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Supporting Information

LiO_4 tetrahedra lock alignment of π-conjugated layers to maximize optical anisotropy in metal hydroisocyanurates

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Experimental procedures

1. Synthesis

All chemicals containing $LiOH·H_2O$ (98%, Aladdin), NaOH (98%, Aladdin), $Ca(OH)_2$ (98%, Aladdin), $Ba(OH)_2·8H_2O$ (99%, Alfa Aesar) and $H_3C_3N_3O_3$ (98%, Aladdin) were used without further purification. **LCHCY**/**NBHCY** crystals were grown by dissolving $LiOH·H_2O$/NaOH (2 mmol), $Ca(OH)_2$/$Ba(OH)_2·8H_2O$ (1 mmol) and $H_3C_3N_3O_3$ (4 mmol) in 30 mL of demineralized water in a clean beaker with stirring and heating using magnetic stirrer at the boiling point until the solution was concentrated to 15 mL. Then the beaker was put in the open air to cool down naturally. Colorless crystals were obtained after cooling down to room temperature.

2. Powder X-ray diffraction

The powder X-ray diffraction (PXRD) data were collected on Bruker D8 Focus diffractometer equipped with Cu Kα radiation (λ=1.5418 Å) in the 2θ range of 5-70° at room temperature.

3. UV–vis–NIR diffuse reflectance spectrum

The UV–vis–NIR diffuse reflectance spectra were measured in the wavelength range from 200 nm to 1400 nm with $BaSO_4$ as a reference material by Cary 7000 UV-vis-NIR universal measurement spectrophotometer under an integrating sphere.

4. Infrared spectrum

Infrared spectroscopy was collected on a Varian Excalibur 3100 spectrometer in the 400 - 3600 cm^{-1} range. **LCHCY** and KBr samples were mixed thoroughly with mass ratio about 1:100, respectively.

5. Raman spectrum

Raman spectra were measured using an InVia Raman spectrometer (Renishaw, Inc.) with exciting wavelength at 532 nm in the 50 - 2000 cm^{-1} range at room temperature.

6. Thermal analysis

Thermal gravimetric (TG) analysis were carried out on NETZSCH STA 409 CD thermal analyzer in the temperature range of 50-600 °C for **LCHCY** with a heating rate of 10 K/min under nitrogen atmosphere.

7. Single crystal structure determination

The single-crystal X-ray diffraction data was gathered on a Rigaku AFC10 single-crystal diffractometer equipped with graphite-monochromatic Mo Kα radiation (λ= 0.71073 Å) and Saturn CCD detector at 293 K. The intensity data, data reduction and cell refinement were captured by the CrystalClear program. The crystal structures were settled by the direct method with grogram SHELXS-97 and further refined by full matrix least squares on F^2 by SHELXL-97 programs. The structure was confirmed by the ADDSYM algorithm from the program PLATON with no higher symmetry discovered. The crystallographic data are given in Table S1 - S5.

8. Computational methods

The theoretical simulations for **LCHCY** and **NBHCY** were performed by first principles density functional theory[1] from CASTEP module,[2] which has been utilized on metal cyanurates and hydro-cyanurates successfully.[3-7] The exchange–correlation (XC) functional was modeled by the generalized gradient density approximation (GGA)[8] and the norm-conserving pseudopotentials[9] were applied for all elements. In this model, Li 2s, Na 2$p^6$3s, Ba 5$p^6$6s^2, Ca 3$p^6$4s^2, C 2$s^2$2p^2, N 2$s^2$2p^3, O 2$s^2$2p^4 and H 1s electrons were modeled as the outer valence electrons, respectively. The kinetic energy cutoff of 770 eV and dense k-point meshes[10] (4×4×5 for **LCHCY** and 2×2×4 for **NBHCY**) in the first Brillouin zone were chosen to guarantee the sufficient calculation accuracy. In order to elaborate the origin of large birefringence in **LCHCY**, the optical properties of two isostructural compounds, $K_2(HC_3N_3O_3)$[11], were also calculated for comparison.

Result and discussion

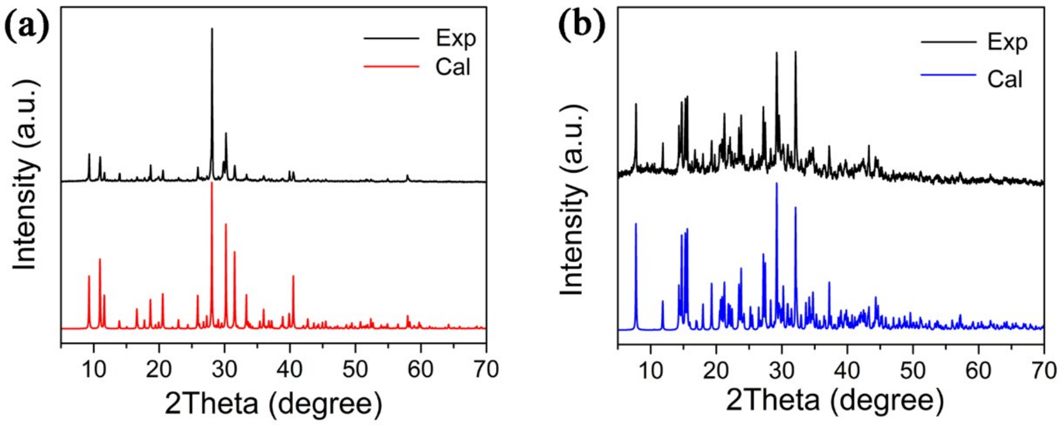

Figure S1. Experimental and calculated XRD patterns for **LCHCY** and **NBHCY**.

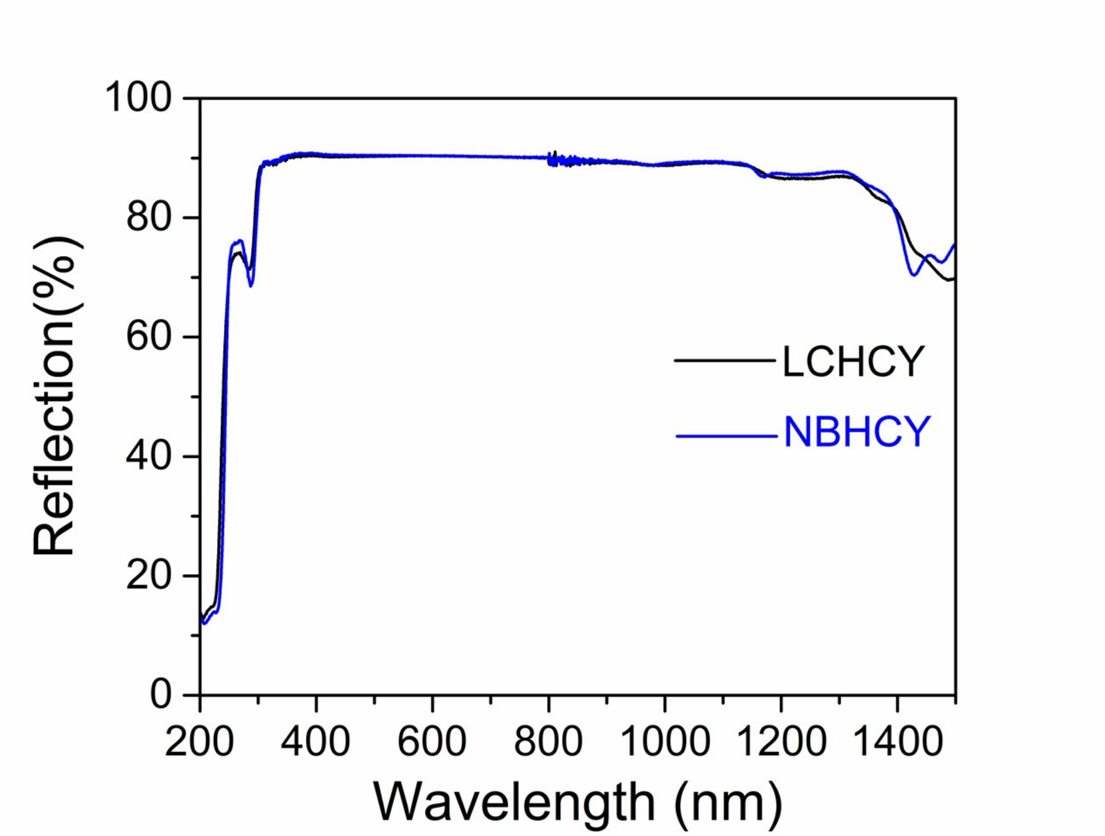

Figure S2. UV–vis–NIR diffuse reflectance spectra of **LCHCY** and **NBHCY**.

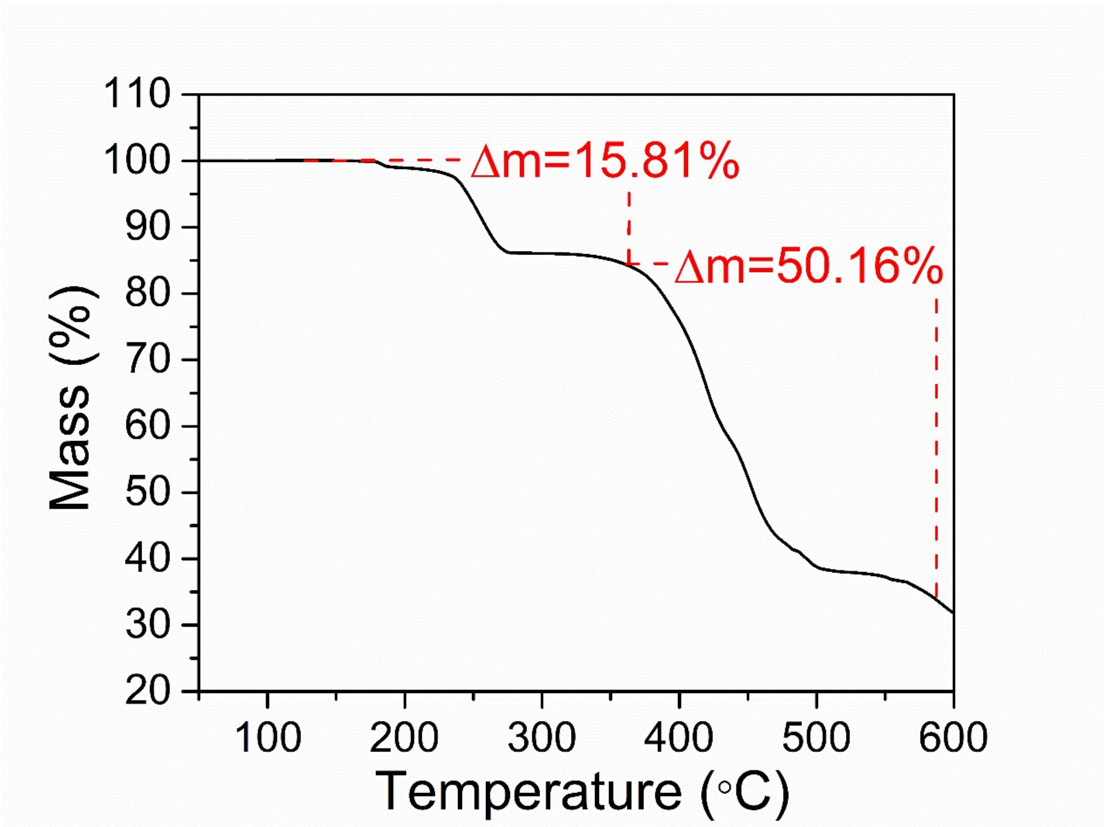

Figure S3. TG curve of **LCHCY**.

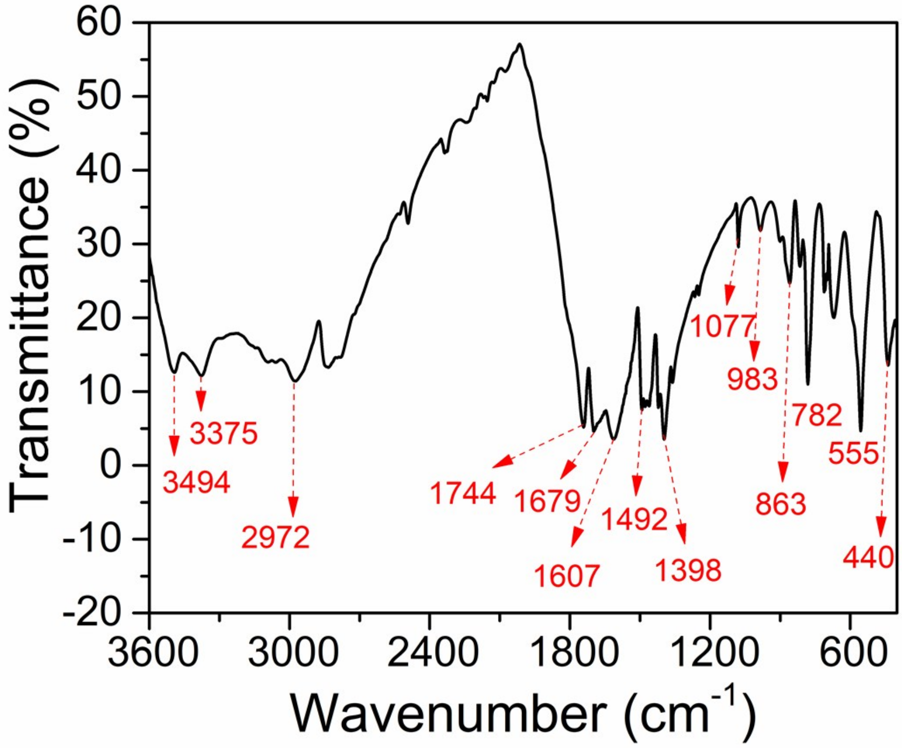

Figure S4. IR spectrum of **LCHCY**.

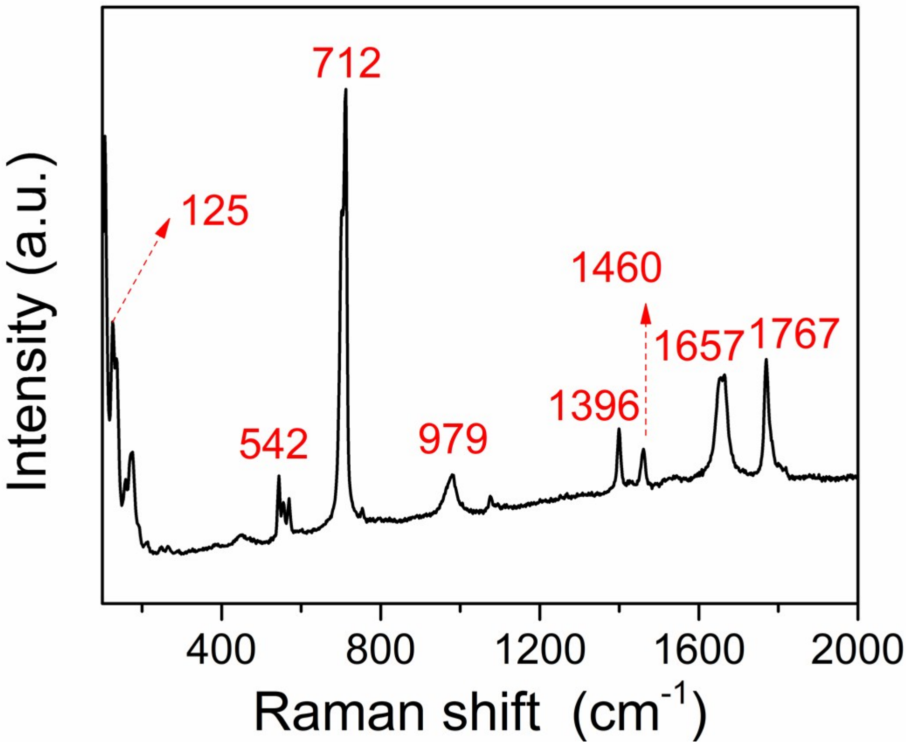

Figure S5. Raman spectrum of **LCHCY**.

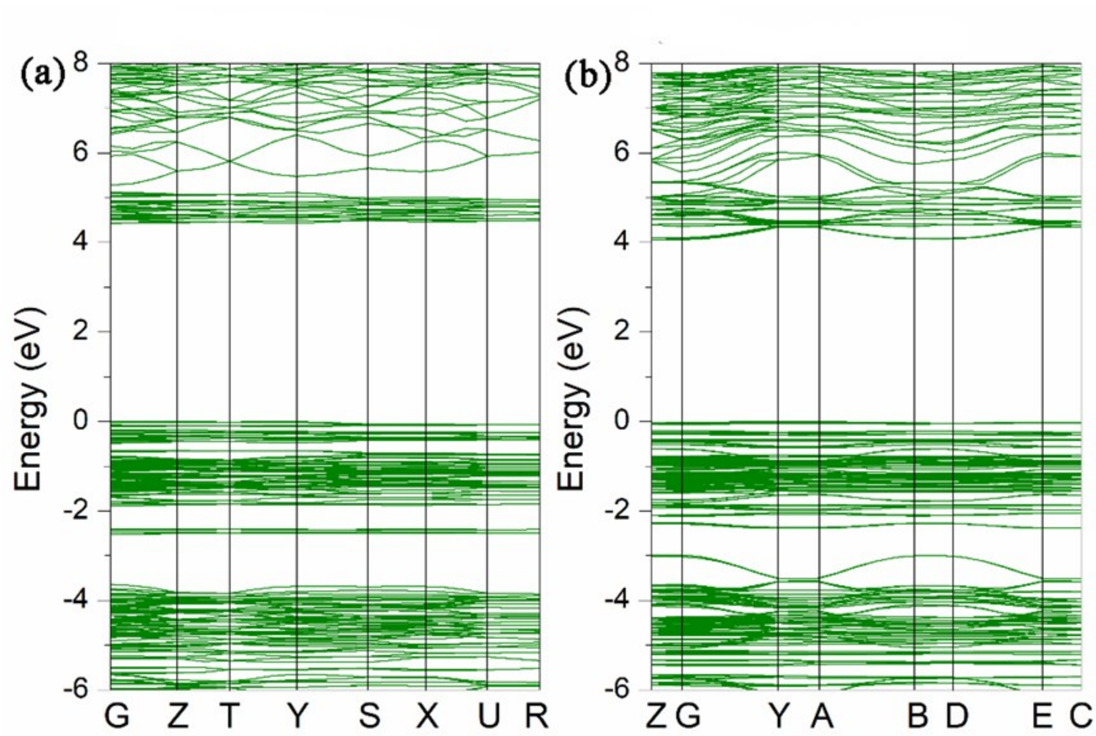

Figure S6. Band structures of (a) **LCHCY** and (b) **NBHCY**.

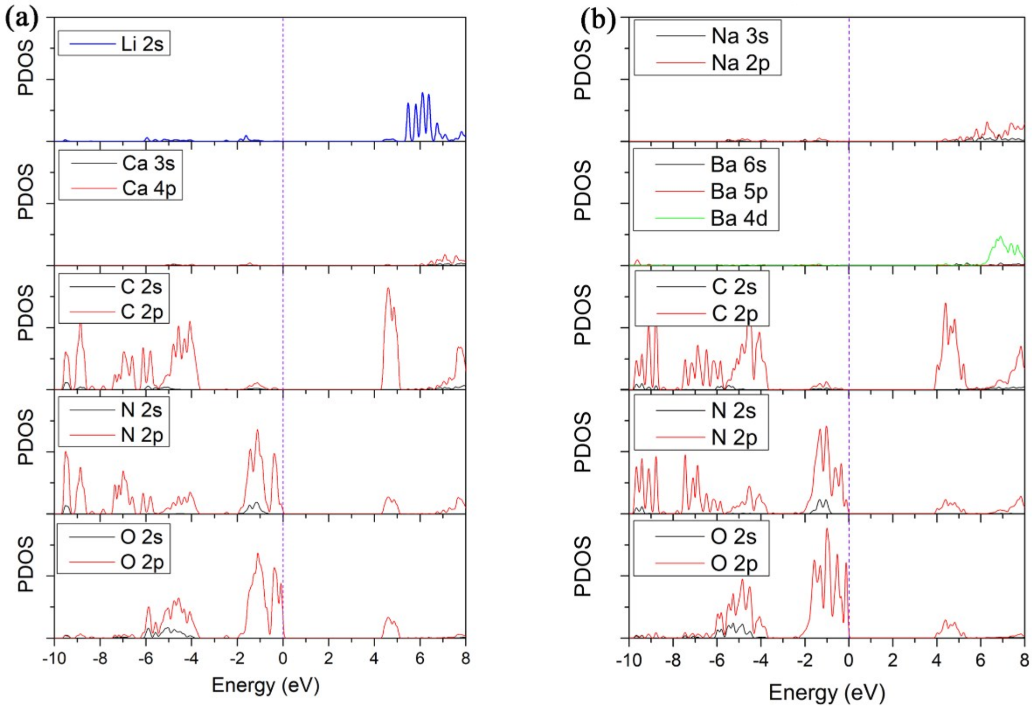

Figure S7. The partial density of states projected constituent atoms of (a) **LCHCY** and (b) **NBHCY** (The contribution from H_2O molecule was omitted for simplification).

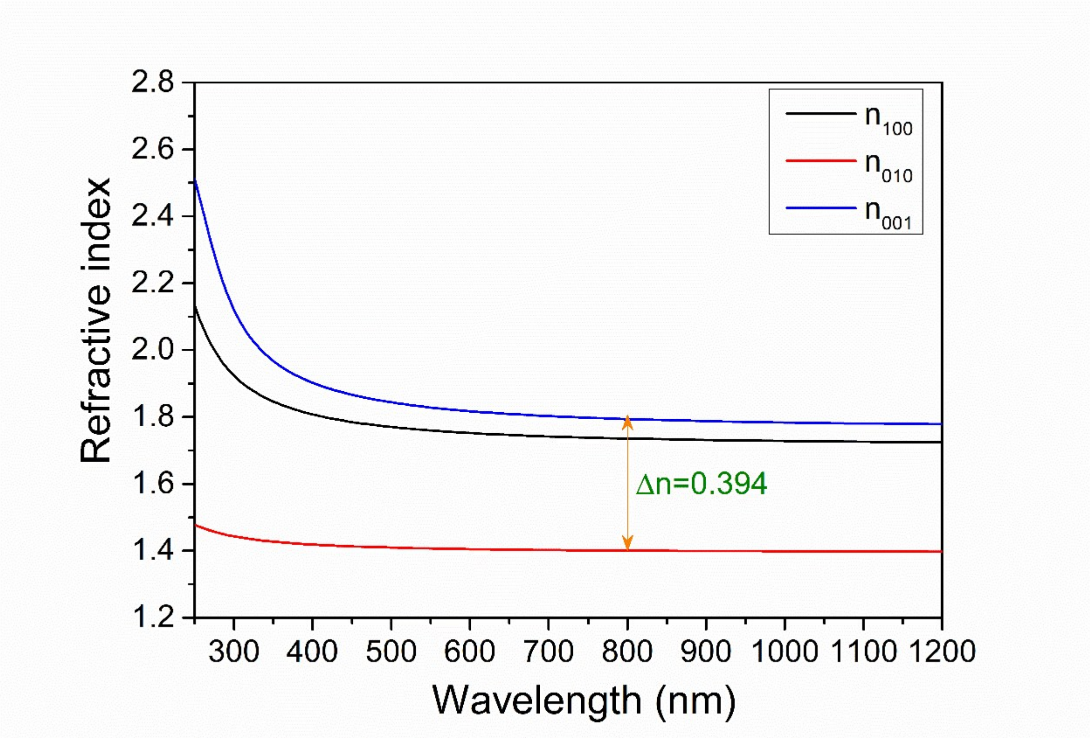

Figure S8. The refractive dispersion curves of **NBHCY**.

Table S1. Crystal data and structure refinement for **LCHCY** and **NBHCY**.

Formula	$Li_2Ca(H_2C_3N_3O_3)_4 \cdot 6H_2O$	$Na_2Ba(H_2C_3N_3O_3)_4 \cdot 6H_2O$
Formula weight(g/mol)	674.36	803.72
Temperature/K	293	293
Crystal system	orthorhombic	monoclinic
Space group	*C*mcm	*C*2/c
a/Å	16.1096(10)	17.0294(6)
b/Å	11.7548(6)	6.5546(2)
c/Å	12.7052(9)	23.1652(8)
α/°	90	90
β/°	90	101.245(3)
γ/°	90	90
Volume/Å^3	2405.9(3)	2536.08(15)
Z	4	4
ρ_{calc}g/cm^3	1.862	2.105
μ/mm^{-1}	0.377	1.712
F(000)	1384	1592.0
Radiation	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
Independent reflections	1334 [R_{int} = 0.0534]	2599 [R_{int} = 0.0295]
Goodness-of-fit on F^2	1.046	1.090
Final R indexes [I>=2σ (I)]	R_1 = 0.0355, wR_2 = 0.1013	R_1 = 0.0183, wR_2 = 0.0453
Final R indexes [all data]	R_1 = 0.0431, wR_2 = 0.1068	R_1 = 0.0188, wR_2 = 0.0456

Table S2. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for **LCHCY**.

LCHCY				
Atom	x	y	z	U(eq)
Ca1	0.5000	0.71839 (6)	0.7500	0.0253 (2)
Li1	0.5000	0.1827 (5)	0.7500	0.0315 (13)
Li2	0.5000	0.4301 (5)	0.7500	0.0370 (15)
O1	0.14538 (10)	−0.06612 (13)	0.7500	0.0262 (4)
O2	0.15127 (10)	0.31675 (14)	0.7500	0.0315 (4)
O3	0.39261 (11)	0.11658 (15)	0.7500	0.0378 (5)
O4	0.10890 (11)	0.5000	0.5000	0.0399 (5)
O5	0.35154 (7)	0.30758 (9)	0.51355 (11)	0.0293 (3)
O6	0.5000	0.29623 (15)	0.63401 (15)	0.0301 (4)
O7	0.5000	0.55559 (14)	0.62993 (14)	0.0261 (4)
O8	0.5000	0.84410 (18)	0.89344 (19)	0.0454 (6)
N1	0.14383 (11)	0.12676 (16)	0.7500	0.0228 (4)
N2	0.26899 (11)	0.02506 (16)	0.7500	0.0227 (4)
N3	0.27370 (12)	0.22029 (16)	0.7500	0.0240 (5)
N4	0.23051 (8)	0.40273 (11)	0.50494 (11)	0.0242 (4)
N5	0.35836 (11)	0.5000	0.5000	0.0229 (4)
C1	0.18327 (14)	0.02641 (19)	0.7500	0.0195 (5)
C2	0.18803 (14)	0.22310 (19)	0.7500	0.0215 (5)
C3	0.31735 (15)	0.1208 (2)	0.7500	0.0236 (5)
C4	0.18434 (15)	0.5000	0.5000	0.0243 (5)
C5	0.31604 (10)	0.40134 (13)	0.50685 (13)	0.0213 (4)

Table S3. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for **NBHCY**.

		NBHCY		
Atom	x	y	z	U(eq)
Ba1	0.5000	0.30296 (2)	0.7500	0.02101 (6)
Na1	0.51333 (5)	0.48259 (14)	0.57942 (4)	0.03295 (19)
C1	0.17847 (11)	0.5058 (3)	0.47514 (8)	0.0222 (4)
C2	0.69355 (11)	0.4306 (3)	0.75666 (8)	0.0224 (4)
C3	0.81927 (11)	0.4483 (3)	0.72422 (8)	0.0223 (4)
C4	0.69103 (11)	0.4430 (3)	0.65701 (8)	0.0225 (4)
C5	0.30432 (11)	0.4853 (3)	0.54415 (9)	0.0245 (4)
C6	0.17650 (11)	0.4770 (3)	0.57470 (8)	0.0227 (4)
N1	0.26106 (9)	0.5031 (3)	0.48840 (7)	0.0240 (3)
N2	0.13688 (9)	0.4941 (3)	0.51875 (7)	0.0236 (3)
N3	0.77445 (9)	0.4467 (3)	0.66915 (7)	0.0259 (4)
N4	0.65164 (9)	0.4305 (3)	0.70169 (7)	0.0240 (3)
N5	0.77632 (9)	0.4402 (3)	0.76774 (7)	0.0232 (3)
N6	0.25898 (9)	0.4717 (3)	0.58625 (7)	0.0267 (4)
O1	0.65940 (8)	0.4208 (3)	0.79960 (6)	0.0320 (3)
O2	0.89301 (8)	0.4568 (2)	0.73433 (6)	0.0285 (3)
O3	0.49934 (9)	0.1558 (2)	0.63571 (7)	0.0301 (3)
O4	0.49946 (9)	0.7351 (2)	0.50644 (8)	0.0327 (3)
O5	0.14509 (8)	0.5207 (3)	0.42272 (6)	0.0322 (3)
O6	0.65657 (8)	0.4525 (2)	0.60495 (6)	0.0305 (3)
O7	0.49380 (11)	0.6557 (3)	0.67521 (9)	0.0435 (4)
O8	0.14158 (8)	0.4638 (2)	0.61689 (6)	0.0303 (3)
O9	0.37685 (8)	0.4793 (3)	0.55520 (7)	0.0390 (4)

Table S4. Selected bond lengths (Å) and bond angles (degree) for **LCHCY**.

LCHCY			
Ca1—O8	2.346 (2)	Li2—O1^{iii}	2.3424 (16)
Ca1—O8^{i}	2.346 (2)	O1—C1	1.247 (3)
Ca1—O7	2.4473 (17)	O2—C2	1.250 (3)
Ca1—O7^{i}	2.4473 (17)	O3—C3	1.213 (3)
Ca1—N1^{ii}	2.5551 (19)	O4—C4	1.215 (3)
Ca1—N1^{iii}	2.5551 (19)	O5—C5	1.245 (2)
Ca1—O2^{ii}	2.6972 (17)	N1—C2	1.338 (3)
Ca1—O2^{iii}	2.6972 (17)	N1—C1	1.340 (3)
Li1—O3	1.897 (3)	N2—C3	1.369 (3)
Li1—O3^{iv}	1.897 (3)	N2—C1	1.381 (3)
Li1—O6^{i}	1.988 (4)	N3—C3	1.364 (3)
Li1—O6	1.988 (4)	N3—C2	1.380 (3)
Li2—O7^{i}	2.122 (4)	N4—C4	1.3654 (19)
Li2—O7	2.122 (4)	N4—C5	1.378 (2)
Li2—O6	2.156 (5)	N5—C5	1.3481 (19)
Li2—O6^{i}	2.156 (5)	N5—C5^{vi}	1.3481 (19)
Li2—O1^{ii}	2.3424 (16)	C4—N4^{vi}	1.3654 (19)
C2—N1—C1	119.5 (2)	N1—C2—N3	120.8 (2)
C3—N2—C1	124.0 (2)	O3—C3—N3	123.4 (2)
C3—N3—C2	122.39 (19)	O3—C3—N2	122.3 (2)
C4—N4—C5	123.74 (15)	N3—C3—N2	114.3 (2)
C5—N5—C5^{vi}	119.2 (2)	O4—C4—N4^{vi}	123.01 (10)
O1—C1—N1	122.4 (2)	O4—C4—N4	123.01 (10)
O1—C1—N2	118.6 (2)	N4^{vi}—C4—N4	114.0 (2)
N1—C1—N2	119.0 (2)	O5—C5—N5	122.27 (16)
O2—C2—N1	119.6 (2)	O5—C5—N4	118.11 (15)
O2—C2—N3	119.7 (2)	N5—C5—N4	119.62 (15)

Symmetry codes: (i) x, y, $-z+3/2$; (ii) $-x+1/2$, $y+1/2$, $-z+3/2$; (iii) $x+1/2$, $y+1/2$, z; (iv) $-x+1$, y, $-z+3/2$; (v) $x-1/2$, $y-1/2$, z; (vi) x, $-y+1$, $-z+1$.

Table S5. Selected bond lengths (Å) and bond angles (degree) for **NBHCY**.

Ba1—O3	2.8157 (15)	C1—N2	1.344 (2)
Ba1—O3^{i}	2.8157 (15)	C1—N1	1.380 (2)
Ba1—O1^{i}	2.8406 (13)	C2—O1	1.248 (2)
Ba1—O1	2.8406 (14)	C2—N4	1.333 (2)
Ba1—O7	2.8788 (18)	C2—N5	1.384 (2)
Ba1—O7^{i}	2.8788 (18)	C3—O2	1.233 (2)
Ba1—O2^{ii}	2.8881 (15)	C3—N3	1.353 (2)
Ba1—O2^{iii}	2.8881 (14)	C3—N5	1.357 (2)
Ba1—N4	3.1220 (15)	C4—O6	1.236 (2)
Ba1—N4^{i}	3.1220 (15)	C4—N4	1.341 (2)
Na1—O9	2.2822 (16)	C4—N3	1.393 (2)
Na1—O4	2.3446 (18)	C5—O9	1.212 (2)
Na1—O6	2.4034 (15)	C5—N6	1.360 (2)
Na1—O4^{iv}	2.4228 (19)	C5—N1	1.361 (2)
Na1—O3	2.5430 (18)	C6—O8	1.242 (2)
Na1—O7	2.571 (2)	C6—N2	1.344 (2)
C1—O5	1.240 (2)	C6—N6	1.378 (2)
O5—C1—N2	122.16 (17)	O9—C5—N1	122.94 (18)
O5—C1—N1	118.14 (16)	N6—C5—N1	114.09 (16)
N2—C1—N1	119.70 (17)	O8—C6—N2	122.50 (17)
O1—C2—N4	121.04 (16)	O8—C6—N6	118.14 (17)
O1—C2—N5	118.07 (17)	N2—C6—N6	119.36 (16)
N4—C2—N5	120.89 (16)	C5—N1—C1	123.49 (16)
O2—C3—N3	123.07 (17)	C6—N2—C1	119.38 (16)
O2—C3—N5	122.50 (17)	C3—N3—C4	123.77 (16)
N3—C3—N5	114.43 (16)	C2—N4—C4	118.82 (16)
O6—C4—N4	122.85 (17)	C4—N4—Ba1	150.01 (12)
O6—C4—N3	117.88 (16)	C3—N5—C2	122.75 (16)
N4—C4—N3	119.26 (16)	C5—N6—C6	123.97 (16)
O9—C5—N6	122.97 (18)		

Symmetry codes: (i) $-x+1$, y, $-z+3/2$; (ii) $x-1/2$, $y-1/2$, z; (iii) $-x+3/2$, $y-1/2$, $-z+3/2$; (iv) $-x+1$, $-y+1$, $-z+1$; (v) $x+1/2$, $y+1/2$, z.

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