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Supporting information for article:

A new polymorph of 1-hydroxy-2-naphthoic acid obtained during failed co-crystallization experiments

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S1. Experimental

S1.1. Materials

HNA raw material is purchased from Aladdin Reagent Company Limited and all analytical grade solvents were purchased from Sinopharm Chemical Reagent Company Limited, and used without further purification.

S1.2. Preparation of HNA Polymorphs

HNA form I and form II were prepared by slow evaporation at room temperature from diethyl ether and acetonitrile, repectively.

S1.3. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis was carried out in a Netzsch TG209 F3 equipment, using N_2 as dry air with a flow of 20 mL/min and a scan rate of 10 ℃/min.

S1.4. Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry was performed with a PerkinElmer DSC 8500 instrument. Samples weighting 3-5 mg were heated in standard aluminum pans at scan rates from 2 ℃/min to 80 ℃/min under nitrogen gas flow of 20 mL/min. Two-point calibration using indium and tin was carried out to check the temperature axis and heat flow of the equipment.

S1.5. Single crystal X-ray diffraction

Single crystal X-ray diffraction measurements for were conducted on a Bruker Smart Apex II diffractometer using Mo-Kα radiation (λ= 0.71073 Å) with a graphite monochromator. Integration and scaling of intensity data was accomplished using the SAINT program (Bruker, 2000). The structures were solved by Direct Methods using SHELXS97 (Sheldrick, 2008) and refinement was carried out by full-matrix least-squares technique using SHELXL97 (Sheldrick, 2008). The heavy atoms were refined anisotropically. The O-H hydrogens were located from difference electron density maps and their coordinates were allowed to refine

freely while their displacement parameters were set to Uiso (H) = 1.5 Ueq (O). The C-H hydrogens were placed in calculated positions and refined using a riding model with C-H = 0.93 Å and with Uiso (H) = 1.2 Ueq (C).

S1.6. Powder X-ray Diffraction

PXRD were measured on a Bruker D8-ADVANCE X-ray diffractometer using a Cu-Kα radiation (λ = 1.5418 Å). The voltage and current were 40 kV and 40 mA, respectively. Samples were measured in reflection mode in the 2θ range 3–40° with a scan speed of 15 ^{o}/min (step size 0.025^o, step time 0.1 s) using a LynxEye detector. All data were acquired at ambient temperature. Data were imaged and integrated with RINT Rapid and peak-analyzed with Jade 6.0 software from Rigaku. Calibration of the instrument was performed using Corindon (Bruker AXS Korundprobe) standard.

Variable-temperature X-ray powder diffraction patterns were recorded with a XPH-300 hot stage (Changfang, China) attached to the Bruker D8 Advance diffractometer (Bruker, Germany). A heating rate of 10 ∘C/min was used during all of these determinations. Approximately 50 mg samples were weighed into the sample holder, taking care not to introduce a preferential orientation of crystals.

S1.7. Fourier-transform Infrared (FTIR)

Fourier-transform Infrared (FTIR) spectra were collected by a Nicolet-Magna FT-IR 750 spectrometer in the range of 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1} at ambient conditions.

S1.8. Hot-Stage Microscopy (HSM)

All HSM examinations were performed on a XPV-400E Polarizing microscope and a XPH-300 hot stage coupled with a JVC TK-C9201 EC digital video recorder (Shanghai Changfang Optical Instrument Company).

Table S1   Crystallographic data for HNA polymorphs

For all structures: $C_{11}H_8O_3$, M_r = 188.17. Experiments were carried out at 296 K with Mo $K\alpha$ radiation.

H atoms were treated by a mixture of independent and constrained refinement.

	mo_I	mo_II
Crystal data		
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $C2/c$
a, b, c (Å)	6.9798 (9), 3.8107 (6), 32.790 (5)	20.920 (5), 6.9926 (14), 14.688 (3)
β (°)	93.901 (8)	125.339 (10)
V (Å^3)	870.1 (2)	1752.7 (6)
Z	4	8
μ (mm^{-1})	0.11	0.11
Crystal size (mm)	0.44 × 0.32 × 0.11	0.42 × 0.34 × 0.11
Data collection		
Absorption correction	–	–
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	6187, 1491, 1020	7678, 2015, 1239
R_{int}	0.038	0.034
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.594	0.651
Refinement		

$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.038,　0.097,　0.96	0.068,　0.226,　1.04
No. of reflections	1491	2015
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.15, -0.16	0.49, -0.27

* Computer programs: *SHELXS97* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 2008).

The crystallographic data of forms I and II (CCDC 1019893-1019894) is also available through

Cambridge Crystallographic Data Centre

Table S2   Hydrogen bond parameters and short O···O contacts

Polymorphs	Form I	Form II
(O3-H2)/Å	0.93(2)	0.93(4)
(H2···O2^i)/Å	1.72(2)	1.74(4)
(O3···O2^i)/Å	2.650(2)	2.650(2)
symmetry operation for (i)	-x+1, -y+2, -z+2	-x+1, y, -z+0.5
(O1-H1)/Å	0.92(2)	0.86(4)
(H1···O2)/Å	1.77(2)	1.83(3)
(O1···O2)/Å	2.600 (2)	2.616 (2)
(O1···O1^{ii})/Å	-	2.979 (2)
Symmetry operation for (ii)	-	-x+1.5, -y+0.5, -z+1

Table S3   Table S3. Columnar stacking parameters

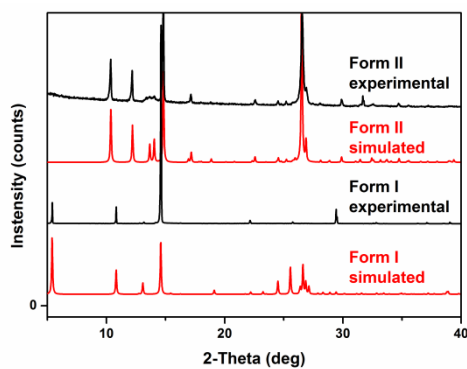| Polymorphs	Form I	Form II
Centroid* to centroid distance (Å)	3.811 (2)	3.849 (3)
Centroid to plane distance (Å)	3.474(2)	3.536(3); 3.451(3)
Interplanar angle (°)	0	4.7
Angle between b-direction and the axis of the stack (°)	0	24.7(1)
Symmetry operations	x, y+1, z	-x+1.5, y-0.5, -z+0.5
		-x+1.5, y+0.5, -z+0.5

* The centroids were calculated by atoms C1, C2, C3, C4, C5 and C10.
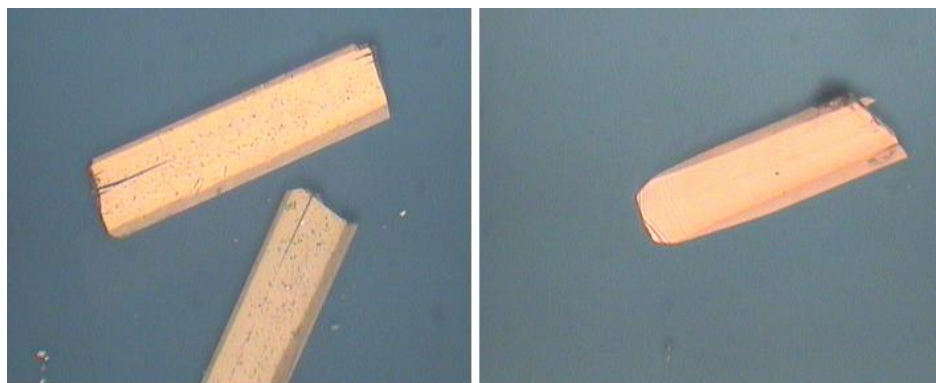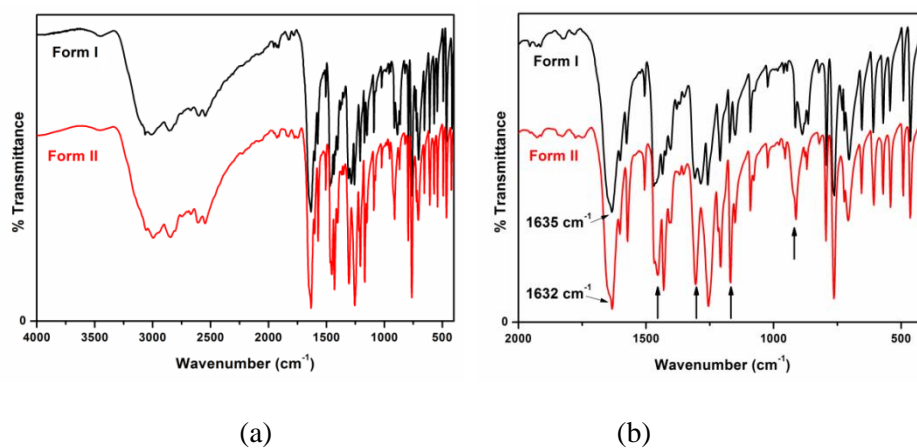
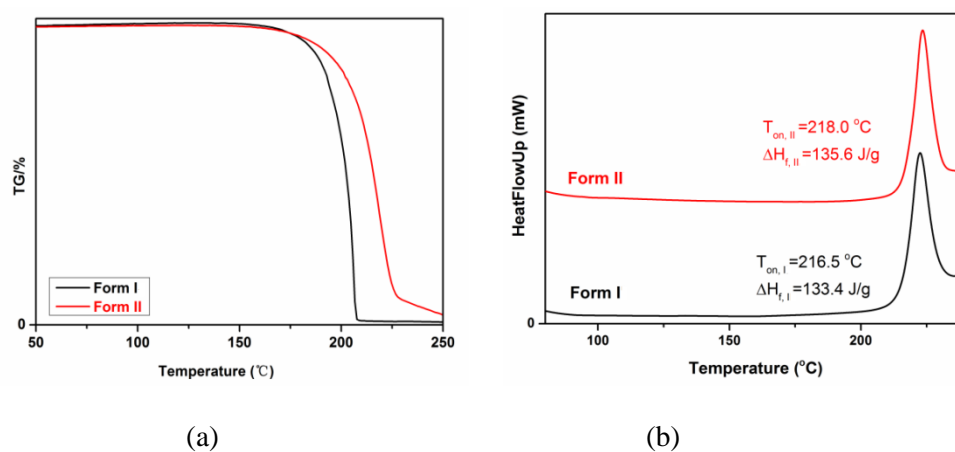**Figure S1** HSM photographs of HNA Form I (left) and Form II (right).
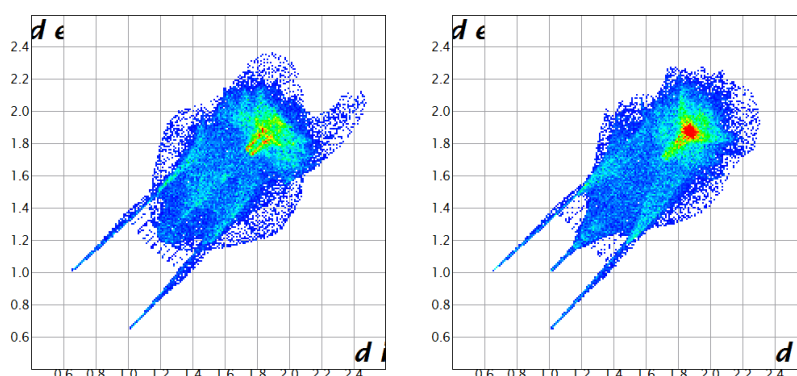
Figure S2 2D fingerprint plots of HNA Form I (left) and Form II (right).
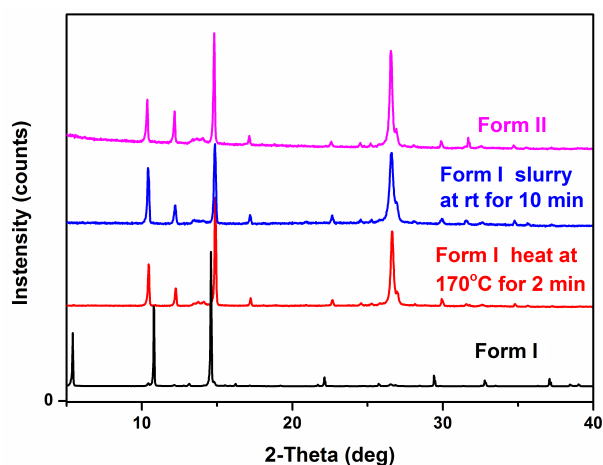

Figure S3 Compared PXRD patterns of HNA polymorphs.

(a)   (b)

Figure S4 Compared FT-IR spectra of HNA polymorphs (a) full range, (b) 2000 -400 cm^{-1}.

(a)   (b)
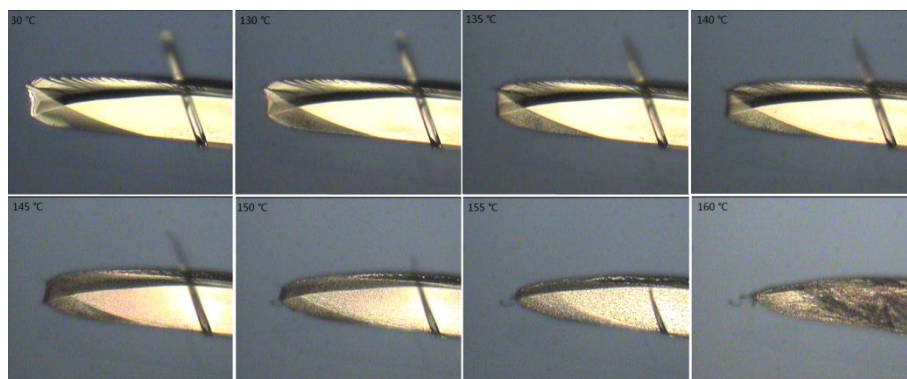
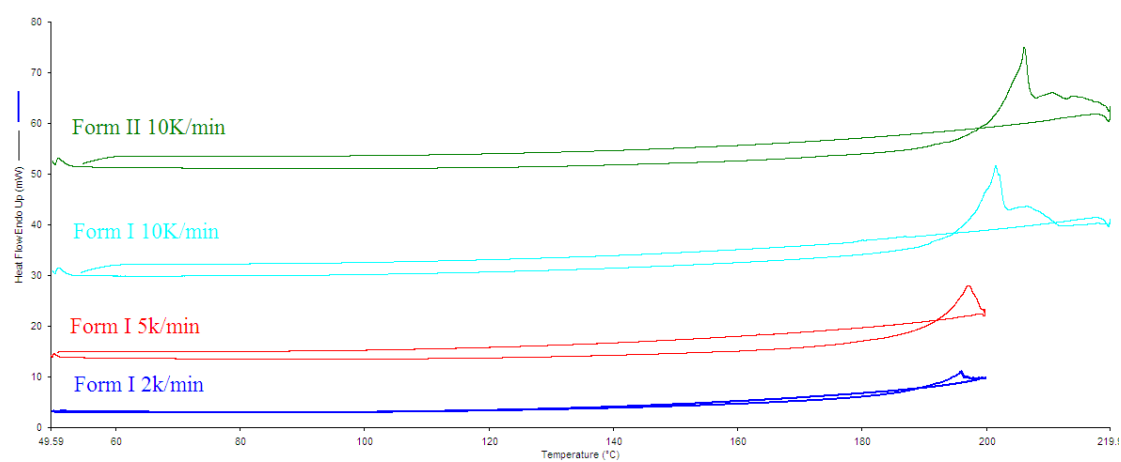**Figure S5** Compared TGA (a) and DSC (b) thermograms of HNA polymorphs.

Figure S6 Compared PXRD patterns for HNA form transformations.

Figure S7 HSM photographs of HNA Form I heated at different temperatures.

Figure S8 DSC thermograms of HNA polymorphs using lower heating/cooling-rate.