Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting information

Ambient *L*-Lactic Acid Crystal Polymorphism

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LLA Form I CheckCIF: [Form I_120bek1h_checkcif.pdf]

LLA Form II CheckCIF: [Form II_18bek65h_checkcif.pdf]

LLA Form III CheckCIF: [Form III_18bek42h_checkcif.pdf]

Corresponding CIF Files can be evaluated at these links.

https://www.ccdc.cam.ac.uk/structures/Search?access=referee&ccdc=2062531&Author=Jingxiang+Yang
https://www.ccdc.cam.ac.uk/structures/Search?access=referee&ccdc=1962562&Author=Jingxiang+Yang
https://www.ccdc.cam.ac.uk/structures/Search?access=referee&ccdc=1962561&Author=Jingxiang+Yang

Materials and methods. All solvents used here were reagent grade and used as received (Sigma-Aldrich, St. Louis, MO). L-lactic acid (LLA, CAS Number 79-33-4) was obtained from Sigma-Aldrich and used as received.

Raman spectroscopy. Raman spectra were recorded on a Raman microscope (DXR, Thermo Fisher Scientific, Waltham, MA) using a 532 nm excitation laser operating at 2 mW, with a 2 cm^{-1} resolution and slit width of 50 μm. The data was analyzed using the Omnic software package.

Single crystal structure determination. The X-ray intensity data of LLA Forms II and III were recorded on a Bruker D8 APEX-II CCD system using a graphite monochromator, 0.5 mm MonoCap-collimated Mo-Kα radiation (λ = 0.71073 Å), and the ω scan method at 100 K. Temperature was controlled by an Oxford Cryosystems 700+ Cooler. The datasets were processed with the INTEGRATE program of the APEX2 software for reduction and cell refinement. Multi-scan absorption corrections were applied by the SCALE program for the area detector. Both structures were solved by intrinsic phasing methods (SHELXT) and the structure models were completed and refined using the full-matrix least-square methods on F^2 (SHELXL). Non-hydrogen atoms in the structures were refined with anisotropic displacement parameters, and hydrogen atoms on carbons were placed in idealized positions (C-H = 0.95-1.00 Å) and included as riding with $U_{iso(H)}$ = 1.2 or 1.5 $U_{eq(non\text{-}H)}$. The selected crystallographic parameters were listed in Table S1. The crystallographic information files (CIFs) including the HKL and RES data are deposited in the CCDC with numbers 1962562 (Form II) and 1962561 (Form III). Crystal indexing was performed using the Crystal Faces program of the APEX2 software.

Polarized light microscopy. A microscope fitted with crossed polarizers (Olympus BX50) and equipped with a digital camera was used to record the phase behavior among LLA polymorphs. A microscope hot stage (Mettler FP82HT) was used for temperature control.

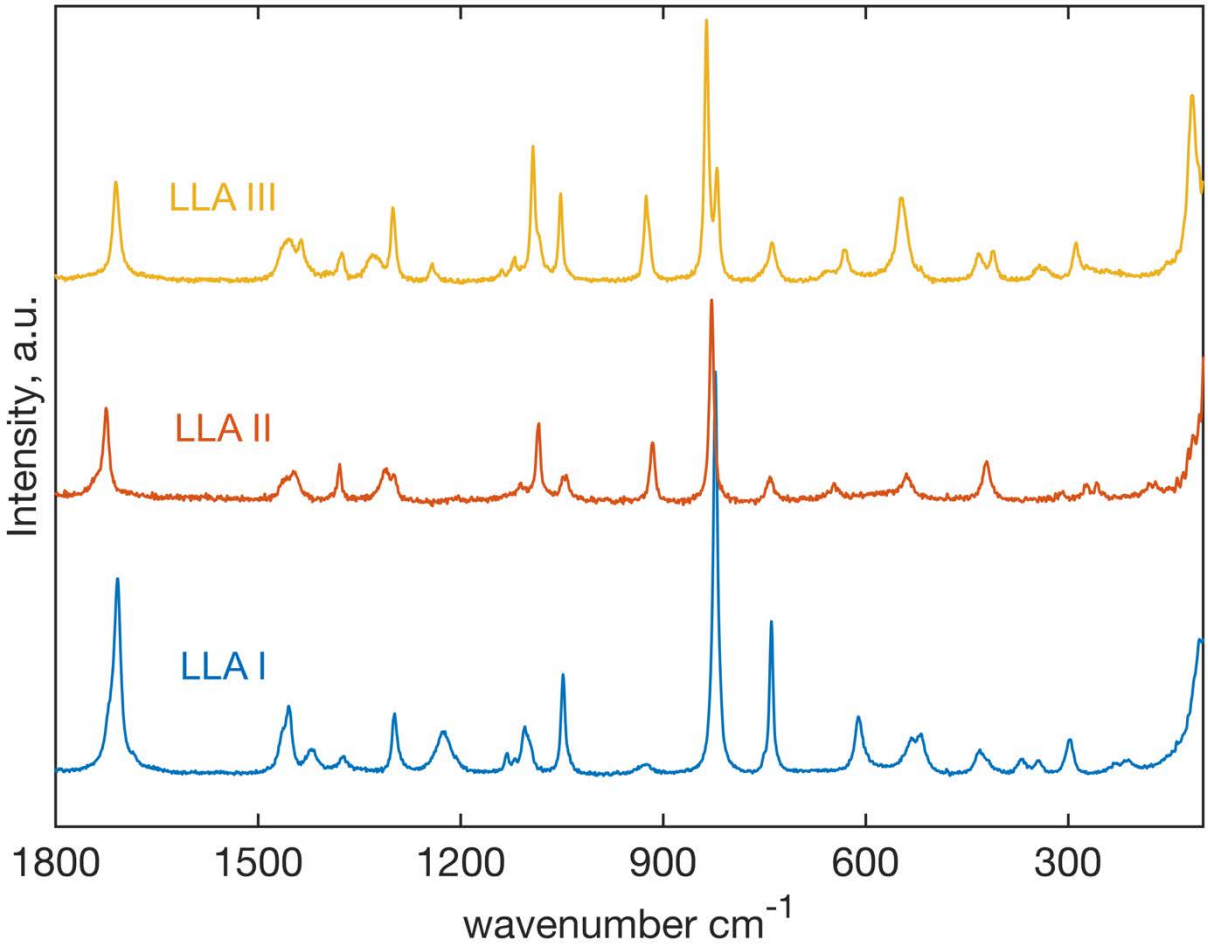

Figure S1. Raman spectra of single crystals of LLA Forms **I** (black), Form **II** (red) and Form **III** (blue). The size of the laser beam was 0.7 μm.

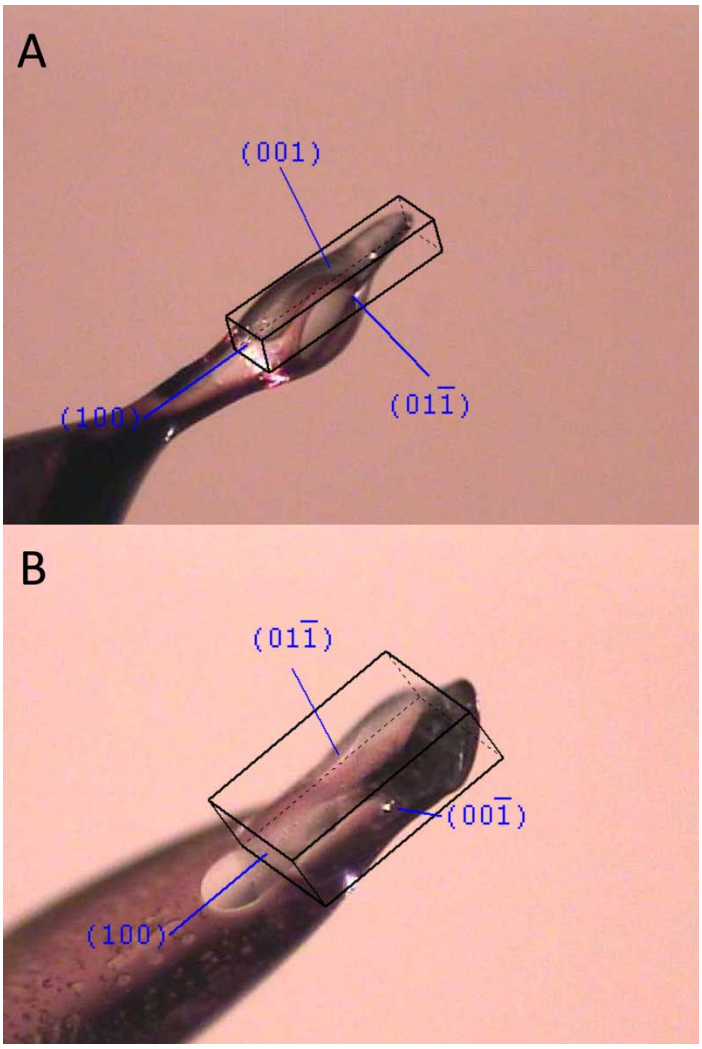

Figure S2. Single crystals of LLA **II** (A) and LLA **III** (B) with Miller indices. The crystal faces were rounded by LLA's hydroscopicity.

Table S1. Selected single crystal data for LLA Forms **I**, **II** and **III**.

	LLA Form I	LLA Form II	LLA Form III
Formula	$C_3H_6O_3$	$C_3H_6O_3$	$C_3H_6O_3$
Formula weight	90.08	90.08	90.08
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group (no.)	$P2_12_12_1$ (19)	$P2_12_12_1$ (19)	$P2_12_12_1$ (19)
***a* (Å)**	5.4954(4)	5.759(3)	5.7323(3)
***b* (Å)**	8.4298(5)	5.772(3)	9.0190(5)
***c* (Å)**	9.3517(6)	12.492(7)	17.3579(10)
***V* (Å^3)**	433.22(1)	415.3(4)	897.49(9)
Z	4	4	8
***D*$_c$ (g cm^{-3})**	1.385	1.441	1.333
μ(mm^{-1})	0.12	0.131	0.121
***F*(000)**	192	192	384
Total reflections	1508	8526	14087
Unique reflections	976	1247	2237
***R*$_{int}$**	0.012	0.0735	0.0310
GOF (all data)	1.09	1.062	1.051
***R*$_1$[a] [*I* > 2σ(*I*)]**	0.030	0.0493	0.0283
***wR*$_2$[b] (all data)**	0.074	0.1226	0.0717
T/K	100	100	100

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; [b] $wR^2=\{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$