Supporting information

# Large Optical Anisotropy-Oriented Construction of Carbonate-Nitrate Chloride as Potential Ultraviolet Birefringent Materials

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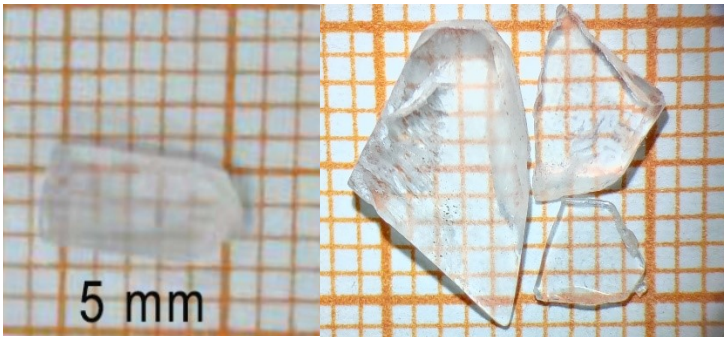

Figure S1. Photograph of crystals grown via mild solvent evaporation method.

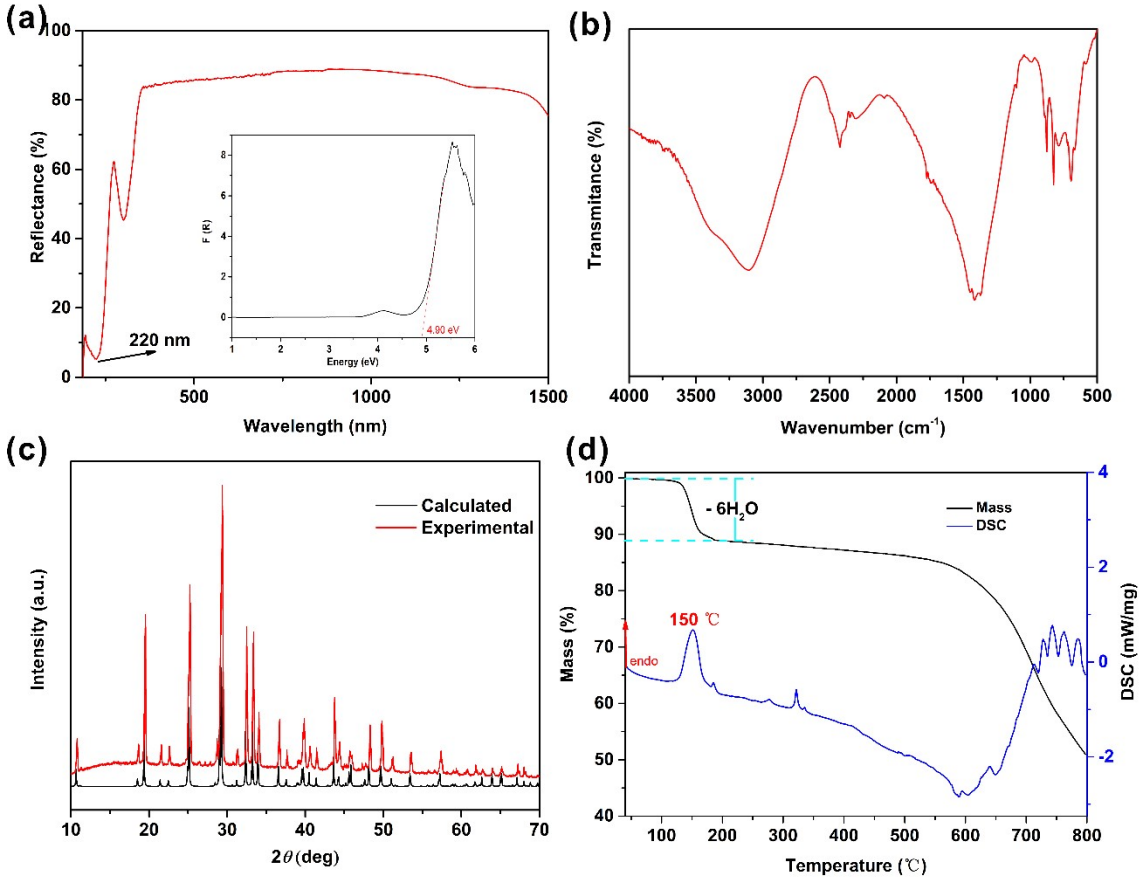


Figure S2. (a) UV−vis-NIR diffuse reflectance spectra for $Na_3Rb_6(CO_3)_3(NO_3)_2Cl\cdot(H_2O)_6$; (b) IR spectrum for $Na_3Rb_6(CO_3)_3(NO_3)_2Cl\cdot(H_2O)_6$; (c) XRD patterns; (d) TG and DSC curves of $Na_3Rb_6(CO_3)_3(NO_3)_2Cl\cdot(H_2O)_6$ in the temperature region from 40 to 800 ℃.

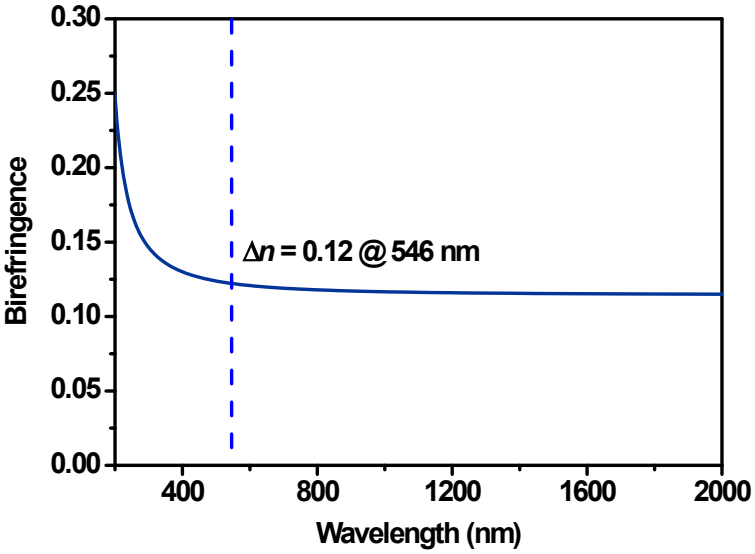


Figure S3. Calculated birefringence curve.

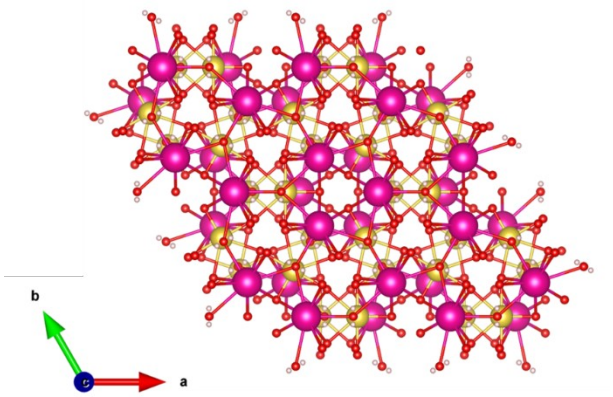


Figure S4. The structure of the title compounds in the *ab* plane excluding C, N and Cl atoms.

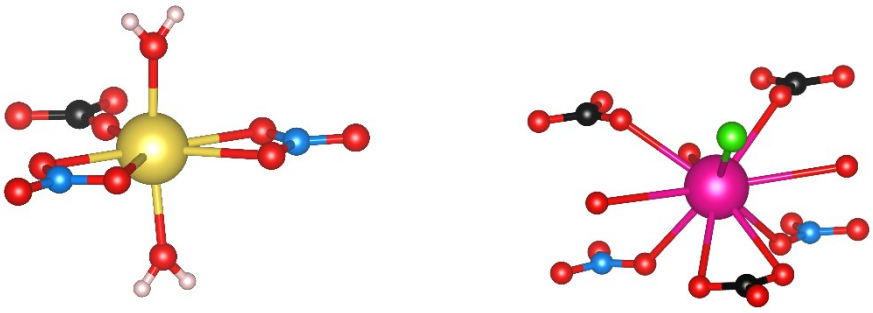

Figure S5. Alignments of planar triangular anion groups by the $NaO_5(H_2O)_2$ and $RbO_9Cl$ polyhedra.

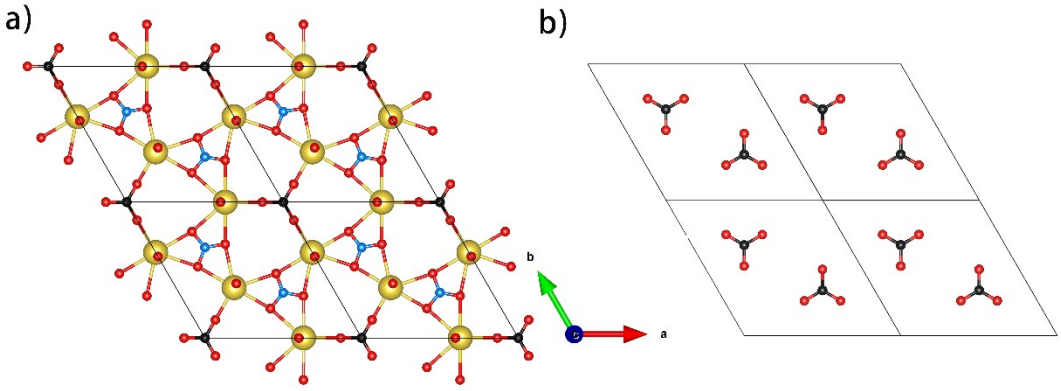


Figure S6. a) Two-dimensional (2D) layer of $NaO_7$ pentagonal bipyramid, $C(1)O_3$ and $NO_3$ trigonal plane units; b) The $C(2)O_3$ trigonal plane units in the *ab* plane.

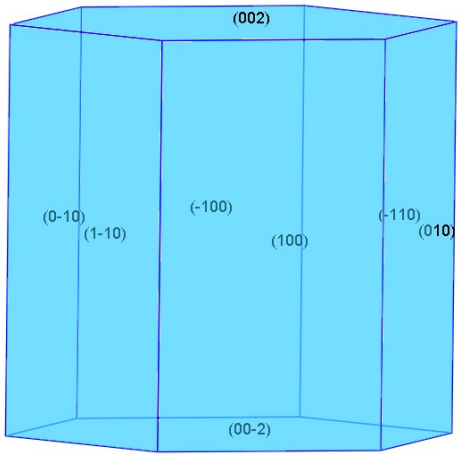


Figure S7. Theoretical crystal morphology of $Na_3Rb_6(CO_3)_3(NO_3)_2Cl\cdot(H_2O)_6$.

Table S1. Atomic coordinates ($\times 10^4$), equivalent isotropic displacement parameters ($Å^2 \times 10^3$) and bond valence sum (BVS) calculation for $Na_3Rb_6(CO_3)_3(NO_3)_2Cl\cdot(H_2O)_6$. U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

| | **Wyckoff sites** | ***x*** | ***y*** | ***z*** | ***U(eq)*** | **BVS** |
|---|---|---|---|---|---|---|
| Na(1) | 6g | 3703(2) | 0 | 2500 | 24(1) | 1.22 |
| Rb(1) | 12k | 2737(1) | 2737(1) | 1192(1) | 27(1) | 1.10 |
| C(1) | 2a | 0 | 0 | 2500 | 16(2) | 4.08 |
| C(2) | 4d | 6667 | 3333 | 0 | 24(2) | 4.04 |
| N(1) | 4c | 6667 | 3333 | 2500 | 22(1) | 4.91 |
| O(1) | 6g | 0 | 1334(4) | 2500 | 28(1) | 2.09 |
| O(2) | 12j | 5123(4) | 2562(2) | 0 | 33(1) | 1.60 |
| O(3) | 12k | 5997(4) | 5997(4) | 1053(2) | 36(1) | 0.45 |
| O(4) | 6g | 5256(4) | 3088(4) | 2500 | 34(1) | 2.08 |
| Cl(1) | 2b | 0 | 0 | 0 | 29(1) | 1.26 |

Table S2. Selected bond distances (Å) and angles (deg) for $Na_3Rb_6(CO_3)_3(NO_3)_2Cl\cdot(H_2O)_6$.

| Bond | Distances (Å) |
|---|---|
| Na(1)-O(4) | 2.560(3) |
| Na(1)-O(4)#4 | 2.715(4) |
| Na(1)-O(4)#11 | 2.560(3) |
| Na(1)-O(4)#12 | 2.715(4) |
| Na(1)-O(3)#4 | 2.307(3) |
| Na(1)-O(3)#13 | 2.307(3) |
| Na(1)-O(1)#6 | 2.268(4) |
| Rb(1)-Cl(1) | 3.2282(4) |
| Rb(1)-O(4) | 3.066(2) |
| Rb(1)-O(4)#2 | 3.066(2) |
| Rb(1)-O(2) | 3.030(2) |
| Rb(1)-O(2)#3 | 3.030(2) |
| Rb(1)-O(3)#4 | 3.400(3) |
| Rb(1)-O(3) | 3.128(4) |
| Rb(1)-O(3)#5 | 3.400(3) |
| Rb(1)-O(1) | 3.0718(4) |
| Rb(1)-O(1)#6 | 3.0718(4) |
| C(1)-O(1)#1 | 1.277(4) |
| C(1)-O(1) | 1.277(4) |
| C(1)-O(1)#6 | 1.277(4) |
| C(2)-O(2)#4 | 1.280(3) |
| C(2)-O(2)#17 | 1.280(3) |
| N(1)-O(4)#15 | 1.250(3) |
| N(1)-O(4)#4 | 1.250(3) |

| Bond | Angles (deg) | Bond | Angles (deg) |
|---|---|---|---|
| O(4)#4-Na(1)-O(4)#12 | 82.91(13) | O(2)#3-Rb(1)-Cl(1) | 85.41(4) |
| O(4)#11-Na(1)-O(4)#12 | 48.36(13) | O(2)-Rb(1)-O(4)#2 | 132.40(7) |
| O(4)-Na(1)-O(4)#12 | 131.27(8) | O(2)#3-Rb(1)-O(4)#2 | 81.55(5) |
| O(4)-Na(1)-O(4)#4 | 48.36(13) | O(2)-Rb(1)-O(4) | 81.55(5) |
| O(4)#11-Na(1)-O(4)#4 | 131.27(8) | O(2)#3-Rb(1)-O(4) | 132.40(7) |
| O(4)-Na(1)-O(4)#11 | 179.63(17) | O(2)#3-Rb(1)-O(2) | 88.984(13) |
| O(3)#13-Na(1)-O(4)#12 | 84.62(8) | O(2)#3-Rb(1)-O(3) | 66.93(5) |
| O(3)#13-Na(1)-O(4)#4 | 84.62(8) | O(2)-Rb(1)-O(3)#4 | 49.30(5) |
| O(3)#13-Na(1)-O(4)#11 | 89.977(11) | O(2)-Rb(1)-O(3) | 66.93(5) |
| O(3)#4-Na(1)-O(4)#11 | 89.977(11) | O(2)#3-Rb(1)-O(3)#4 | 135.74(6) |

| | | | |
|---|---|---|---|
| O(3)#4-Na(1)-O(4)#4 | 84.62(8) | O(2)#3-Rb(1)-O(3)#5 | 49.30(5) |
| O(3)#4-Na(1)-O(4)#12 | 84.62(8) | O(2)-Rb(1)-O(3)#5 | 135.74(6) |
| O(3)#4-Na(1)-O(4) | 89.977(11) | O(2)#3-Rb(1)-O(1)#6 | 153.72(7) |
| O(3)#13-Na(1)-O(4) | 89.977(11) | O(2)-Rb(1)-O(1)#6 | 113.09(6) |
| O(3)#13-Na(1)-O(3)#4 | 165.6(2) | O(2)-Rb(1)-O(1) | 153.72(7) |
| O(1)#6-Na(1)-O(4)#12 | 138.55(7) | O(2)#3-Rb(1)-O(1) | 113.09(6) |
| O(1)#6-Na(1)-O(4)#4 | 138.55(7) | O(3)-Rb(1)-Cl(1) | 140.24(6) |
| O(1)#6-Na(1)-O(4)#11 | 90.19(8) | O(3)-Rb(1)-O(3)#4 | 101.65(4) |
| O(1)#6-Na(1)-O(4) | 90.19(8) | O(3)#5-Rb(1)-O(3)#4 | 154.95(9) |
| O(1)#6-Na(1)-O(3)#4 | 97.18(11) | O(3)-Rb(1)-O(3)#5 | 101.65(4) |
| O(1)#6-Na(1)-O(3)#13 | 97.18(11) | O(1)#6-Rb(1)-Cl(1) | 82.51(3) |
| Cl(1)-Rb(1)-O(3)#5 | 78.12(5) | O(1)-Rb(1)-Cl(1) | 82.51(3) |
| Cl(1)-Rb(1)-O(3)#4 | 78.12(5) | O(1)-Rb(1)-O(3)#5 | 63.81(8) |
| O(4)#2-Rb(1)-Cl(1) | 139.29(6) | O(1)-Rb(1)-O(3) | 133.72(7) |
| O(4)-Rb(1)-Cl(1) | 139.29(6) | O(1)#6-Rb(1)-O(3)#5 | 105.15(8) |
| O(4)-Rb(1)-O(4)#2 | 71.74(10) | O(1)#6-Rb(1)-O(3)#4 | 63.81(8) |
| O(4)#2-Rb(1)-O(3)#4 | 135.11(7) | O(1)-Rb(1)-O(3)#4 | 105.15(8) |
| O(4)-Rb(1)-O(3)#5 | 135.11(7) | O(1)#6-Rb(1)-O(3) | 133.72(7) |
| O(4)#2-Rb(1)-O(3) | 66.45(7) | O(1)#6-Rb(1)-O(1) | 42.18(13) |
| O(4)#2-Rb(1)-O(3)#5 | 64.18(7) | O(1)-C(1)-O(1)#1 | 120 |
| O(4)-Rb(1)-O(3) | 66.45(7) | O(1)-C(1)-O(1)#6 | 120.000(1) |
| O(4)-Rb(1)-O(3)#4 | 64.18(7) | O(1)#1-C(1)-O(1)#6 | 120 |
| O(4)-Rb(1)-O(1)#6 | 67.88(8) | O(2)#4-C(2)-O(2) | 120.000(1) |
| O(4)#2-Rb(1)-O(1)#6 | 92.59(4) | O(2)#4-C(2)-O(2)#17 | 120 |
| O(4)-Rb(1)-O(1) | 92.59(4) | O(4)#4-N(1)-O(4)#15 | 120.000(1) |
| O(4)#2-Rb(1)-O(1) | 67.88(8) | O(4)#4-N(1)-O(4) | 120 |
| O(2)-Rb(1)-Cl(1) | 85.41(4) | O(4)#15-N(1)-O(4) | 120 |

Symmetry transformations used to generate equivalent atoms:

| | | |
|---|---|---|
| # 1 x-y,x,-z | #2 y,x,z | # 3-y,x-y,z |
| # 4 -x+y,-x+1,z | #5 -y+1,x-y,z | # 6-x,-y,-z |
| # 7 y,-x+y,-z | #8 -x+y,-x,z | # 9-y+1,x-y,-z+1/2 |
| # 10 x-y,-y,-z+1/2 | #11 -x+1,-x+y,z | # 12y,x-1,z |
| # 13 x,y,-z+1/2 | #14 -x+y,-x,-z+1/2 | # 15-x+y+1,-x+1,-z+1/2 |
| # 16 -y+1,x-y+1,z | # 17-x+y+1,-x+1,z | # 18-y,x-y,-z+1/2 |

Table S3. Anisotropic displacement parameters for $Na_3Rb_6(CO_3)_3(NO_3)_2Cl\cdot(H_2O)_6$.

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| Na(1) | 21(1) | 24(1) | 26(1) | 0 | 0 | 12(1) |
| Rb(1) | 26(1) | 26(1) | 28(1) | 0(1) | 0(1) | 11(1) |
| C(1) | 21(3) | 21(3) | 6(4) | 0 | 0 | 10(2) |
| C(2) | 26(2) | 26(2) | 19(4) | 0 | 0 | 13(1) |
| N(1) | 21(2) | 21(2) | 25(3) | 0 | 0 | 10(1) |
| Cl(1) | 27(1) | 27(1) | 31(1) | 0 | 0 | 14(1) |
| O(1) | 33(2) | 19(2) | 35(3) | 0 | 0 | 16(1) |
| O(2) | 24(2) | 30(1) | 44(2) | 4(1) | 0 | 12(1) |
| O(3) | 46(2) | 46(2) | 26(2) | -3(1) | -3(1) | 31(2) |
| O(4) | 19(2) | 39(2) | 48(2) | 0 | 0 | 16(1) |

Table S4. Hydrogen bonds for $Na_3Rb_6(CO_3)_3(NO_3)_2Cl\cdot(H_2O)_6$.

| D-H···A | d(D-A)/Å | D-H···A/° |
|---|---|---|
| O(3)-H(3)···O(2)#1 | 2.702(5) | 176(3) |

Symmetry transformations used to generate equivalent atoms:
# 1 1-x+y,1-x,z

Table S5. HOMO-LUMO energy gap and polarizability anisotropy of $BO_3$, $NO_3$, and $CO_3$.

| | **Energy gap (eV)** | **δ** |
|---|---|---|
| **$BO_3$** | 7.84 | 9.45 |
| **$NO_3$** | 5.39 | 17.67 |
| **$CO_3$** | 7.36 | 12.80 |

Table S6. Real-space atom-cutting analysis of calculated birefringence in $Na_3Rb_6(CO_3)_3(NO_3)_2Cl\cdot(H_2O)_6$. The cutting radii of Na, Rb, C, N, O ($CO_3$, $NO_3$, $H_2O$), Cl, and H were set as 0.76, 0.94, 0.28, 0.63, (1.01, 0.63, 0.72) and 0.27 Å, respectively.

| **Cut unit** | **Birefringence （@ 546 nm）** |
|---|---|
| None | 0.12 |
| $H_2O$ | 0.12 |
| Na, Rb, Cl, and $H_2O$ | 0.14 |
| $CO_3$ | 0.09 |
| $NO_3$ | 0.07 |
| $CO_3$ + $NO_3$ | 0.03 |