Regulating the Spherulitic Evolution of 3-nitro-1,2,4-triazol-5-one via Controlled Supersaturation in Cooling Crystallization: Growth Mechanism and Morphological Consequences

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Table S1. Specific parameters of the cooling process crystallization

Type of solvent	Initial temperature (°C)	Final temperature (°C)	Cooling rate (°C/min)	Temperature of crystal precipitation point (°C)	C (g/mL)	C_{eq} (g/mL)	S_{max}
MT	55	10	1	30	0.0870	0.0515	1.69
	55	10	3	25	0.0870	0.0463	1.88
	55	10	5	20	0.0870	0.0414	2.10
	55	10	8	15	0.0870	0.0370	2.35
EtOH	65	10	1	35	0.0718	0.0386	1.86
	65	10	3	30	0.0718	0.0342	2.10
	65	10	5	20	0.0718	0.0272	2.64
	65	10	8	15	0.0718	0.0239	3.00
NPA	85	10	1	55	0.0516	0.0324	1.59
	85	10	3	50	0.0516	0.0286	1.80
	85	10	5	40	0.0516	0.0210	2.46
	85	10	8	30	0.0516	0.0161	3.20
IPA	75	10	1	55	0.0526	0.0353	1.49
	75	10	3	40	0.0526	0.0231	2.28
	75	10	5	30	0.0526	0.0173	3.04
	75	10	8	25	0.0526	0.0147	3.58
NBA	90	10	1	55	0.0379	0.0204	1.86
	90	10	3	45	0.0379	0.0155	2.44
	90	10	5	35	0.0379	0.0119	3.18
	90	10	8	30	0.0379	0.0106	3.58

Table S2. Specific parameters of NTO cooling rate at 1 °C /min in NPA solvent at 85 °C

Stirring rate/rpm	Initial concentration (g/mL)/C (g/mL)	Temperature of crystal precipitation point (°C)	C_{eq} (g/mL)	S_{max}
300	0.038	10	0.0068	5.59
300	0.042	15	0.0086	4.88
300	0.046	20	0.0102	4.51
450	0.038	30	0.0161	2.36
450	0.042	40	0.0210	2.00
450	0.046	40	0.0210	2.19
600	0.038	45	0.0240	1.58
600	0.042	45	0.0240	1.75
600	0.046	45	0.0240	1.92

Table S3. The comparison of the experimental and optimized lattice parameters of NTO

Lattice parameter	a/Å	b/Å	c/Å	β/°
Experiment	5.123	10.314	17.998	97.810
Dreiding	5.630	9.141	19.491	98.686
Compass	4.856	11.412	16.610	98.429
cvff	5.335	9.916	19.796	105.631
CompassII	5.723	8.827	18.958	90.000
pcff	5.119	11.869	17.416	107.095

Table S4. Related data on NTO's modified adsorption energy calculation

（1）

The parameters of the main crystal faces of NTO

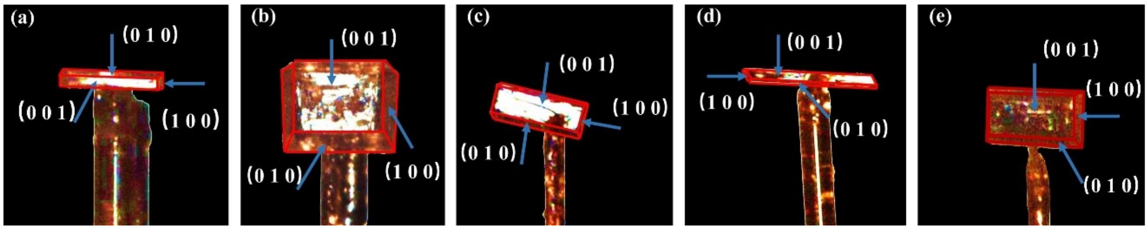
	(0 0 1)	(0 1 0)	(0 1 -1)	(1 0 0)
A_{hkl}/Å^2	52.84	92.21	92.24	185.63
A_{box}/Å^2	951.15	1096.25	1096.48	1067.31
z_{hkl}	2	2	2	2
E_{att}/kcal mol^{-1}	-11.35	-23.31	-23.33	-52.38

（2）

The interaction energy and corrected adhesion energy of different crystal planes of NTO in five alcohol solvents

	E/kcal mol^{-1}	(0 0 1)	(0 1 0)	(0 1 -1)	(1 0 0)
MT	E_{int}	-372.404	-370.471	-361.36	-425.045
	E_s	-10.427	-15.597	-15.213	-36.979
	E_{att}'	-0.924	-7.708	-8.114	-15.404
EtOH	E_{int}	-437.975	-337.924	-327.268	-420.851
	E_s	-12.263	-14.227	-13.778	-36.614
	E_{att}'	0.912	-9.101	-9.527	-15.769
NPA	E_{int}	-369.446	-349.961	-324.95	-444.35
	E_s	-10.344	-14.733	-13.680	-38.658
	E_{att}'	-1.006	-8.594	-9.625	-13.725
IPA	E_{int}	-387.9	-388.628	-343.206	-462.006
	E_s	-10.860	-16.360	-14.449	-40.194
	E_{att}'	-0.491	-6.967	-17.856	-12.189
NBA	E_{int}	-370.753	-326.673	-321.555	-433.834
	E_s	-10.381	-13.753	-13.537	-37.743
	E_{att}'	-0.970	-9.574	-9.768	-14.640

Figure S1. Picture of single crystal indexing; The value below the picture represents the indexing rate.



53 % 67 % 88 % 71 % 77 %

Figure S2. Simulated crystal morphology under different solvents

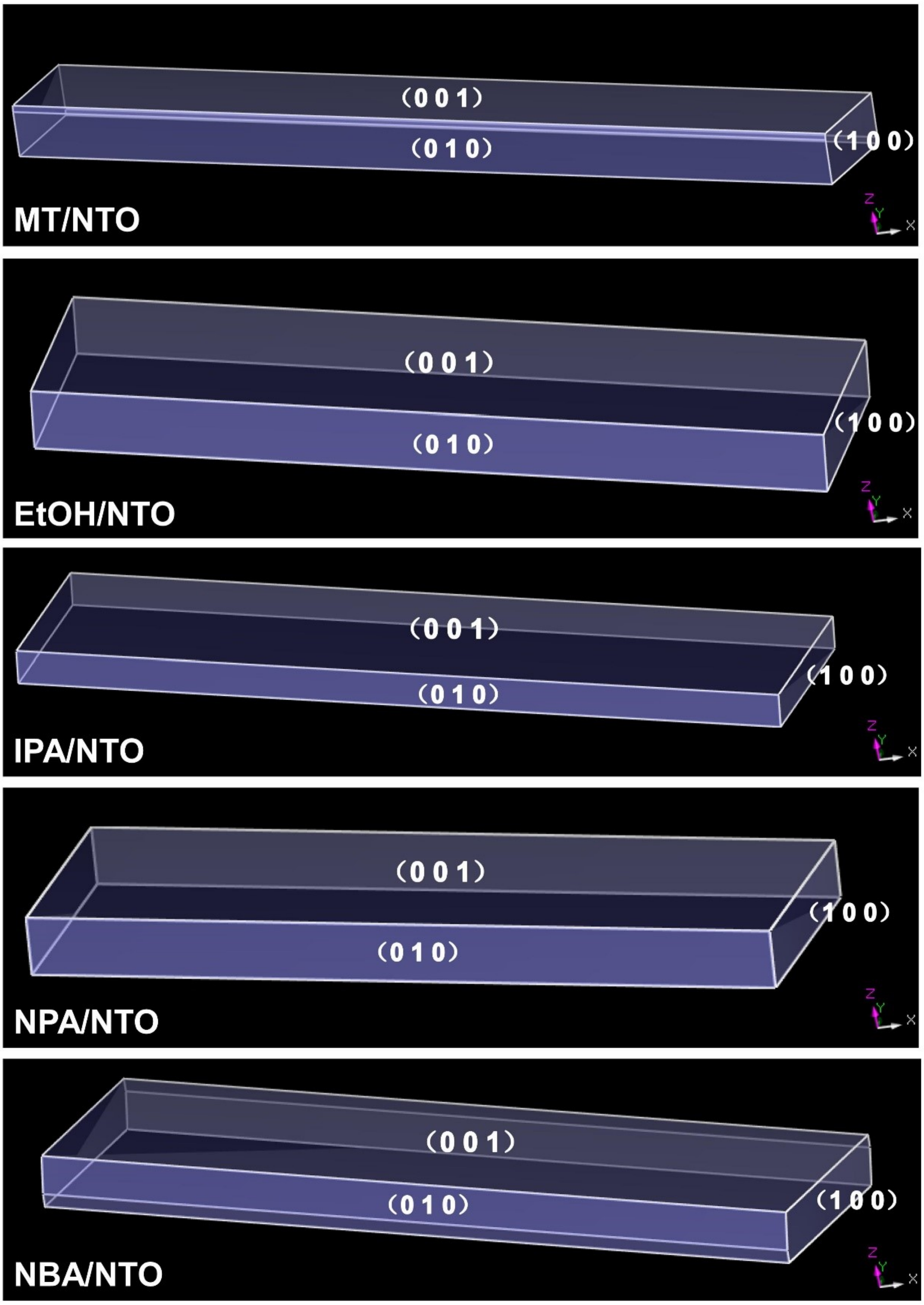


Figure S3. SEM images of NTO quenching in five solvent systems

spherulites were found to form in all five alcohol solvents by temperature quenching on a glass slide. Since methanol, ethanol, and isopropanol have large particle size particles, only the surfaces in contact with the solution form spherulites when they precipitate on the glass sheet, thus forming a hemisphere-like state. In n-propanol and n-butanol complete spherulites can be formed because of the relatively small particles. Electron microscope images of NTO precipitation from different alcohols: (a) methanol (b) ethanol (c) n-propanol (d) isopropanol (e) n-butanol

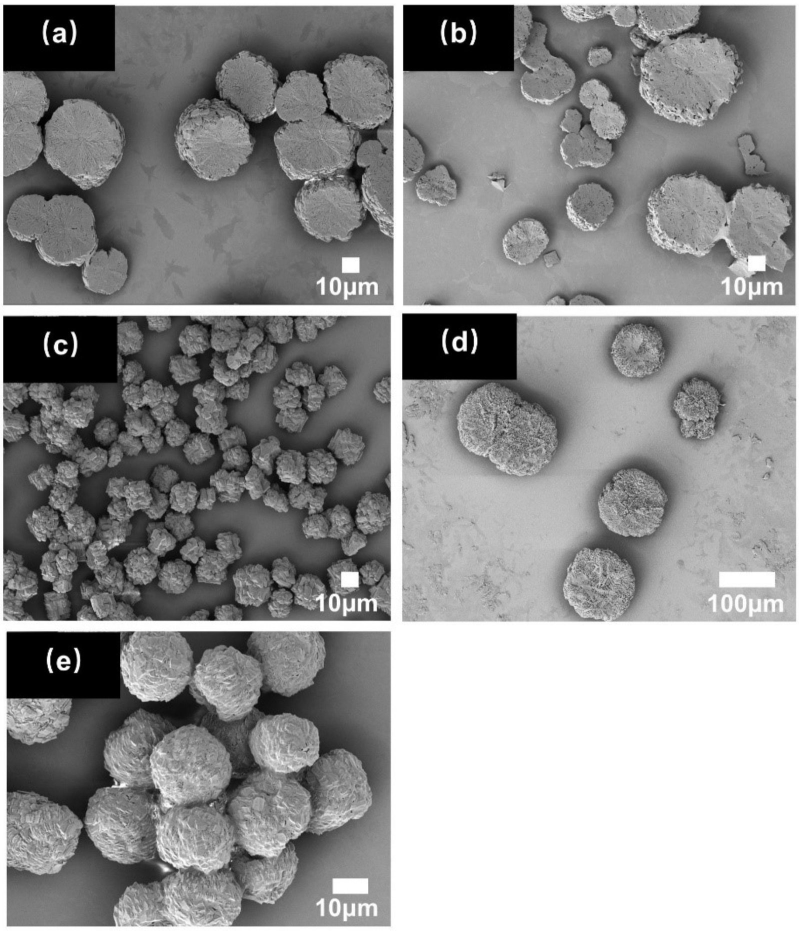
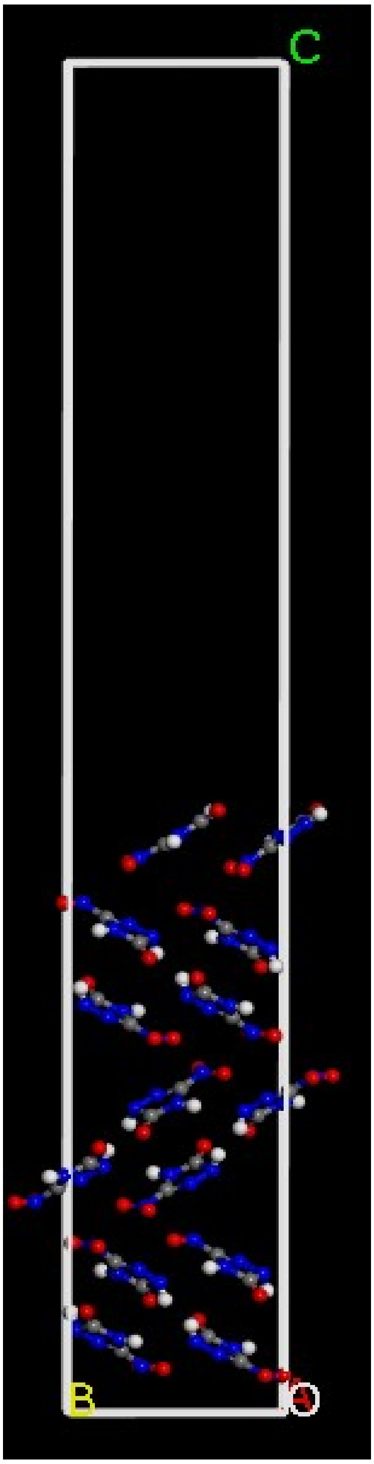


Figure S4. Model construction and computational details of NTO

The left figure shows the normal growth configuration of NTO, and the right figure shows the growth configuration of NTO after torsion.

Computational Details: First principles calculations of geometric optimization in this work have been performed using Cambridge Serial Total Energy Package (CASTEP) module[1] implemented in Materials Studio 8.0 program suite within the generalized gradient approximation (GGA). Exchange and correlation interactions were described using the functional parameterized by Perdew-Burke-Ernzerhof (PBE)[2]. The electronic wave functions have been expanded in a plane wave basis set with an energy cutoff of 490 eV. The SCF tolerance was set to be equal 1×10^{-6} eV per atom and the force convergence criterion during optimizations was set to be 1×10^{-2} eV/Å.


C
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A
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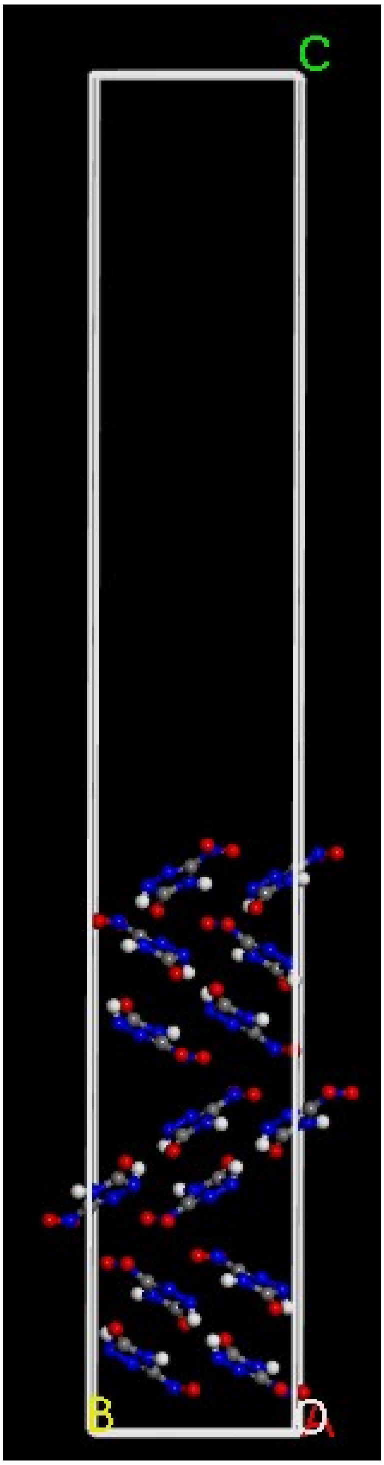

C
B
A

Figure S5. Supplementary TG-DSC data of other spherulites

(a) represents the TG-DSC figure of the spherulites in the methanol system; (b) represents the TG-DSC figure of the spherulites in the ethanol system; (c) represents the TG-DSC figure of the spherulites in the isopropanol system; (d) represents the TG-DSC figure of the spherulites in the n-butanol system;

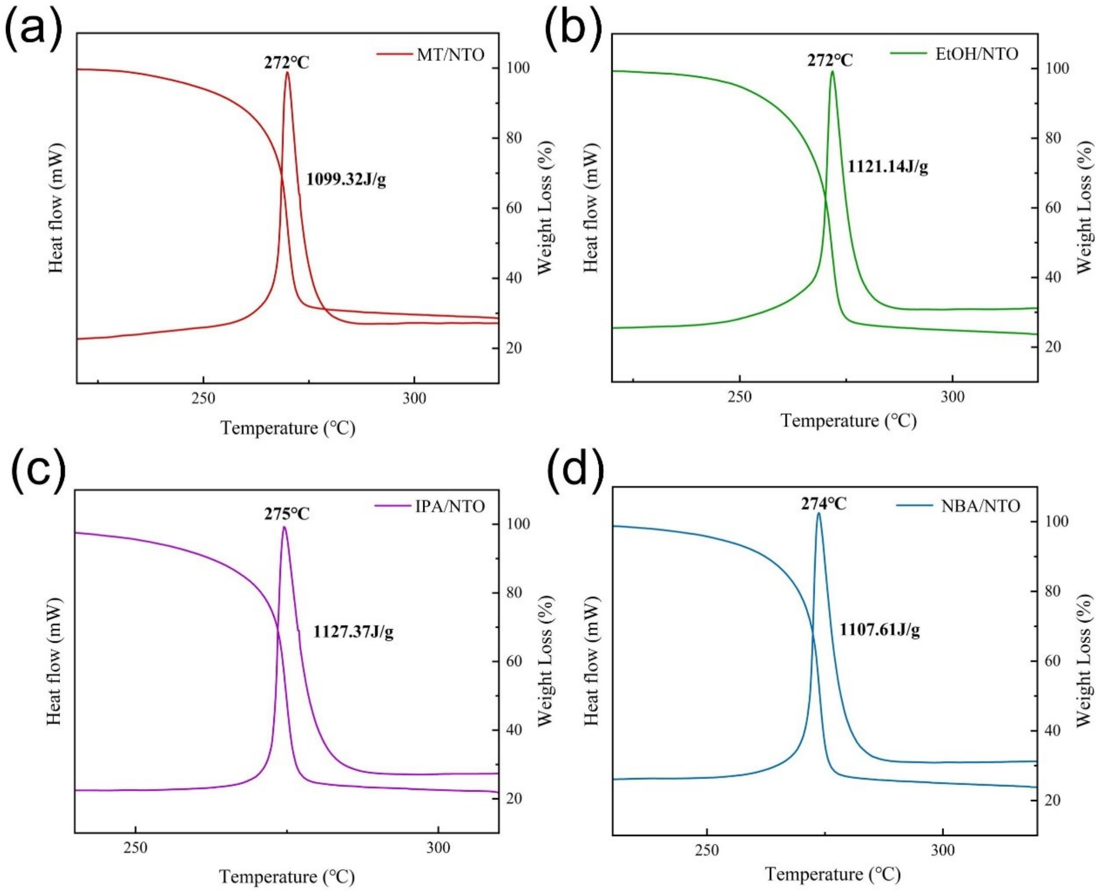
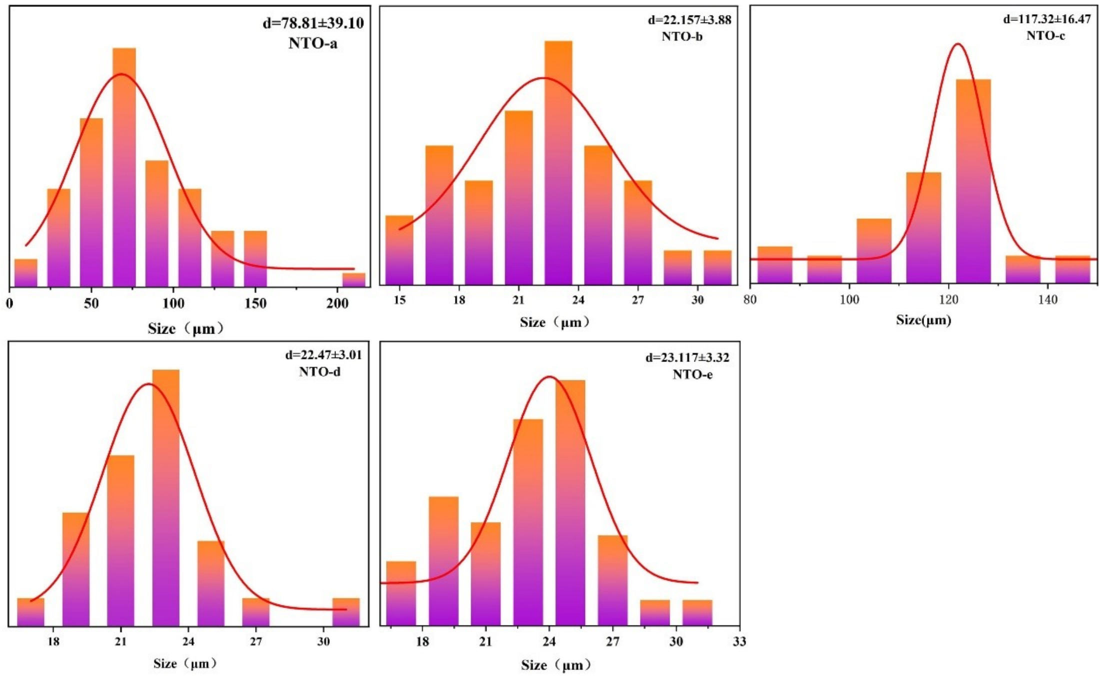


Figure S6. Analysis of data on average particle size

Since NTO has good water solubility and is dissolved to varying degrees for most organic solvents, it is not possible to use a dedicated laser particle sizer for testing, so all the average particle sizes involved in this paper were calculated using Nano Measurer 1.2 software combined with SEM images, and the results are as follows:



TextS1. Details of solubility determination

First, mix the excess NTO and 5 mL solvent in a 20 mL glass bottle, adjust the temperature and place it on a heating mixer with an accuracy of ± 0.1 K. To ensure the uniformity and accuracy of the temperature, water bath is used as the medium; After controlling the temperature, run at a speed of 300 rpm for 24 hours to achieve solid-liquid equilibrium. When the system reaches equilibrium, keep the solution stationary for at least 10 hours to allow all suspended particles to settle within the experimental temperature range. Subsequently, filter the supernatant (1mL) through a preheated or cooled membrane (0.45 μm) Filter into a clean glass bottle with a known weight (M_1) and immediately weigh it as M_2. Finally, let the solvent in the glass bottle stand and evaporate completely before placing it in a vacuum oven at 80℃for another 2 hours to ensure that the solvent has completely evaporated. Then, weigh again and record it as M_3. The same group of experiments should be repeated at least 3 times. The error analysis between the average value and the measured value shows that the maximum error range is less than 5 %, which is within a reasonable error range, further proving the accuracy of the solubility results.

Mass of saturated solution at set temperature：$m_1 = M_2 - M_1$

Mass of solute at set temperature：$m_2 = M_3 - M_1$

Type of solvent	MT	EtOH	NPA	IPA	NBA
Number of temperature points	10	12	16	14	17

Text S2. The details of molecular dynamic (MD) simulation

After single crystal indexing, it was found that there were differences in morphology under different solvent systems. Therefore, the reason for the morphology differences was explained from a thermodynamic perspective through the calculation of related adhesion energies. The operation details and steps are as follows:

The initial structure of α-NTO crystal was obtained from CCDC (286331) crystal database. The optimization of crystal structure is carried out using the Forcit module in Materials Studio 8.0. Choose COMPASS[3, 4] (Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies) force field to simulate the morphology of NTO. The calculation in Table S3 proves that the COMPASS force field error is the smallest. All force fields used in the calculation are COMPASS. The optimized structure uses a morphology module and growth morphology method to calculate the crystal morphology of NTO under vacuum. Therefore, the main growth surface and adhesion energy (E_{att}) of NTO under vacuum conditions were obtained.

The calculation for correcting adsorption energy in a solvent system is as follows, using the NTO (0 0 1) surface as an example. First, the COMPASS (Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies) force field was used to optimize the five alcohol molecules. The NTO cell was then faceted along the morphological growth surface (0 0 1) using the "cleave" method to obtain a faceted layer with a depth of 5×dhkl. A periodical structure with a length and width of about 40 Å is constructed using a "super-cell"[3, 5]. Five solvent boxes corresponding to the crystal plane size were also built by the Amorphous Cell module. and respectively set the density of Methanol to 0.7918 g/cm^3, Ethanol to 0.789 g/cm^3, Isopropanol to 0.785 g/cm^3, n-Propanol to 0.804 g/cm^3, and n-Butanol to 0.8098 g/cm^3. Geometric optimization of the compass force field was applied. The five (0 0 1)/alcohol interfaces are modeled separately under the Build layer module, with the periodic structure of the (0 0 1) crystal plane set as layer1, the corresponding solvent box set as layer2, the fixed crystal plane layer, the unconstrained solvent layer and the vacuum layer (50 Å to eliminate boundary effects), and the geometric optimization of the built interface models. Finally, the forcite module was used to perform molecular dynamics calculations for the five interface models. The parameters were set as follows: temperature was controlled by an Anderse thermostat at 298 K, molecular dynamics (MD) simulations were performed using the NVT system synthesis, and Ewald summation-based methods with a cut-off distance of 15.5 Å were used to calculate electrostatic and van der Waals interactions with a time step of 1 fs and a total MD time of 1 ns, and data were collected every 500 steps[6]. The system is considered to be in equilibrium when the temperature and energy fluctuations are within 5 %. The energy task in the focite module is then used to calculate the energy of the system, the crystal layer and the solvent layer separately. (0 1 0)、(0 1 -1) and (1 0 0) crystal surface is the same manner as described above. The corresponding calculation equation is as follows:

The solvent affects the adhesion energy of the different crystal faces of the explosive crystal in its ideal state by interacting with the molecules exposed to the different surfaces of the crystal, which is called the modified adhesion energy[7] and is denoted by $E_{a_{tt}}^{'}$:

$$E_{a_{tt}}^{'} = E_{att} - E_s \tag{1}$$

E_{att} denotes the adhesion energy of the explosive crystal surface calculated by AE model in the ideal state without solvent influence, and Es denotes the solvent effect.

$$E_s = E_{int} \cdot A_{hkl}/(A_{box} \cdot z_{hkl}) \tag{2}$$

E_{int} represents the crystal surface/solvent interface interaction energy, A_{hkl} is the surface area of slices per unit cell (hkl), A_{box} is the total surface area of the supercell, and z_{hkl} represents the number of solute molecules per unit crystal surface.

$$E_{int} = E_{tot} \text{ - } (E_{cry} - E_{sol}) \tag{3}$$

where E_{tot}, E_{cry} and E_{sol} are the potential energy obtained for each component after performing the MD simulation.

Generate new crystal morphology: Modify the main crystal plane E_{att} under vacuum to the calculated $E_{a_{tt}}^{'}$, select the main crystal plane hkl and the corrected adhesion energy $E_{a_{tt}}^{'}$ data, and run the Generate Habit task through the morphology module to simulate the morphology of crystals in the solvent system.

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