---H3...N2»12	0.85	2.43	3.256	163.9°
O4---H4...N2»11	0.83	2.12	2.927	165.8°
O2»1---H1»1...N3»7	0.84	2.02	2.851	174.2°
O2»2---H1»2...N3	0.84	2.02	2.851	174.2°
O2»3---H1»3...N3»8	0.84	2.02	2.851	174.2°
O2»3---H2»3...O1»16	0.82	2.23	3.012	159.5°
O3»3---H3»3...N2»16	0.85	2.43	3.256	163.9°
O4»3---H4»3...N2»15	0.83	2.12	2.927	165.8°
O2»4---H1»4...N3»11	0.84	2.02	2.851	174.2°
O2»4---H2»4...O1»1	0.82	2.23	3.012	159.5°
O3»4---H3»4...N2»1	0.85	2.43	3.256	163.9°
O4»4---H4»4...N2»2	0.83	2.12	2.927	165.8°
O2»5---H1»5...N3»13	0.84	2.02	2.851	174.2°
O2»6---H1»6...N3»15	0.84	2.02	2.851	174.2°
O2»6---H2»6...O1»10	0.82	2.23	3.012	159.5°
O3»6---H3»6...N2»10	0.85	2.43	3.256	163.9°
O4»6---H4»6...N2»8	0.83	2.12	2.927	165.8°
O2»7---H1»7...N3»1	0.84	2.02	2.851	174.2°
O2»7---H2»7...O1»11	0.82	2.23	3.012	159.5°
O3»1---H3»7...N2»11	0.85	2.43	3.256	163.9°
O2»8---H1»8...N3»3	0.84	2.02	2.851	174.2°
O4»2---H4»9...N2»12	0.83	2.12	2.927	165.8°
O2»11---H1»11...N3»4	0.84	2.02	2.851	174.2°
O2»13---H1»13...N3»5	0.84	2.02	2.851	174.2°
O2»15---H1»15...N3»6	0.84	2.02	2.851	174.2°

X-ray single crystal analysis of K_2-btbq·2H_2O

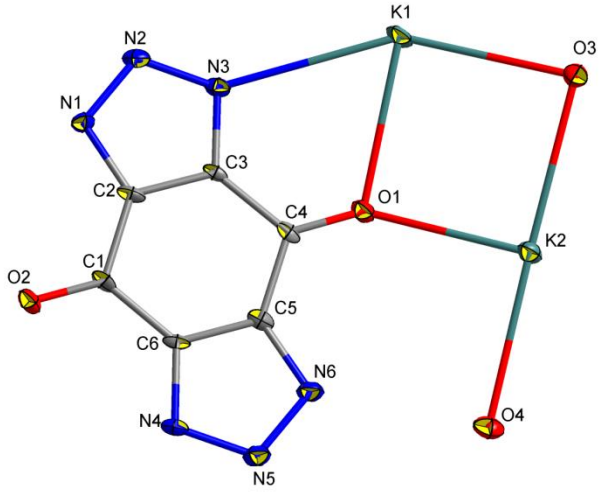


Fig. S14 ORTEP-style plot of the asymmetric units K_2-btbq·2H_2O. Thermal ellipsoids probability: 50 %. Hydrogen atoms have been omitted for clarity.

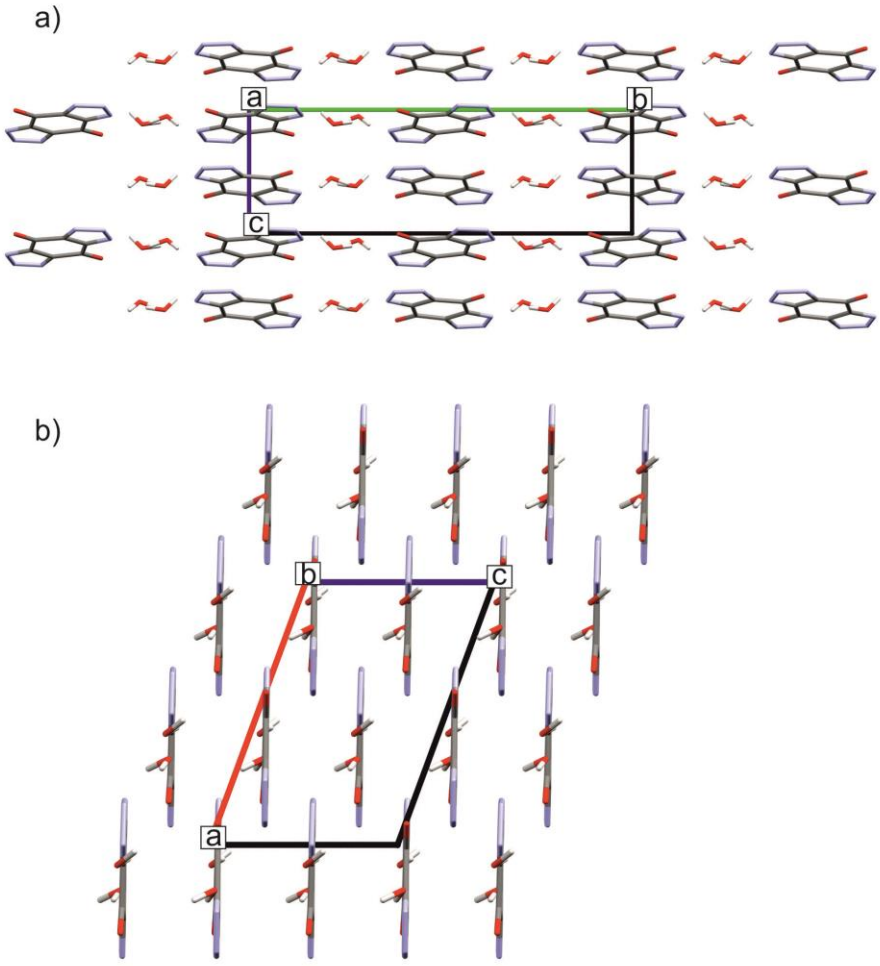


Fig. S15 Packing diagram of the structure of K_2-btbq·2H_2O, view in *a*- (a) and *b*-direction (b). K-cations are omitted for clarity.

Table S10. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) of of K_2-btbq·$2H_2O$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
K(1)	1269(1)	5766(1)	2423(1)	18(1)
K(2)	3740(1)	7477(1)	5941(2)	16(1)
O(1)	8346(3)	3865(2)	7006(5)	15(1)
O(2)	4200(3)	6096(2)	5059(4)	15(1)
O(3)	6730(3)	7790(2)	6180(5)	17(1)
O(4)	774(3)	7142(2)	5521(5)	18(1)
N(1)	7560(3)	6321(2)	6714(5)	13(1)
N(2)	9038(4)	6139(2)	7447(6)	14(1)
N(3)	9223(4)	5414(2)	7556(6)	13(1)
N(4)	3323(3)	4536(2)	4663(5)	13(1)
N(5)	3512(4)	3807(2)	4732(6)	16(1)
N(6)	4986(4)	3627(2)	5428(6)	17(1)
C(1)	5131(4)	5596(2)	5527(6)	12(1)
C(2)	6779(4)	5697(2)	6356(6)	13(1)
C(3)	7812(4)	5128(2)	6876(6)	10(1)
C(4)	7415(4)	4359(2)	6613(5)	11(1)
C(5)	5763(4)	4260(2)	5828(5)	11(1)
C(6)	4731(4)	4825(2)	5351(6)	11(1)

Table S11. Bond lengths [Å] and angles [°] of of K_2-btbq·$2H_2O$.

K(1)-O(2)	2.757(3)
K(1)-O(1)#1	2.759(3)
K(1)-O(3)#2	2.851(3)
K(1)-N(3)#1	2.926(3)
K(1)-N(4)	3.000(3)
K(1)-N(4)#3	3.075(3)
K(1)-N(3)#4	3.091(3)
K(1)-N(2)#4	3.204(3)
K(1)-N(5)#3	3.237(4)
K(1)-O(4)	3.338(3)

K(1)-C(4)#1	3.495(3)
K(1)-C(1)	3.502(3)
K(2)-O(2)	2.674(3)
K(2)-O(1)#5	2.703(3)
K(2)-O(4)	2.783(3)
K(2)-O(3)	2.828(3)
K(2)-O(4)#6	2.959(3)
K(2)-O(3)#2	2.999(3)
K(2)-N(1)#2	3.356(3)
K(2)-N(6)#7	3.363(4)
K(2)-N(5)#7	3.433(4)
K(2)-N(2)#2	3.452(4)
K(2)-K(1)#6	3.9364(12)
K(2)-H(3)	3.02(5)
O(1)-C(4)	1.227(5)
O(1)-K(2)#8	2.703(3)
O(1)-K(1)#9	2.759(3)
O(2)-C(1)	1.234(4)
O(3)-K(1)#6	2.851(3)
O(3)-K(2)#6	2.999(3)
O(3)-H(1)	0.88(2)
O(3)-H(2)	0.89(2)
O(4)-K(2)#2	2.959(3)
O(4)-H(3)	0.891(19)
O(4)-H(4)	0.873(19)
N(1)-C(2)	1.342(5)
N(1)-N(2)	1.349(4)
N(1)-K(2)#6	3.356(3)
N(2)-N(3)	1.346(5)
N(2)-K(1)#10	3.204(3)
N(2)-K(2)#6	3.452(4)
N(3)-C(3)	1.354(5)
N(3)-K(1)#9	2.926(3)
N(3)-K(1)#10	3.091(3)
N(4)-C(6)	1.354(4)
N(4)-N(5)	1.354(5)

N(4)-K(1)#7	3.075(3)
N(5)-N(6)	1.346(5)
N(5)-K(1)#7	3.237(4)
N(5)-K(2)#3	3.433(4)
N(6)-C(5)	1.354(5)
N(6)-K(2)#3	3.363(4)
C(1)-C(6)	1.464(6)
C(1)-C(2)	1.469(5)
C(2)-C(3)	1.390(5)
C(3)-C(4)	1.461(5)
C(4)-C(5)	1.472(5)
C(4)-K(1)#9	3.495(3)
C(5)-C(6)	1.385(5)
O(2)-K(1)-O(1)#1	139.59(9)
O(2)-K(1)-O(3)#2	75.26(9)
O(1)#1-K(1)-O(3)#2	89.19(9)
O(2)-K(1)-N(3)#1	132.71(9)
O(1)#1-K(1)-N(3)#1	62.60(9)
O(3)#2-K(1)-N(3)#1	150.01(9)
O(2)-K(1)-N(4)	62.10(8)
O(1)#1-K(1)-N(4)	133.69(9)
O(3)#2-K(1)-N(4)	134.51(9)
N(3)#1-K(1)-N(4)	75.47(8)
O(2)-K(1)-N(4)#3	71.92(8)
O(1)#1-K(1)-N(4)#3	142.50(9)
O(3)#2-K(1)-N(4)#3	79.97(9)
N(3)#1-K(1)-N(4)#3	115.61(10)
N(4)-K(1)-N(4)#3	72.71(8)
O(2)-K(1)-N(3)#4	143.18(9)
O(1)#1-K(1)-N(3)#4	72.43(9)
O(3)#2-K(1)-N(3)#4	91.26(9)
N(3)#1-K(1)-N(3)#4	71.50(8)
N(4)-K(1)-N(3)#4	113.10(10)
N(4)#3-K(1)-N(3)#4	72.05(8)
O(2)-K(1)-N(2)#4	136.80(9)
O(1)#1-K(1)-N(2)#4	63.84(9)

O(3)#2-K(1)-N(2)#4	68.79(9)
N(3)#1-K(1)-N(2)#4	88.45(9)
N(4)-K(1)-N(2)#4	136.46(10)
N(4)#3-K(1)-N(2)#4	78.82(9)
N(3)#4-K(1)-N(2)#4	24.61(9)
O(2)-K(1)-N(5)#3	64.33(8)
O(1)#1-K(1)-N(5)#3	134.50(9)
O(3)#2-K(1)-N(5)#3	55.82(9)
N(3)#1-K(1)-N(5)#3	138.77(10)
N(4)-K(1)-N(5)#3	90.08(9)
N(4)#3-K(1)-N(5)#3	24.60(9)
N(3)#4-K(1)-N(5)#3	79.65(9)
N(2)#4-K(1)-N(5)#3	75.79(8)
O(2)-K(1)-O(4)	77.88(8)
O(1)#1-K(1)-O(4)	62.07(8)
O(3)#2-K(1)-O(4)	61.26(7)
N(3)#1-K(1)-O(4)	108.66(9)
N(4)-K(1)-O(4)	119.58(9)
N(4)#3-K(1)-O(4)	135.72(9)
N(3)#4-K(1)-O(4)	125.55(8)
N(2)#4-K(1)-O(4)	103.84(9)
N(5)#3-K(1)-O(4)	112.01(8)
O(2)-K(1)-C(4)#1	151.15(9)
O(1)#1-K(1)-C(4)#1	18.21(9)
O(3)#2-K(1)-C(4)#1	105.68(9)
N(3)#1-K(1)-C(4)#1	45.08(9)
N(4)-K(1)-C(4)#1	119.19(9)
N(4)#3-K(1)-C(4)#1	136.93(8)
N(3)#4-K(1)-C(4)#1	65.24(9)
N(2)#4-K(1)-C(4)#1	64.81(8)
N(5)#3-K(1)-C(4)#1	140.57(8)
O(4)-K(1)-C(4)#1	77.71(8)
O(2)-K(1)-C(1)	18.23(8)
O(1)#1-K(1)-C(1)	152.21(9)
O(3)#2-K(1)-C(1)	90.63(9)
N(3)#1-K(1)-C(1)	118.98(9)

N(4)-K(1)-C(1)	44.86(9)
N(4)#3-K(1)-C(1)	64.41(8)
N(3)#4-K(1)-C(1)	135.35(9)
N(2)#4-K(1)-C(1)	140.69(9)
N(5)#3-K(1)-C(1)	65.02(9)
O(4)-K(1)-C(1)	93.79(8)
C(4)#1-K(1)-C(1)	154.39(9)
O(2)-K(2)-O(1)#5	177.69(10)
O(2)-K(2)-O(4)	89.94(10)
O(1)#5-K(2)-O(4)	90.81(9)
O(2)-K(2)-O(3)	88.54(9)
O(1)#5-K(2)-O(3)	90.80(9)
O(4)-K(2)-O(3)	177.49(11)
O(2)-K(2)-O(4)#6	109.51(9)
O(1)#5-K(2)-O(4)#6	68.21(9)
O(4)-K(2)-O(4)#6	115.79(11)
O(3)-K(2)-O(4)#6	66.63(8)
O(2)-K(2)-O(3)#2	74.03(8)
O(1)#5-K(2)-O(3)#2	108.27(9)
O(4)-K(2)-O(3)#2	66.62(8)
O(3)-K(2)-O(3)#2	111.01(11)
O(4)#6-K(2)-O(3)#2	175.38(10)
O(2)-K(2)-N(1)#2	119.59(9)
O(1)#5-K(2)-N(1)#2	62.57(8)
O(4)-K(2)-N(1)#2	91.45(9)
O(3)-K(2)-N(1)#2	87.57(9)
O(4)#6-K(2)-N(1)#2	123.45(9)
O(3)#2-K(2)-N(1)#2	52.00(8)
O(2)-K(2)-N(6)#7	64.31(8)
O(1)#5-K(2)-N(6)#7	113.52(9)
O(4)-K(2)-N(6)#7	89.56(9)
O(3)-K(2)-N(6)#7	91.57(9)
O(4)#6-K(2)-N(6)#7	52.72(9)
O(3)#2-K(2)-N(6)#7	131.84(9)
N(1)#2-K(2)-N(6)#7	175.97(10)
O(2)-K(2)-N(5)#7	62.88(9)

O(1)#5-K(2)-N(5)#7	115.47(9)
O(4)-K(2)-N(5)#7	67.08(9)
O(3)-K(2)-N(5)#7	113.88(9)
O(4)#6-K(2)-N(5)#7	69.63(9)
O(3)#2-K(2)-N(5)#7	114.93(9)
N(1)#2-K(2)-N(5)#7	158.53(8)
N(6)#7-K(2)-N(5)#7	22.81(8)
O(2)-K(2)-N(2)#2	120.92(9)
O(1)#5-K(2)-N(2)#2	60.67(9)
O(4)-K(2)-N(2)#2	113.83(9)
O(3)-K(2)-N(2)#2	65.40(8)
O(4)#6-K(2)-N(2)#2	106.63(9)
O(3)#2-K(2)-N(2)#2	68.79(8)
N(1)#2-K(2)-N(2)#2	22.81(7)
N(6)#7-K(2)-N(2)#2	155.21(9)
N(5)#7-K(2)-N(2)#2	175.77(10)
O(2)-K(2)-K(1)#6	134.77(6)
O(1)#5-K(2)-K(1)#6	44.46(6)
O(4)-K(2)-K(1)#6	135.26(8)
O(3)-K(2)-K(1)#6	46.36(6)
O(4)#6-K(2)-K(1)#6	55.75(7)
O(3)#2-K(2)-K(1)#6	119.68(7)
N(1)#2-K(2)-K(1)#6	69.79(6)
N(6)#7-K(2)-K(1)#6	106.85(6)
N(5)#7-K(2)-K(1)#6	125.37(6)
N(2)#2-K(2)-K(1)#6	50.88(6)
O(2)-K(2)-K(1)	41.87(6)
O(1)#5-K(2)-K(1)	139.81(6)
O(4)-K(2)-K(1)	54.11(7)
O(3)-K(2)-K(1)	123.69(7)
O(4)#6-K(2)-K(1)	140.47(7)
O(3)#2-K(2)-K(1)	44.14(6)
N(1)#2-K(2)-K(1)	95.95(6)
N(6)#7-K(2)-K(1)	87.81(6)
N(5)#7-K(2)-K(1)	71.90(6)
N(2)#2-K(2)-K(1)	112.10(6)

K(1)#6-K(2)-K(1)	161.30(4)
O(2)-K(2)-H(3)	106.8(6)
O(1)#5-K(2)-H(3)	73.9(6)
O(4)-K(2)-H(3)	17.0(5)
O(3)-K(2)-H(3)	164.7(6)
O(4)#6-K(2)-H(3)	106.7(9)
O(3)#2-K(2)-H(3)	74.5(10)
N(1)#2-K(2)-H(3)	85.1(10)
N(6)#7-K(2)-H(3)	94.8(11)
N(5)#7-K(2)-H(3)	74.3(10)
N(2)#2-K(2)-H(3)	105.4(10)
K(1)#6-K(2)-H(3)	118.3(6)
K(1)-K(2)-H(3)	70.6(6)
C(4)-O(1)-K(2)#8	143.1(2)
C(4)-O(1)-K(1)#9	117.2(2)
K(2)#8-O(1)-K(1)#9	92.21(9)
C(1)-O(2)-K(2)	144.3(2)
C(1)-O(2)-K(1)	117.5(2)
K(2)-O(2)-K(1)	97.80(8)
K(2)-O(3)-K(1)#6	87.77(9)
K(2)-O(3)-K(2)#6	106.96(10)
K(1)#6-O(3)-K(2)#6	88.76(9)
K(2)-O(3)-H(1)	130(9)
K(1)#6-O(3)-H(1)	74(9)
K(2)#6-O(3)-H(1)	119(8)
K(2)-O(3)-H(2)	102(7)
K(1)#6-O(3)-H(2)	167(8)
K(2)#6-O(3)-H(2)	80(8)
H(1)-O(3)-H(2)	105(10)
K(2)-O(4)-K(2)#2	109.26(11)
K(2)-O(4)-K(1)	83.40(8)
K(2)#2-O(4)-K(1)	77.12(7)
K(2)-O(4)-H(3)	97(4)
K(2)#2-O(4)-H(3)	88(4)
K(1)-O(4)-H(3)	164(4)
K(2)-O(4)-H(4)	140(3)

K(2)#2-O(4)-H(4)	109(3)
K(1)-O(4)-H(4)	93(3)
H(3)-O(4)-H(4)	96(5)
C(2)-N(1)-N(2)	106.6(3)
C(2)-N(1)-K(2)#6	135.4(2)
N(2)-N(1)-K(2)#6	82.6(2)
N(3)-N(2)-N(1)	111.4(3)
N(3)-N(2)-K(1)#10	73.0(2)
N(1)-N(2)-K(1)#10	129.9(2)
N(3)-N(2)-K(2)#6	137.6(3)
N(1)-N(2)-K(2)#6	74.6(2)
K(1)#10-N(2)-K(2)#6	72.40(8)
N(2)-N(3)-C(3)	105.9(3)
N(2)-N(3)-K(1)#9	144.2(2)
C(3)-N(3)-K(1)#9	106.6(2)
N(2)-N(3)-K(1)#10	82.4(2)
C(3)-N(3)-K(1)#10	127.2(2)
K(1)#9-N(3)-K(1)#10	89.69(9)
C(6)-N(4)-N(5)	106.1(3)
C(6)-N(4)-K(1)	104.8(2)
N(5)-N(4)-K(1)	145.2(2)
C(6)-N(4)-K(1)#7	128.8(2)
N(5)-N(4)-K(1)#7	84.4(2)
K(1)-N(4)-K(1)#7	88.65(9)
N(6)-N(5)-N(4)	111.3(3)
N(6)-N(5)-K(1)#7	132.4(2)
N(4)-N(5)-K(1)#7	71.0(2)
N(6)-N(5)-K(2)#3	75.7(2)
N(4)-N(5)-K(2)#3	134.5(2)
K(1)#7-N(5)-K(2)#3	138.30(11)
N(5)-N(6)-C(5)	106.2(3)
N(5)-N(6)-K(2)#3	81.5(2)
C(5)-N(6)-K(2)#3	133.5(2)
O(2)-C(1)-C(6)	124.2(3)
O(2)-C(1)-C(2)	124.6(4)
C(6)-C(1)-C(2)	111.2(3)

O(2)-C(1)-K(1)	44.32(17)
C(6)-C(1)-K(1)	81.58(19)
C(2)-C(1)-K(1)	162.6(3)
N(1)-C(2)-C(3)	107.9(3)
N(1)-C(2)-C(1)	128.2(4)
C(3)-C(2)-C(1)	123.9(4)
N(3)-C(3)-C(2)	108.2(3)
N(3)-C(3)-C(4)	126.7(3)
C(2)-C(3)-C(4)	125.0(3)
O(1)-C(4)-C(3)	124.0(3)
O(1)-C(4)-C(5)	125.1(4)
C(3)-C(4)-C(5)	110.9(3)
O(1)-C(4)-K(1)#9	44.62(19)
C(3)-C(4)-K(1)#9	80.49(19)
C(5)-C(4)-K(1)#9	164.8(2)
N(6)-C(5)-C(6)	108.3(3)
N(6)-C(5)-C(4)	127.5(3)
C(6)-C(5)-C(4)	124.2(4)
N(4)-C(6)-C(5)	108.1(3)
N(4)-C(6)-C(1)	127.2(3)
C(5)-C(6)-C(1)	124.7(3)

Symmetry transformations used to generate equivalent atoms:

#1 x-1,-y+1,z-1/2 #2 x-1/2,-y+3/2,z-1/2 #3 x,-y+1,z-1/2

#4 x-1,y,z-1 #5 x-1/2,y+1/2,z #6 x+1/2,-y+3/2,z+1/2

#7 x,-y+1,z+1/2 #8 x+1/2,y-1/2,z #9 x+1,-y+1,z+1/2

#10 x+1,y,z+1

Table S12. Anisotropic displacement parameters ($Å^2 x\ 10^3$) of K_2-btbq·$2H_2O$.

The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
K(1)	6(1)	23(1)	22(1)	4(1)	1(1)	-1(1)
K(2)	10(1)	19(1)	18(1)	-3(1)	4(1)	0(1)

O(1)	10(1)	17(1)	17(1)	2(1)	3(1)	2(1)
O(2)	9(1)	19(1)	14(1)	-2(1)	2(1)	3(1)
O(3)	18(1)	16(1)	20(1)	-1(1)	10(1)	-1(1)
O(4)	16(1)	25(2)	18(1)	-1(1)	10(1)	-2(1)
N(1)	10(1)	12(2)	16(2)	-2(1)	1(1)	-2(1)
N(2)	10(1)	18(2)	15(2)	3(1)	3(1)	-4(1)
N(3)	10(1)	16(2)	12(1)	3(1)	3(1)	-1(1)
N(4)	8(1)	18(2)	13(1)	1(1)	4(1)	-3(1)
N(5)	12(1)	17(2)	17(2)	-1(1)	2(1)	-4(1)
N(6)	10(1)	17(2)	20(2)	2(1)	2(1)	-2(1)
C(1)	6(1)	19(2)	8(2)	1(1)	-1(1)	3(1)
C(2)	6(1)	21(2)	10(1)	0(1)	2(1)	-2(1)
C(3)	6(1)	17(2)	6(1)	1(1)	2(1)	1(1)
C(4)	10(2)	18(2)	8(2)	-1(1)	6(1)	2(1)
C(5)	9(1)	19(2)	6(1)	0(1)	2(1)	0(1)
C(6)	7(1)	18(2)	6(1)	1(1)	2(1)	-3(1)

Table S13. Hydrogen Bonds for K_2-btbq·$2H_2O$

Donor---Hydrogen...Acceptor	Don--Hyd [Å]	Hyd--Acc [Å]	Don--Acc [Å]	D--H-----A
O3---H2...N1	0.89	1.97	2.805	156.9°
O4---H3...N6»2	0.89	2.02	2.831	150.8°
O3»1---H2»1...N1»1	0.89	1.97	2.805	156.9°
O4»1---H3»1...N6	0.89	2.02	2.831	150.8°
O3»2---H2»2...N1»2	0.89	1.97	2.805	156.9°
O3»3---H1»3...N5»6	0.88	2.05	2.870	154.6°
O3»3---H2»3...N1»3	0.89	1.97	2.805	156.9°
O4»3---H3»3...N6»10	0.89	2.02	2.831	150.8°
O3»4---H1»4...N5»9	0.88	2.05	2.870	154.6°
O3»4---H2»4...N1»4	0.89	1.97	2.805	156.9°
O4»4---H3»4...N6»5	0.89	2.02	2.831	150.8°
O3»5---H2»5...N1»5	0.89	1.97	2.805	156.9°
O3»6---H2»6...N1»6	0.89	1.97	2.805	156.9°
O4»6---H4»6...N2»10	0.87	2.13	2.994	173.2°
O3»7---H2»7...N1»7	0.89	1.97	2.805	156.9°
O3»8---H2»8...N1»8	0.89	1.97	2.805	156.9°
O3»9---H2»9...N1»9	0.89	1.97	2.805	156.9°
O4»9---H4»9...N2»5	0.87	2.13	2.994	173.2°
O3»10---H2»10...N1»10	0.89	1.97	2.805	156.9°