Electronic Supplementary Information

Explore Short-Wavelength Birefringent Crystals *via* Triggering Cooperative Arrangement Between Different π-Conjugated Groups

Xiao Wang,[a] Tingwen Han,[a] Kenneth R. Poeppelmeier,[b] Xueling Hou,[c] Shilie Pan[c] and Fangfang Zhang*[a, c]

[a]*College of Materials Science and engineering, Xinjiang University, Urumqi 830017, China*
[b]*Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208-3113, United States*
[c]*Research Center for Crystal Materials, State Key Laboratory of Functional Materials and Devices for Special Environmental Conditions, Xinjiang Key Laboratory of Functional Crystal Materials, Xinjiang Technical Institute of Physics and Chemistry of CAS, 40-1 South Beijing Road, Urumqi 830011, China*
**To whom correspondence should be addressed, E-mail: ffzhang@ms.xjb.ac.cn*

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1.Experimental Section

Reagents. K_2CO_3 (Aladdin, 99 %), Cs_2CO_3 (Aladdin, 99 %), H_3BO_3 (Aladdin, 99.99 %), $H_2C_4O_4$ (Macklin, 98 %) and $H_2C_2O_4·2H_2O$ (Aladdin, AR) were used as reagents without further purification.

Single-Crystal Growth. $K_2C_2O_4·B(OH)_3$ **(I)**, $Cs_4(HC_2O_4)_2(C_2O_4)·[B(OH)_3]_2$ **(II)** and $K(C_4O_4)_{0.5}·B(OH)_3$ **(III)** were synthesized by adopting a slow evaporation procedure at room temperature. Powder of K_2CO_3 (0.811 g, 5.87 mmol), H_3BO_3 (0.484 g, 7.83 mmol) and $H_2C_2O_4·2H_2O$ (0.705 g, 5.59 mmol) was dissolved in 15 mL deionized water for **I**. Cs_2CO_3 (0.587 g, 1.80 mmol), H_3BO_3 (0.311g, 5.03 mmol) and $H_2C_2O_4·2H_2O$ (0.459g, 3.64 mmol) was dissolved in 15 mL deionized water for **II**. Powder of K_2CO_3 (0.88 g, 6.37 mmol), H_3BO_3 (0.726 g, 11.74 mmol) and $H_2C_4O_4$ (0.394 g, 3.45 mmol) was dissolved in 15ml deionized water for **III**. The reactants were thoroughly mixed under ultrasonic vibration for 0.5 h, and magnetic agitation for 2 h. Then the beaker was covered by preservative film with small holes and allowed to crystallize through evaporating the solvent at room temperature (25 °C). The millimeter-sized crystals of **I** and **III** and the micron-sized crystals of **II** were obtained, respectively.

2.Characterizations and Measurements

Single-Crystal Structure Determination. Single-crystal XRD data of the three compounds were collected on Bruker D8 Venture diffractometer assembled with monochromatic Mo-Kα (λ = 0.71073 Å) as the radiation source. By using the Bruker SAINT program,[1] data integration was performed. The crystal structures of all compounds were settled down by the direct method and refined through SHELXTL system[2] with the Olex2 software.[3] The atomic coordinates for all atoms were determined through full matrix least-squares optimization. PLATON was utilized to verify the space group,[4] and no higher symmetry was observed. For detailed crystallographic data, refer to Table S1, while additional relevant data can be found in Tables S1−S4.

Powder X-ray Diffraction. Powder X-ray diffraction (XRD) data of the three compounds were measured using a Bruker D2 PHASER diffractometer equipped with Cu Kα radiation (λ = 1.5418 Å). The scanning step width was 0.02 ° in the 2θ range from 5 to 60°, and the fixed time of each step was 1 s.

Thermal Analysis. A NETZSCH STA 449 F3 simultaneous analyzer instrument was applied to measure the thermal gravimetric analysis (TGA)-differential scanning calorimetry (DSC) curves. The powder samples of $K_2C_2O_4·B(OH)_3$, $Cs_4(HC_2O_4)_2(C_2O_4)·[B(OH)_3]_2$ and $K(C_4O_4)_{0.5}·B(OH)_3$ were placed in Pt crucibles to heat, respectively, with the temperature ranging from 40 to 600 °C at a heating rate of 5 °C·min^{-1} under a N_2 atmosphere.

Infrared Spectroscopy. The powder samples of $K_2C_2O_4·B(OH)_3$, $Cs_4(HC_2O_4)_2(C_2O_4)·[B(OH)_3]_2$ and $K(C_4O_4)_{0.5}·B(OH)_3$ were mixed with KBr in a ratio of 1:100 and compressed into tablets. A Shimadzu IR Affinity transform infrared

spectrometer was used to collect infrared data in the range of 400-4000 cm^{-1}.

Transmittance Spectra and UV-vis-NIR Diffuse Reflectance Spectrum. The transmittance spectra of $K_2C_2O_4 \cdot B(OH)_3$ and $K(C_4O_4)_{0.5} \cdot B(OH)_3$ and the UV-vis-NIR diffuse reflectance spectrum of $Cs_4(HC_2O_4)_2(C_2O_4) \cdot [B(OH)_3]_2$ were measured with a Shimadzu SolidSpec-3700 DUV spectrophotometer for a range of 200–1600 nm.

3.Computation Details

Theoretical Calculations. The electronic band structures, total/partial density of states (DOS/PDOS) and birefringence values of three compounds were calculated using density functional theory (DFT) calculations performed with the CASTEP program.[5, 6] The exchange-correlation potential was calculated using the generalized gradient approximation (GGA) with Perdew-Bruker-Ernzerhof (PBE) functional.[7, 8] Using the norm-conserving pseudopotential (NCP), the following orbital electrons were treated as valence electrons: K: $3s^2\ 3p^6\ 4s^1$, Cs: $5s^2\ 5p^6\ 6s^1$, B: $2s^2\ 2p^1$, O:$2s^2\ 2p^4$, C: $2s^2\ 2p^2$ and H: $1s^1$. The cutoff energy was set as 750 eV, and the numerical integration of the Brillouin zone was performed via utilizing Monkhorst–Pack[9] *k*-point meshes 4 × 7 × 6 for $K_2C_2O_4 \cdot B(OH)_3$, 4 × 2 × 12 for $Cs_4(HC_2O_4)_2(C_2O_4) \cdot [B(OH)_3]_2$ and 3 × 2 × 2 for $K(C_4O_4)_{0.5} \cdot B(OH)_3$. The default values of the CASTEP code served as the other calculation parameters and convergent criteria. The optical properties of the compounds were calculated based on the dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$, the imaginary part of $\varepsilon_2(\omega)$ was obtained from the equation:

$$\varepsilon_2\left(q \to O_{\hat{u}}, h\omega\right) = (2e^2\pi/\Omega\varepsilon_o) \sum_{kcv} \left|\left\langle \varphi_k^c | u \cdot r | \varphi_k^v \right\rangle\right|^2 \delta\left[E_k^c - E_k^v - E\right],$$

where *h* stands for Planck's constant, *e* stands for the elementary charge, *r* is the position operator, *u* stands for the vector which defines the incident polarization, Ω is the volume of the unit cell, ε_o is the dielectric constant, $\left\langle \varphi_k^c | u \cdot r | \varphi_k^v \right\rangle$ represent the transition of momentum matrix element, E_k^c and E_k^v are used to represent energies of the occupied and unoccupied electronic states. Then, the birefringence Δn is determined by the real section of the dielectric function $\varepsilon_1(\omega)$ via the Kramers-Kronig transformation.

4.Tables and Figures

Table S1 Crystal data and structure refinement parameters for $K_2C_2O_4 \cdot B(OH)_3$, $Cs_4(HC_2O_4)_2(C_2O_4) \cdot [B(OH)_3]_2$ and $K(C_4O_4)_{0.5} \cdot B(OH)_3$.

Formula	$K_2C_2O_4 \cdot B(OH)_3$	$Cs_4(HC_2O_4)_2(C_2O_4) \cdot [B(OH)_3]_2$	$K(C_4O_4)_{0.5} \cdot B(OH)_3$
Formula weight	228.05	921.38	156.95
Temperature/K		302	
Crystal system	orthorhombic	orthorhombic	triclinic
Space group	*Pnma*	*Pbam*	$P\bar{1}$
a/Å	13.1577(13)	11.2578(15)	6.5081(6)
b/Å	7.0592(9)	24.484(3)	6.8597(7)
c/Å	7.8332(7)	3.9326(6)	7.7226(6)
α/°			94.604(4)
β/°			109.002(4)
γ/°			117.725(4)
Volume/Å^3	727.57(13)	1084.0(3)	277.27(5)
Z	4	2	2
ρ_{calc}/g·cm^{-3}	2.082	2.823	1.88
μ/mm^{-1}	1.297	6.751	0.897
F(000)	456.0	836	158
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2*θ* range for data collection/°	6.052 to 55.188	3.326 to 55.08	6.984 to 55.056
Index ranges	$-16 \le h \le 17$, $-9 \le k \le 9$, $-10 \le l \le 9$	$-14 \le h \le 14$, $-31 \le k \le 30$, $-5 \le l \le 5$	$-8 \le h \le 8$, $-8 \le k \le 8$, $-9 \le l \le 10$
Reflections collected	5151	7888	6077
Independent reflections	907 [R_{int} = 0.0670, R_{sigma} = 0.0474]	1420 [R_{int} = 0.0876, R_{sigma} = 0.0563]	1233 [R_{int} = 0.0538, R_{sigma} = 0.0359]
Data/restraints/parameters	907/0/71	1420/0/90	1233/0/94
Goodness-of-fit on F^2	1.055	1.046	1.082
Final *R* indexes [$I \ge 2\sigma(I)$][a]	R_1 = 0.0327, wR_2 = 0.0742	R_1 = 0.0340, wR_2 = 0.0642	R_1 = 0.0284, wR_2 = 0.0626
Final *R* indexes [all data][a]	R_1 = 0.0520, wR_2 = 0.0826	R_1 = 0.0644, wR_2 = 0.0725	R_1 = 0.0330, wR_2 = 0.0668
Largest diff. peak/hole/e·Å^{-3}	0.35/–0.28	0.81/–0.67	0.34/–0.30

[a] $R_1 = \Sigma||F_o| - |F_o||/\Sigma|F_o|$ and $wR_2 = [\Sigma w(F_o^2 - F_o^2)^2 / \Sigma wF_o^4]^{1/2}$

Table S2 Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for $K_2C_2O_4{\cdot}B(OH)_3$, $Cs_4(HC_2O_4)_2(C_2O_4){\cdot}[B(OH)_3]_2$ and $K(C_4O_4)_{0.5}{\cdot}B(OH)_3$. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Atom	*x*	*y*	*z*	U_{eq}
$K_2C_2O_4{\cdot}B(OH)_3$				
K(1)	3939.2(3)	4998.6(8)	8100.8(6)	28.9(2)
B(1)	1476(2)	2500	7365(4)	21.2(7)
C(1)	5905(2)	7500	6168(4)	23.4(7)
C(2)	6414(2)	7500	7978(3)	21.1(7)
O(1)	6441.8(16)	7500	4878(3)	51.5(9)
O(2)	7363.1(16)	7500	8046(3)	30.5(6)
O(3)	5814.8(17)	7500	9199(3)	34.8(6)
O(4)	4957.1(15)	7500	6133(2)	28.5(6)
O(5)	1627.2(15)	2500	5663(2)	28.8(6)
O(6)	2300.2(15)	2500	8423(3)	28.7(6)
O(7)	498.5(16)	2500	7896(3)	33.8(6)
$Cs_4(HC_2O_4)_2(C_2O_4){\cdot}[B(OH)_3]_2$				
Cs(1)	6137.1(5)	1788.5(2)	0	43.0(2)
Cs(2)	1454.4(4)	588.2(2)	10000	35.25(18)
B(1)	2938(8)	1890(3)	5000	31(2)
C(1)	-929(6)	1417(3)	5000	29.6(18)
C(2)	-1526(6)	848(3)	5000	30.8(18)
C(3)	4526(6)	223(3)	15000	36(2)
O(1)	3987(4)	2151(2)	5000	38.1(15)
O(2)	1883(3)	2169.2(14)	5000	40.6(15)
O(3)	2894(3)	1331.1(14)	5000	45.9(18)
O(4)	154(4)	1413.5(19)	5000	49.2(18)
O(5)	-1588(5)	1809.4(19)	5000	65(2)
O(6)	-2669(4)	869(2)	5000	57(2)
O(7)	-956(5)	433(2)	5000	57(2)
O(8)	3458(4)	78(2)	15000	45.8(17)
O(9)	4859(5)	711(2)	15000	66(2)
$K(C_4O_4)_{0.5}{\cdot}B(OH)_3$				
K(1)	2447.0(7)	2693.8(7)	230.7(5)	30.26(14)
B(1)	4104(4)	8465(3)	2328(3)	24.3(4)
C(1)	8764(3)	5381(3)	4100(2)	23.0(3)
C(2)	10097(3)	5964(3)	6162(2)	23.7(3)
O(1)	2854(2)	9600(2)	2353.7(18)	30.1(3)
O(2)	5727(3)	8490(2)	3984.5(17)	34.6(3)
O(3)	3699(2)	7272(2)	639.4(17)	30.5(3)
O(4)	7258(2)	5836(2)	2988.2(16)	32.5(3)
O(5)	10230(2)	7122(2)	7579.3(16)	34.5(3)

Table S3 Selected bond lengths for $K_2C_2O_4 \cdot B(OH)_3$, $Cs_4(HC_2O_4)_2(C_2O_4) \cdot B(OH)_3$ and $K(C_4O_4)_{0.5} \cdot B(OH)_3$.

Bond	Length/Å	Bond	Length/Å
$K_2C_2O_4 \cdot B(OH)_3$			
K(1)-O(1)[4]	2.9675(17)	B(1)-O(5)	1.348(4)
K(1)-O(2)[5]	2.8679(17)	B(1)-O(6)	1.365(4)
K(1)-O(3)[1]	2.7730(17)	B(1)-O(7)	1.352(4)
K(1)-O(3)	3.1541(19)	C(1)-C(2)	1.568(4)
K(1)-O(4)	2.6994(15)	C(1)-O(1)	1.233(3)
K(1)-O(5)[6]	2.7751(16)	C(1)-O(4)	1.248(4)
K(1)-O(6)	2.7973(16)	C(2)-O(2)	1.250(4)
K(1)-O(7)[7]	2.8161(17)	C(2)-O(3)	1.240(3)

Symmetry transformation used to generate equivalent atoms:

[1] +X,3/2-Y,+Z; [2] 1-X,1-Y,2-Z; [3] +X,1/2-Y,+Z; [4] 1-X,1-Y,1-Z; [5] -1/2+X,+Y,3/2-Z; [6] 1/2-X,1-Y,1/2+Z; [7] 1/2+X,+Y,3/2-Z; [8] 1-X,1/2+Y,1-Z; [9] 1/2+X,3/2-Y,3/2-Z; [10] 1-X,1/2+Y,2-Z; [11] 1/2-X,-1/2+Y,-1/2+Z; [12] 1/2-X,1-Y,-1/2+Z; [13] -1/2+X,1/2-Y,3/2-Z

$Cs_4(HC_2O_4)_2(C_2O_4) \cdot [B(OH)_3]_2$			
Cs(1)-O(1)[2]	3.243(4)	Cs(2)-O(7)	3.372(4)
Cs(1)-O(1)	3.243(4)	Cs(2)-O(7)[3]	3.230(4)
Cs(1)-O(2)[5]	3.329(3)	Cs(2)-O(7)[4]	3.230(4)
Cs(1)-O(2)[6]	3.329(3)	Cs(2)-O(7)[1]	3.372(4)
Cs(1)-O(5)[7]	3.229(4)	B(1)-O(1)	1.343(9)
Cs(1)-O(5)[8]	3.229(4)	B(1)-O(2)	1.371(9)
Cs(1)-O(6)[7]	3.277(4)	B(1)-O(3)	1.368(8)
Cs(1)-O(6)[8]	3.277(4)	C(3)-O(8)	1.254(8)
Cs(1)-O(9)[9]	3.590(4)	C(1)-O(4)	1.220(8)
Cs(1)-O(9)[2]	3.590(4)	C(1)-O(5)	1.213(8)
Cs(2)-O(3)[1]	3.131(3)	C(2)-O(7)	1.202(9)
Cs(2)-O(3)	3.131(3)	C(2)-O(6)	1.289(8)
Cs(2)-O(8)	3.242(4)	C(3)-O(9)	1.254(8)
Cs(2)-O(8)[2]	3.242(4)	C(2)-C(1)	1.547(10)
Cs(2)-O(4)	3.177(4)	C(3)[10]-C(3)	1.524(13)
Cs(2)-O(4)[1]	3.177(4)		

Symmetry transformation used to generate equivalent atoms:

[1] +X,+Y,1+Z; [2] +X,+Y,-1+Z; [3] -X,-Y,1-Z; [4] -X,-Y,2-Z; [5] 1/2+X,1/2-Y,+Z; [6] 1/2+X,1/2-Y,-1+Z; [7] 1+X,+Y,+Z; [8] 1+X,+Y,-1+Z; [9] +X,+Y,-2+Z; [10] 1-X,-Y,3-Z

$K(C_4O_4)_{0.5} \cdot B(OH)_3$			
K(1)-O(1)[3]	2.8395(13)	B(1)-O(1)	1.366(2)
K(1)-O(1)[4]	2.8850(13)	B(1)-O(3)	1.358(2)

K(1)-O(4)	2.7616(13)	B(1)-O(2)	1.361(2)
K(1)-O(4)[1]	2.7869(13)	C(1)-O(4)	1.2549(19)
K(1)-O(3)[1]	2.7908(13)	C(2)-O(5)	1.253(2)
K(1)-O(3)	2.8138(14)	C(2)-C(1)	1.457(2)
K(1)-O(5)[5]	2.8286(13)	C(1)-C(2)[6]	1.465(2)

Symmetry transformation used to generate equivalent atoms:

[1] 1-X,1-Y,-Z; [2] -X,-Y,-Z; [3] +X,-1+Y,+Z; [4] -X,1-Y,-Z; [5] 1-X,1-Y,1-Z; [6] 2-X,1-Y,1-Z

Table S4 Selected bond angles for $K_2C_2O_4 \cdot B(OH)_3$, $Cs_4(HC_2O_4)_2(C_2O_4) \cdot [B(OH)_3]_2$ and $K(C_4O_4)_{0.5} \cdot B(OH)_3$.

Bond	Angle/°	Bond	Angle/°
$K_2C_2O_4 \cdot B(OH)_3$			
O(1)[4]-K(1)-O(3)	132.79(6)	O(5)[6]-K(1)-O(2)[5]	68.93(5)
O(2)[5]-K(1)-O(1)[4]	89.86(5)	O(5)[6]-K(1)-O(3)	69.92(5)
O(2)[5]-K(1)-O(3)	107.85(4)	O(5)[6]-K(1)-O(6)	97.41(5)
O(3)[2]-K(1)-O(1)[4]	103.97(4)	O(5)[6]-K(1)-O(7)[7]	142.63(6)
O(3)[2]-K(1)-O(2)[5]	135.64(6)	O6-K(1)-O(1)[4]	64.27(5)
O(3)[2]-K(1)-O(3)	93.25(4)	O6-K(1)-O(2)[5]	81.90(4)
O(3)[2]-K(1)-O(5)[6]	83.36(5)	O6-K(1)-O(3)	158.69(6)
O(3)[2]-K(1)-O(6)	67.68(6)	O6-K(1)-O(7)[7]	101.05(4)
O(3)[2]-K(1)-O(7)[7]	74.22(5)	O(7)[7]-K(1)-O(1)[4]	62.14(6)
O(4)-K(1)-O(1)[4]	91.36(5)	O(7)[7]-K(1)-O(2)[5]	145.65(6)
O(4)-K(1)-O(2)[5]	77.13(5)	O(7)[7]-K(1)-O(3)	81.73(4)
O(4)-K(1)-O(3)	53.22(6)	O(5)-B(1)-O(6)	118.9(3)
O(4)-K(1)-O(3)[2]	142.52(6)	O(5)-B(1)-O(7)	116.4(3)
O(4)-K(1)-O(5)[6]	97.46(4)	O(7)-B(1)-O(6)	124.7(3)
O(4)-K(1)-O6	147.82(6)	O(1)-C(1)-O(4)	123.7(3)
O(4)-K(1)-O(7)[7]	83.68(4)	O(3)-C(2)-O(2)	127.1(3)
O(5)[6]-K(1)-O(1)[4]	154.35(6)		

Symmetry transformation used to generate equivalent atoms:

[1] +X,3/2-Y,+Z; [2] 1-X,1-Y,2-Z; [3]+X,1/2-Y,+Z; [4] 1-X,1-Y,1-Z; [5] -1/2+X,+Y,3/2-Z; [6] 1/2-X,1-Y,1/2+Z; [7] 1/2+X,+Y,3/2-Z; [8] 1-X,1/2+Y,1-Z; [9] 1/2+X,3/2-Y,3/2-Z; [10] 1-X,1/2+Y,2-Z; [11] 1/2-X,-1/2+Y,-1/2+Z; [12] 1/2-X,1-Y,-1/2+Z; [13] -1/2+X,1/2-Y,3/2-Z

$Cs_4(HC_2O_4)_2(C_2O_4) \cdot [B(OH)_3]_2$			
O(3)[1]-Cs(2)-O(3)	77.82(8)	O(1)[2]-Cs(1)-O(2)[5]	67.67(9)
O(3)[1]-Cs(2)-O(8)[2]	104.16(9)	O(1)-Cs(1)-O(2)[6]	67.67(9)
O(3)-Cs(2)-O(8)[2]	58.86(10)	O(1)[2]-Cs(1)-O(6)[7]	149.11(12)
O(3)-Cs(2)-O(8)	104.16(9)	O(1)[2]-Cs(1)-O(6)[8]	97.49(9)

O(3)^{1}-Cs(2)-O(8)	58.86(10)	O(1)-Cs(1)-O(6)^{7}	97.49(9)
O(3)^{1}-Cs(2)-O(4)^{1}	58.68(10)	O(1)-Cs(1)-O(6)^{8}	149.11(12)
O(3)-Cs(2)-O(4)	58.68(10)	O(1)-Cs(1)-O(9)^{9}	103.54(10)
O(3)^{1}-Cs(2)-O(4)	104.93(9)	O(1)^{2}-Cs(1)-O(9)^{2}	103.54(10)
O(3)-Cs(2)-O(4)^{1}	104.93(9)	O(1)^{2}-Cs(1)-O(9)^{9}	64.53(11)
O(3)^{1}-Cs(2)-O(7)^{3}	157.24(11)	O(1)-Cs(1)-O(9)^{2}	64.52(11)
O(3)^{1}-Cs(2)-O(7)^{1}	96.65(8)	O(2)^{6}-Cs(1)-O(2)^{5}	72.40(7)
O(3)-Cs(2)-O(7)^{1}	148.02(10)	O(2)^{5}-Cs(1)-O(9)^{9}	109.91(6)
O(3)-Cs(2)-O(7)^{4}	157.24(11)	O(2)^{6}-Cs(1)-O(9)^{9}	170.93(10)
O(3)^{1}-Cs(2)-O(7)^{4}	99.05(7)	O(2)^{6}-Cs(1)-O(9)^{2}	109.91(6)
O(3)-Cs(2)-O(7)	96.65(8)	O(2)^{5}-Cs(1)-O(9)^{2}	170.93(10)
O(3)^{1}-Cs(2)-O(7)	148.02(10)	O(5)^{7}-Cs(1)-O(1)	102.61(8)
O(3)-Cs(2)-O(7)^{3}	99.05(7)	O(5)^{8}-Cs(1)-O(1)^{2}	102.61(8)
O(8)^{2}-Cs(2)-O(8)	74.66(10)	O(5)^{7}-Cs(1)-O(1)^{2}	163.12(12)
O(8)^{2}-Cs(2)-O(7)	99.35(9)	O(5)^{8}-Cs(1)-O(1)	163.12(12)
O(8)^{2}-Cs(2)-O(7)^{1}	150.43(12)	O(5)^{7}-Cs(1)-O(2)^{5}	98.48(9)
O(8)-Cs(2)-O(7)	150.43(12)	O(5)^{8}-Cs(1)-O(2)^{5}	55.12(10)
O(8)-Cs(2)-O(7)^{1}	99.36(9)	O(5)^{8}-Cs(1)-O(2)^{6}	98.48(9)
O(4)^{1}-Cs(2)-O(8)^{2}	160.20(12)	O(5)^{7}-Cs(1)-O(2)^{6}	55.12(10)
O(4)-Cs(2)-O(8)^{2}	100.96(8)	O(5)^{7}-Cs(1)-O(5)^{8}	75.03(12)
O(4)^{1}-Cs(2)-O(8)	100.96(8)	O(5)^{8}-Cs(1)-O(6)^{7}	92.93(10)
O(4)-Cs(2)-O(8)	160.20(12)	O(5)^{8}-Cs(1)-O(6)^{8}	47.18(11)
O(4)^{1}-Cs(2)-O(4)	76.48(11)	O(5)^{7}-Cs(1)-O(6)^{7}	47.18(11)
O(4)^{1}-Cs(2)-O(7)	93.56(10)	O(5)^{7}-Cs(1)-O(6)^{8}	92.93(10)
O(4)^{1}-Cs(2)-O(7)^{4}	92.03(10)	O(5)^{7}-Cs(1)-O(9)^{9}	131.53(11)
O(4)^{1}-Cs(2)-O(7)^{1}	48.72(12)	O(5)^{8}-Cs(1)-O(9)^{9}	89.77(10)
O(4)-Cs(2)-O(7)^{1}	93.55(10)	O(5)^{8}-Cs(1)-O(9)^{2}	131.53(11)
O(4)-Cs(2)-O(7)^{3}	92.03(10)	O(5)^{7}-Cs(1)-O(9)^{2}	89.77(10)
O(4)-Cs(2)-O(7)^{4}	142.10(13)	O(6)^{7}-Cs(1)-O(2)^{6}	93.94(8)
O(4)^{1}-Cs(2)-O(7)^{3}	142.10(13)	O(6)^{8}-Cs(1)-O(2)^{6}	141.03(10)
O(4)-Cs(2)-O(7)	48.72(12)	O(6)^{8}-Cs(1)-O(2)^{5}	93.94(8)
O(7)^{4}-Cs(2)-O(8)^{2}	101.07(11)	O(6)^{7}-Cs(1)-O(2)^{5}	141.03(10)
O(7)^{4}-Cs(2)-O(8)	56.88(12)	O(6)^{8}-Cs(1)-O(6)^{7}	73.75(11)
O(7)^{3}-Cs(2)-O(8)	101.07(11)	O(6)^{7}-Cs(1)-O(9)^{2}	48.03(11)
O(7)^{3}-Cs(2)-O(8)^{2}	56.88(12)	O(6)^{8}-Cs(1)-O(9)^{9}	48.03(11)
O(7)^{3}-Cs(2)-O(7)	54.39(16)	O(6)^{8}-Cs(1)-O(9)^{2}	89.34(10)
O(7)^{4}-Cs(2)-O(7)	97.34(8)	O(6)^{7}-Cs(1)-O(9)^{9}	89.34(10)
O(7)^{1}-Cs(2)-O(7)	71.34(11)	O(9)^{9}-Cs(1)-O(9)^{2}	66.41(9)
O(7)^{4}-Cs(2)-O(7)^{1}	54.39(16)	O(5)-C(1)-O(4)	128.1(7)
O(7)^{3}-Cs(2)-O(7)^{1}	97.34(8)	O(8)-C3-O(9)	123.7(6)
O(7)^{3}-Cs(2)-O(7)^{4}	75.01(11)	O(7)-C(2)-O(6)	124.6(7)

O(1)-Cs(1)-O(1)^2	74.66(10)	O(1)-B(1)-O(2)	121.6(6)
O(1)-Cs(1)-O(2)^5	109.66(9)	O(1)-B(1)-O(3)	120.6(6)
O(1)^2-Cs(1)-O(2)^6	109.66(9)	O(3)-B(1)-O(2)	117.8(6)

Symmetry transformation used to generate equivalent atoms:

[1] +X,+Y,1+Z; [2] +X,+Y,-1+Z; [3] -X,-Y,1-Z; [4] -X,-Y,2-Z; [5] 1/2+X,1/2-Y,-1+Z; [6] 1/2+X,1/2-Y,+Z; [7] 1+X,+Y,+Z; [8] 1+X,+Y,-1+Z; [9] +X,+Y,-2+Z; [10] -1/2+X,1/2-Y,1+Z; [11] -1/2+X,1/2-Y,+Z; [12] -1+X,+Y,+Z; [13] -1+X,+Y,1+Z; [14] +X,+Y,2+Z; [15] 1-X,-Y,3-Z

$K(C_4O_4)_{0.5}\cdot B(OH)_3$			
O(1)^3-K(1)-O(1)^4	105.43(3)	O(3)^2-K(1)-O(1)^4	125.56(4)
O(4)^2-K(1)-O(1)^4	78.14(4)	O(3)-K(1)-O(1)^4	99.34(4)
O(4)-K(1)-O(1)^3	84.17(4)	O(3)-K(1)-O(1)^3	142.47(4)
O(4)^2-K(1)-O(1)^3	145.80(4)	O(3)^2-K(1)-O(1)^3	85.74(4)
O(4)-K(1)-O(1)^4	163.82(4)	O(3)^2-K(1)-O(3)	102.34(3)
O(4)-K(1)-O(4)^2	101.40(3)	O(3)-K(1)-O(5)^5	80.53(4)
O(4)^2-K(1)-O(3)	66.57(4)	O(3)^2-K(1)-O(5)^5	159.43(4)
O(4)-K(1)-O(3)^2	67.23(4)	O(5)^5-K(1)-O(1)^4	73.15(4)
O(4)-K(1)-O(3)	66.32(4)	O(5)^5-K(1)-O(1)^3	80.23(4)
O(4)^2-K(1)-O(3)^2	66.29(4)	O(3)-B(1)-O(1)	119.88(15)
O(4)^2-K(1)-O(5)^5	131.58(4)	O(3)-B(1)-O(2)	119.60(15)
O(4)-K(1)-O(5)^5	96.24(4)	O(2)-B(1)-O(1)	120.51(15)

Symmetry transformation used to generate equivalent atoms:

[1] -X,-Y,-Z; [2] 1-X,1-Y,-Z; [3] +X,-1+Y,+Z; [4] -X,1-Y,-Z; [5] 1-X,1-Y,1-Z; [6] +X,1+Y,+Z; [7] 2-X,1-Y,1-Z

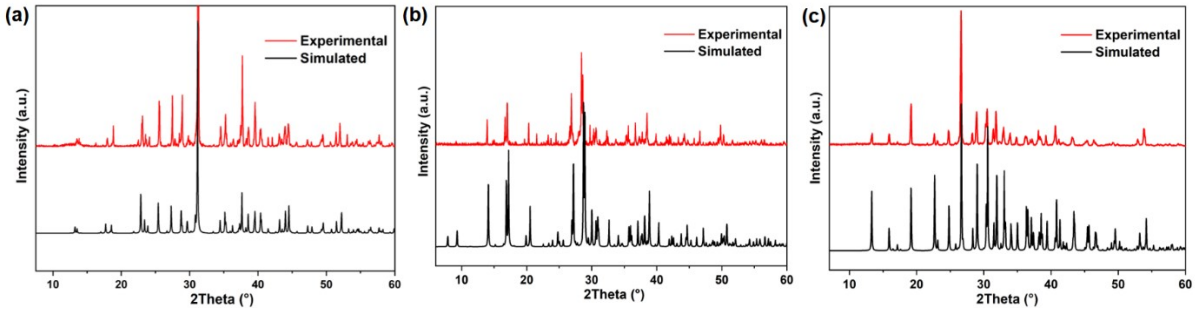

Figure S1. Experimental and simulated XRD patterns for $K_2C_2O_4\cdot B(OH)_3$ (a), $Cs_4(HC_2O_4)_2(C_2O_4)\cdot[B(OH)_3]_2$ (b) and $K(C_4O_4)_{0.5}\cdot B(OH)_3$ (c).

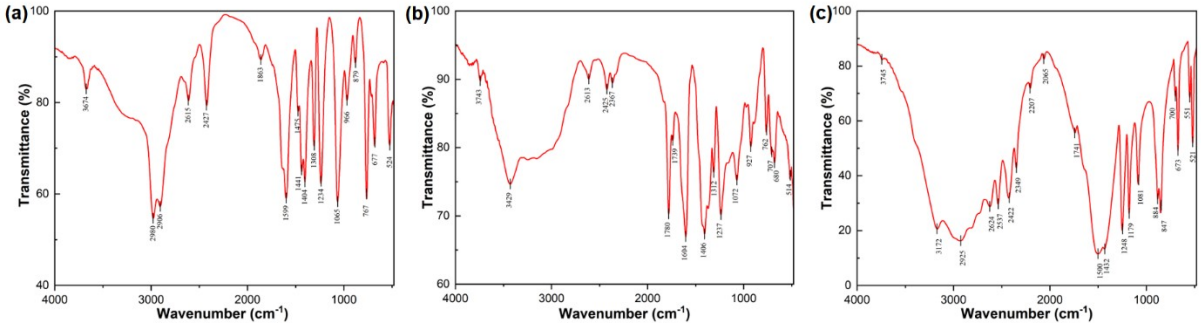

Figure S2. IR spectra of $K_2C_2O_4 \cdot B(OH)_3$ (a), $Cs_4(HC_2O_4)_2(C_2O_4) \cdot [B(OH)_3]_2$ (b) and $K(C_4O_4)_{0.5} \cdot B(OH)_3$ (c).

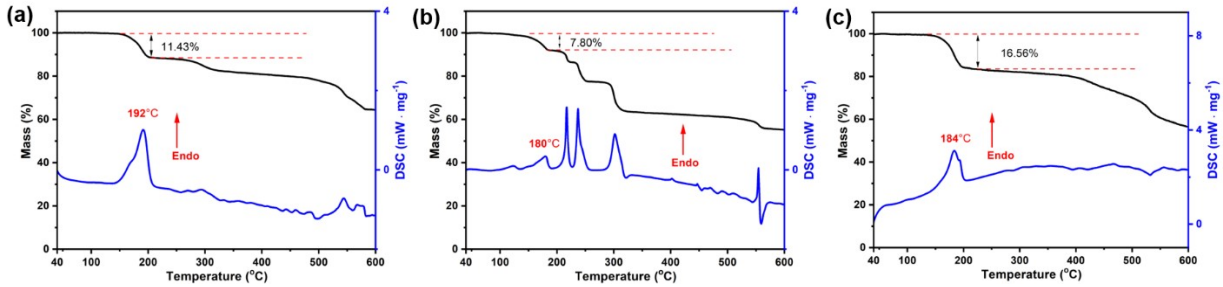

Figure S3. TG-DSC curves of $K_2C_2O_4 \cdot B(OH)_3$ (a), $Cs_4(HC_2O_4)_2(C_2O_4) \cdot [B(OH)_3]_2$ (b) and $K(C_4O_4)_{0.5} \cdot B(OH)_3$ (c).

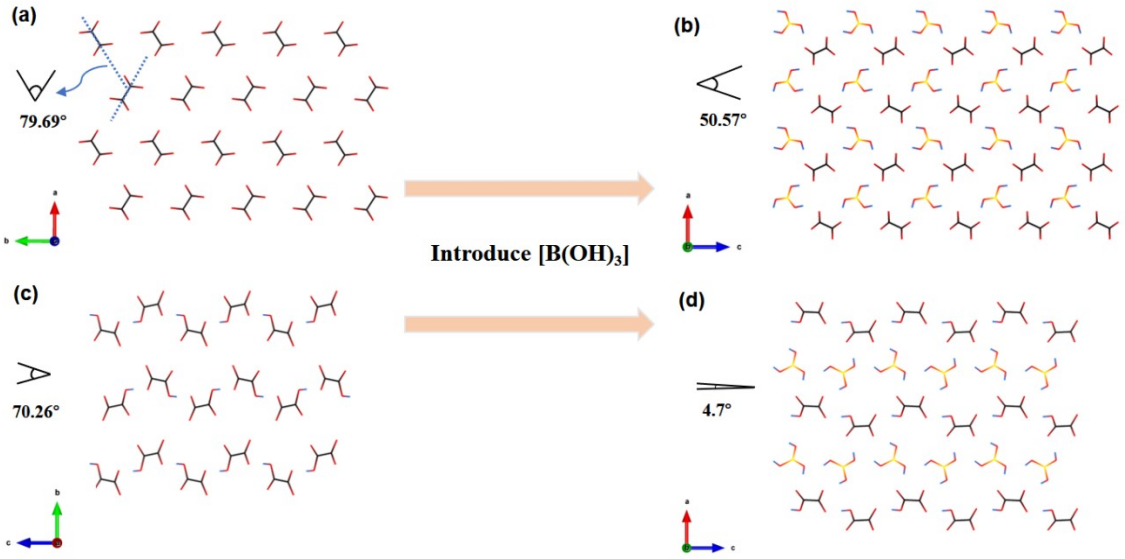

Figure S4. Wireframe representation of the anionic groups in $K_2C_2O_4$[10](a), $K_2C_2O_4 \cdot B(OH)_3$ (b), KHC_2O_4[11] (c) and $KHC_2O_4 \cdot B(OH)_3$[12] (d).

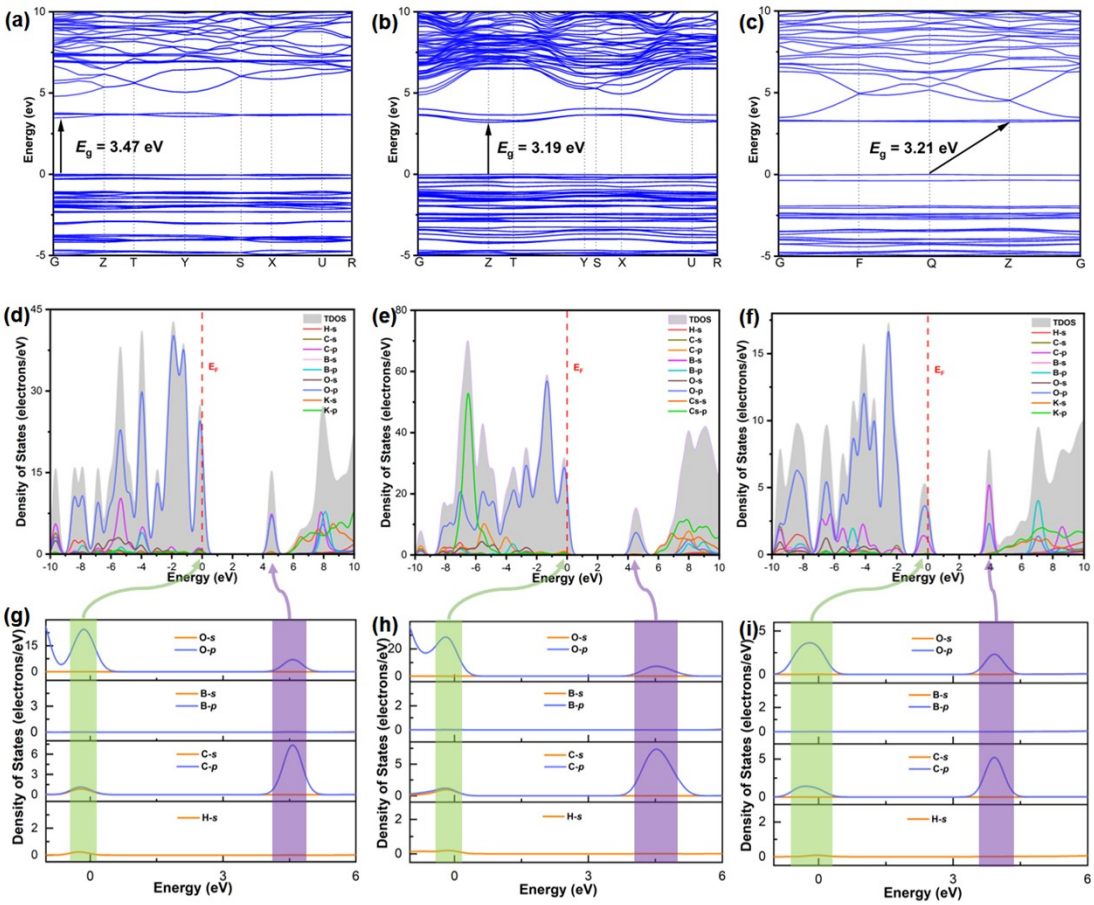

Figure S5. Electronic band structures and total and partial density of states of $K_2C_2O_4{\cdot}B(OH)_3$ (a, d, g) , $Cs_4(HC_2O_4)_2(C_2O_4){\cdot}[B(OH)_3]_2$ (b, e, h) and $K(C_4O_4)_{0.5}{\cdot}B(OH)_3$ (c, f, i).

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