Electronic Supplementary Material (ESI) for CrystEngComm.

ESI: Table 1 Conditions and products of crystallization of discrete compounds in the system of malic acid enantiomers (Designations of the phases, see text)

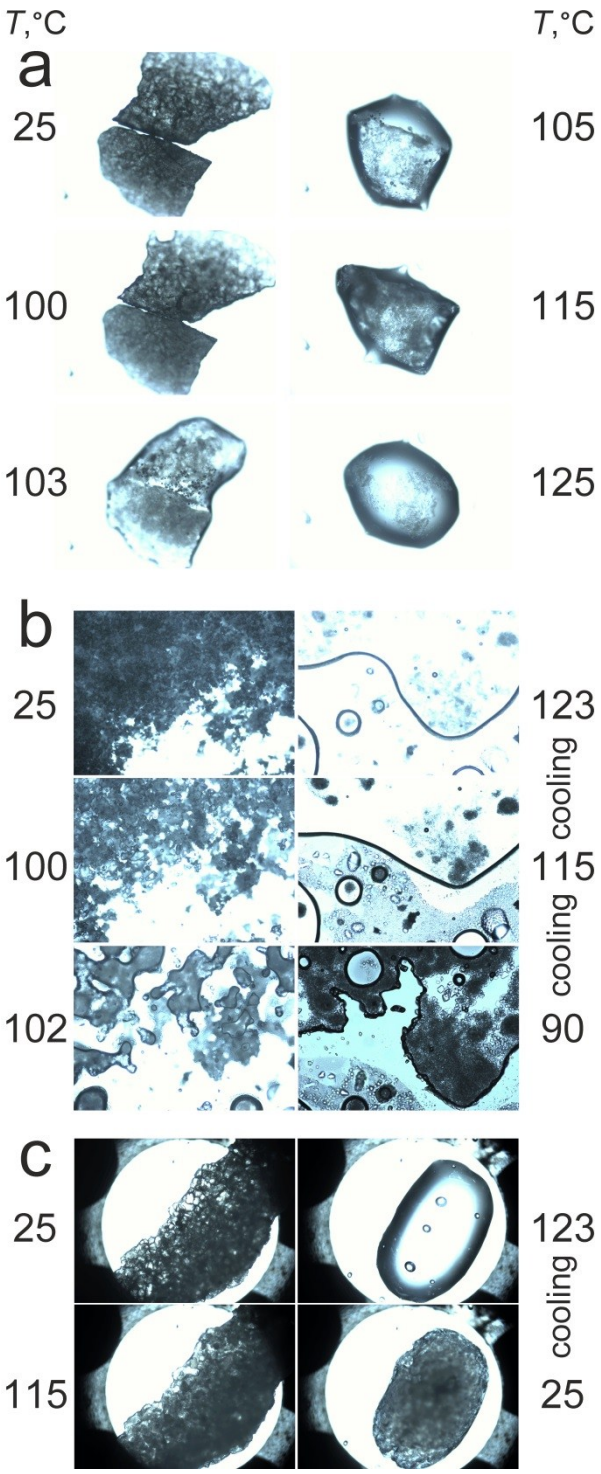
Crystallization medium	Educts	Products of crystallization
Rate of crystallization < 5 minutes		
Water solution	Mixture *S*:*R* = 1:1	Racemate *RS*II
Acetone solution	Mixture *S*:*R* = 1:1	Racemates *RS*II > *RS*III
Ethanol solution	Mixture *S*:*R* = 1:1	Racemate *RS*II
Melt	Mixture *S*:*R* = 1:1	Racemate *RS*II
Melt	Racemate *RS*I	Racemate *RS*II
Rate of crystallization 0.5 – 5 days		
Water solution	Racemate *RS*I	Racemates *RS*II > *RS*I
Acetone solution	Racemate *RS*I	Racemates *RS*III > *RS*II
Ethanol solution	Racemate *RS*I	Racemates *RS*II > *RS*III
Rate of crystallization 4 months		
Water solution	Racemate *RS*I	Racemates *RS*I >> *RS*III
Acetone solution	Racemate *RS*I	Racemates *RS*I >> *RS*III
Rate of crystallization < 5 minutes		
Melt	Mixture *S*:*R* = 3:1	Compound 3*S*1*R*
Rate of crystallization 1 day – 1 month		
Water solution	Mixture *S*:*R* = 3:1	Compounds 3*S*1*R* + S_3R
Acetone solution	Mixture *S*:*R* = 3:1	Compounds 3*S*1*R* + S_3R
Acetonitrile solution	Mixture *S*:*R* = 3:1	Compounds 3*S*1*R* + S_3R
Rate of crystallization 2 months		
Acetonitrile solution	Mixture *S*:*R* = 3:1	Compound S_3R

ESI: Table 2 Crystal structure data and structure refinement for the discrete compound *S*$_3$*R*

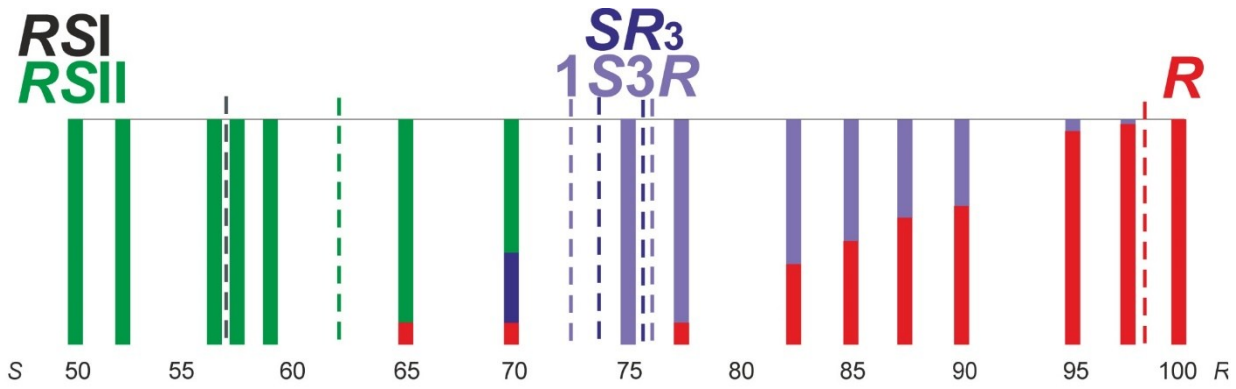
Empirical formula	$C_{16}H_{24}O_{20}$
Formula weight	536.35
Temperature/K	100(2)
Crystal system	triclinic
Space group	*P*1
a/Å	4.8168(6)
b/Å	10.4707(10)
c/Å	11.0951(9)
α/°	107.086(8)
β/°	95.382(9)
γ/°	93.503(9)
Volume/Å^3	530.21(9)
Z	4
ρ_{calc}g/cm^3	1.680
μ/mm^{-1}	1.421
F(000)	280.0
Radiation	$Cu_{K\alpha}$ (λ = 1.54184)
2θ range for data collection/°	8.394 to 134.98
Index ranges	-5 ≤*h*≤5, -12≤*k*≤12, -13≤*l*≤ 12
Reflections collected	8577
Independent reflections	3585 [R_{int}= 0.0449, R_{sigma}= 0.0402]
Data/restraints/parameters	3585/4/340
Goodness-of-fit on F^2	1.034
Final R indexes [I>=2σ (I)]	R_1= 0.0519, wR_2= 0.1375
Final R indexes [all data]	R_1= 0.0557, wR_2= 0.1425
Largest diff. peak/hole / e Å^{-3}	0.84/-0.34
Flack parameter	-0.1(2)

ESI: Table 3 Unit cell parameters (PXRD) of discrete solid phases with determined crystal structures formed in the malic acid system

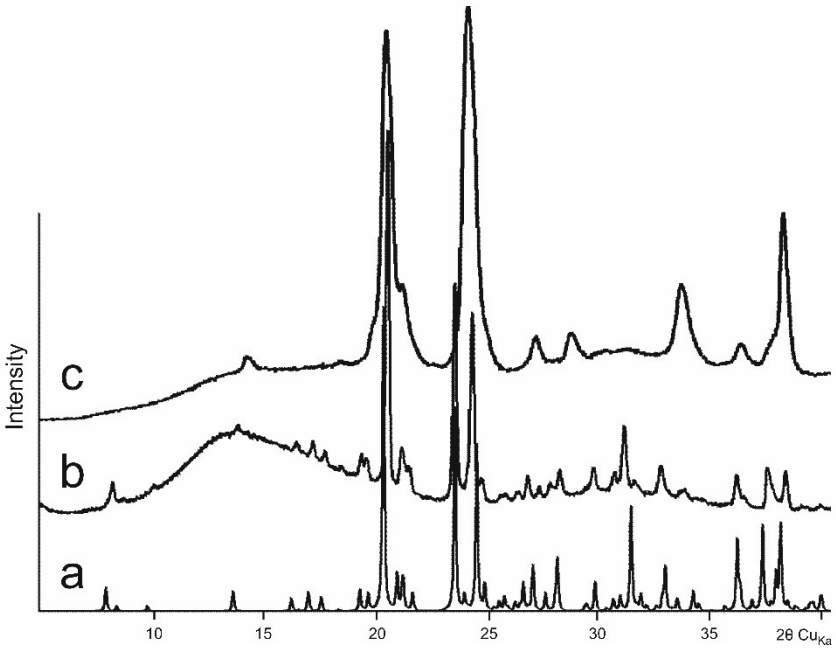
Compound	S. G.	*a*, Å	*b*, Å	*c*, Å	α, deg.	β, deg.	ϒ, deg.	*V*, Å^3
S	$P2_1$	5.043(2)	9.183(2)	11.851(5)	90	94.28(3)	90	547.3(2)
*RS*I	$P2_1/c$	4.893(2)	8.824(2)	13.056(3)	90	102.86(2)	90	549.5(2)
*RS*II	*Cc*	13.094(4)	8.820(3)	4.903(2)	90	103.08(3)	90	551.5(3)
S$_3$*R*	*P*1	4.893(3)	10.606(8)	11.190(8)	106.87(6)	95.54(7)	94.57(6)	549.6(5)



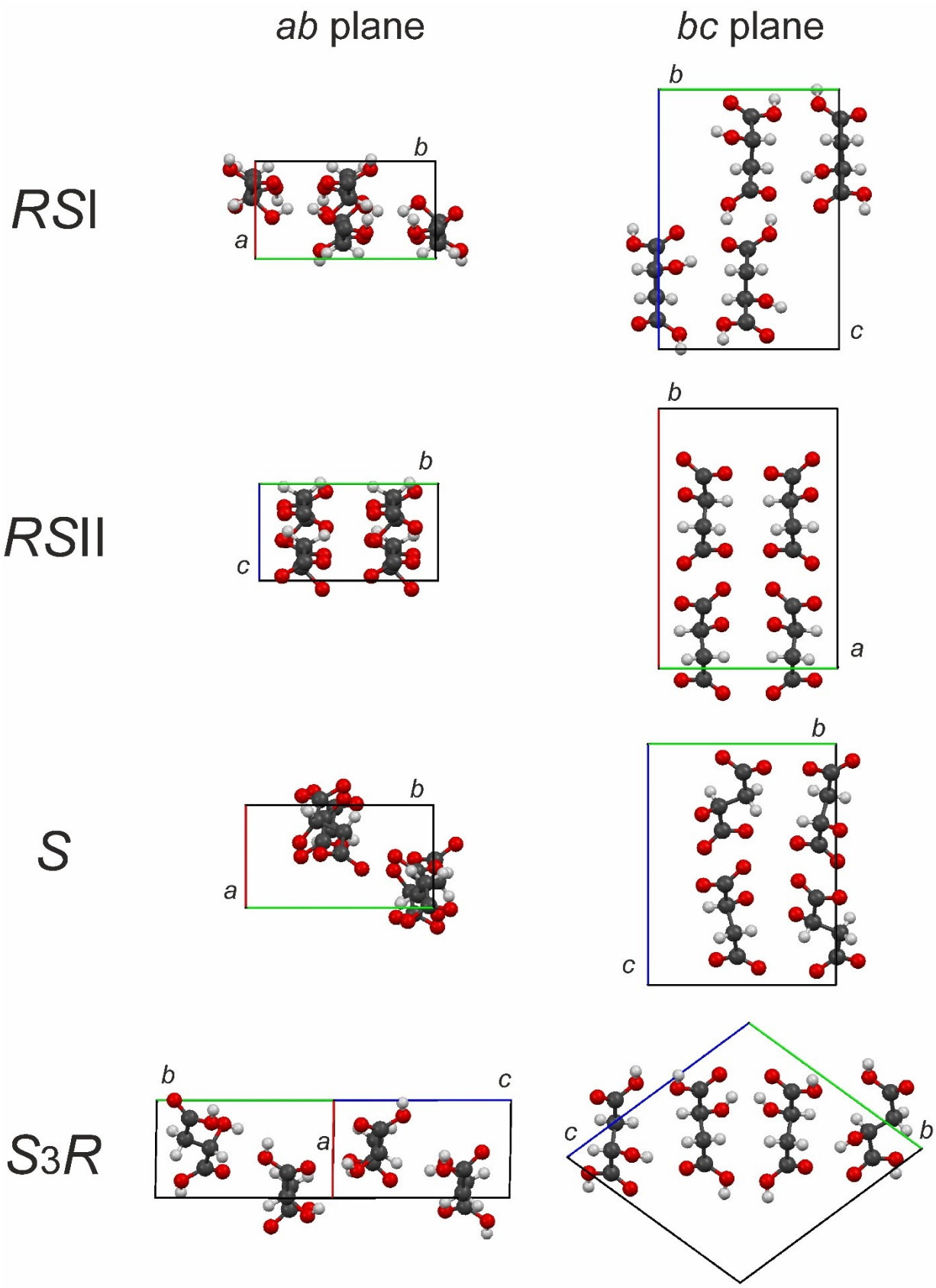
ESI: Fig. 1. HSM of malic acid: (a) two crystallites *S* and *R* before and after their homogenization; (b) physical mixture of powders *S*:*R* = 3:1 before and after its homogenization; (c) recrystallized compound 3*S*1*R*. Explanations are provided in the discussion.



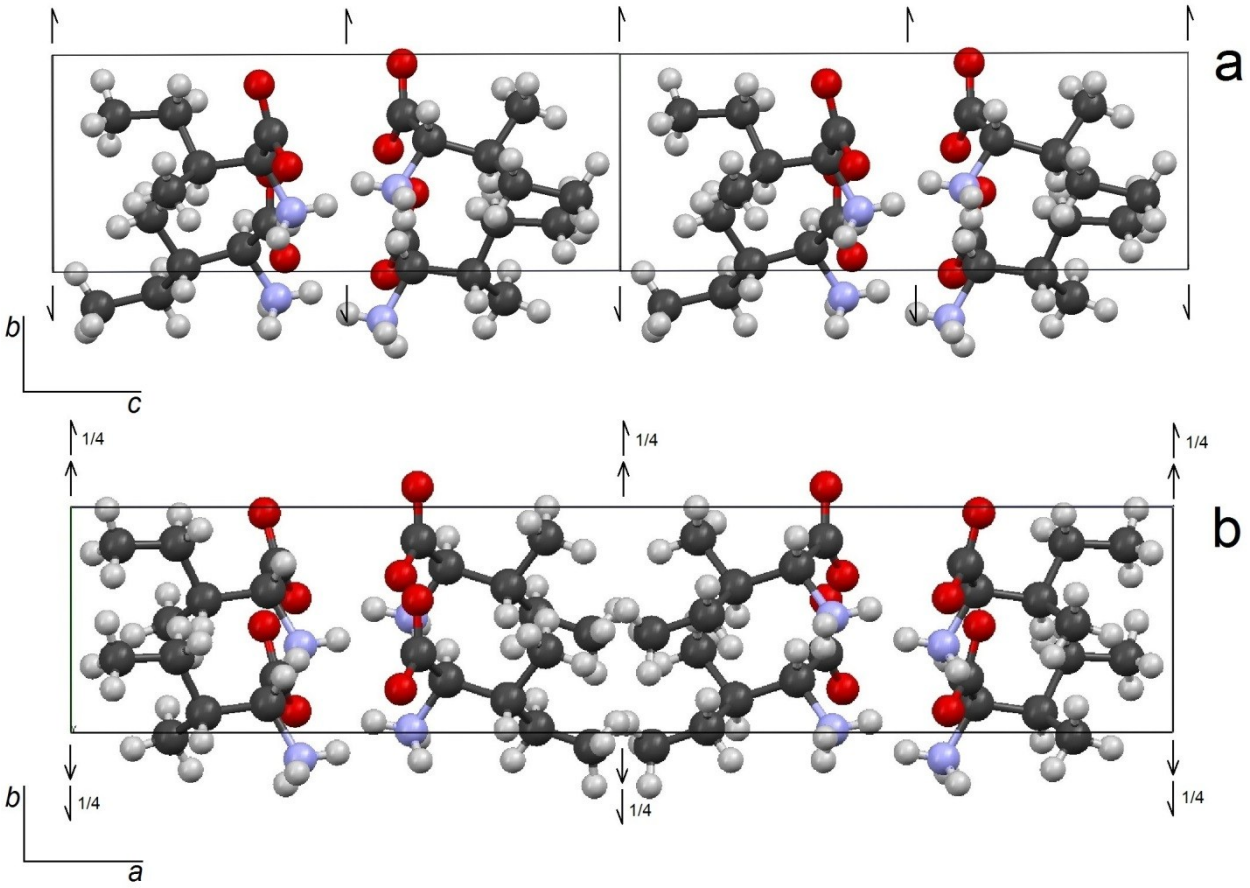
ESI: Fig. 2. Correlation between the phase composition of molten mixtures in the *RS*II — *R* system and the compositions of the starting mixtures. The studied compounds are shown as vertical bars. Each discrete phase and the corresponding solid solutions formed on the basis of the particular phase are designated with the same color. Dashed lines of different colors represent the limits of miscibility in the solid phase.



ESI: Fig. 3. Calculated powder X-ray diffraction pattern of the stable compound S_3R (a) and experimental powder X-ray diffraction patterns of the stable S_3R (b) and metastable 3*S*1*R* (c) compounds of malic acid.



ESI: Fig. 4. Crystal structures of racemic compounds *RS*I and *RS*II, enantiomer *S,* and compound S_3R of malic acid in projections upon the *ab* (left) and *bc* (right) planes.



ESI: Fig. 5. Projections of the coupled monoclinic cells of Ile (a) and the monoclinic cell of the discrete compound V2I (b) on the planes *bc* and *ba* respectively.[34] The structures are fixed in equivalent positions. The projection of coupled monoclinic cells of Ile is plotted using structural data from CSD (identifier LISLEU02).[94] (reprinted from ref. 34, Copyright (2016) with permission from the Americal Chemical Society).