

Electronic Supplementary Information

Polymorphs and transformations of the solid forms of organic salts 5-sulfosalicylic acid and isonicotinamide

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Table S1 Geometric parameters of hydrogen bonding in crystals.

	D-H...A	D-H (Å)	D...A (Å)	H...A (Å)	D-H...A (°)	Symmetry Code
1a form	i	0.858(1)	2.888(1)	2.303(1)	125.52(3)	x,-y+3/2,z+1/2
	ii	0.847(1)	3.1137(1)	2.270(1)	173.21(1)	x-1/2,y+3/2,-z+1
	iii	0.850(1)	2.884 (1)	2.410(2)	115.82(1)	x-1/2,y,-z+3/2
	iv	0.853(1)	2.647(1)	1.796(1)	174.68(1)	-x+3/2,-y+1,z+1/2
	v	0.857(2)	2.984(2)	2.147(2)	165.19(2)	x,y,z
	vi	0.858(1)	2.767(1)	2.063(2)	138.63(1)	x+1/2,y,-z+3/2
1b form	i	0.894(3)	2.703(2)	1.931(3)	143.43(29)	x+1/2,y-1/2,z
	ii	0.852(3)	3.122(2)	2.323(3)	156.03(31)	x, -y+1, z-1/2
	iii	0.861(5)	2.993(2)	2.426(4)	123.87(40)	x-1/2, -y+1/2, z-1/2
	iv	0.832(3)	2.751(2)	1.921(3)	173.75(35)	x-1, y, z
	v	0.791(4)	2.757(3)	1.993(3)	162.07(40)	x, y, z
	vi	0.894(3)	2.913(2)	2.367(3)	119.40(28)	x+1/2,-y+1/2,z+1/2
	vii	0.852(3)	2.975(2)	2.455(3)	120.02(27)	x+1/2,y+1/2,z
	viii	0.809(3)	2.583(2)	1.774(3)	177.28(35)	x+1/2,y-1/2,z
	ix	0.863(4)	3.240(3)	2.394(3)	143.43(29)	x+1,y,z
1c form	i	0.842(4)	2.957(3)	2.281(3)	137.39(3)	-x+1, y-1/2,-Z+1
	ii	0.830(4)	2.912(2)	2.096(3)	167.15(4)	x, y, z+1
	iii	0.989(4)	2.914(2)	2.356(4)	114.81(3)	-x+1, y-1/2,-Z+2
	iv	0.926(3)	2.646(2)	1.722(3)	175.67(3)	x, y, z+1
	v	0.831(6)	2.983(3)	2.220(6)	152.64(6)	x, y, z
	vi	0.842(4)	3.046(3)	2.453(4)	128.01(3)	-x+1, y-1/2,-Z+1
	vii	0.912(3)	3.051(3)	2.176(3)	160.40(3)	-x+1, y-1/2,-Z+2
$(5\text{-SSA-2H})_2^-\cdot(\text{INA-H})_2^+$ (2)	i	0.860(1)	2.932(3)	2.098(1)	163.16(1)	-x,-y+2,-z+1
	ii	0.859(1)	2.861(2)	2.123(1)	143.64(1)	-x,-y+1,-z+1
	iii	0.861(2)	2.926(3)	2.159(2)	148.08(1)	-x,-y+2,-z+1
	iv	0.863(2)	3.154(3)	2.457(2)	138.23(1)	-x+1/2,y+1/2,-z+1/2
	v	0.865(2)	3.203(3)	2.579(2)	129.88(1)	x-1/2,-y+3/2,z+1/2
	vi	0.860(2)	2.886(3)	2.130(2)	146.42(1)	-x,-y+1,-z+1
	vii	0.860(2)	3.304(2)	2.459(1)	124.91(1)	x-1/2,-y+1/2,z-1/2
	viii	0.820(1)	2.589(2)	1.770(1)	176.51(1)	-x+1/2,y-1/2,-z+3/2
$(5\text{-SSA-2H})^-\cdot(\text{INA-H})^+\cdot\text{M}$	i	0.860(1)	2.949(2)	2.107(1)	165.90(1)	x-1/2,-y+3/2,z-1/2
	ii	0.819(0)	2.674(2)	1.859(1)	172.49(1)	-x+3/2,y-1/2,-z+3/2
	iii	0.859(2)	2.799(2)	1.957(2)	165.83(2)	x,y,z

eOH(3)	iv	0.820(2)	2.724(3)	1.907(2)	174.11(1)	x,y,z
	v	0.859(1)	2.858 (3)	2.010(2)	168.33(1)	x+1/2,-y+3/2,z+1/2
(5-SSA-2H)₂⁻·(INA-H)₂⁺· H₂O·MeOH (4)	vi	0.868(3)	3.013(2)	2.448(3)	123.25(2)	x,-y+1/2,z-1/2
	vii	0.818(3)	3.026(2)	2.508(3)	122.31(2)	x,-y+3/2,z+1/2
	viii	0.884(3)	2.653(2)	1.772(3)	174.29(3)	-x+1,-y+3/2,z+1/2
	ix	0.863(2)	2.915(2)	2.064(2)	168.27(2)	x,y,z
	x	0.868(3)	2.773(2)	2.036(2)	142.07(2)	x,-y+1/2,z-1/2
	xi	0.883(3)	3.215(3)	2.372(2)	160.46(2)	x,y,z
(5-SSA-2H)⁻·(INA-H)⁺·(I NA) (5)	i	0.886(2)	2.998(2)	2.117(2)	171.84(2)	-x,y,-z+3/2
	ii	1.027(3)	2.639(2)	1.613(3)	176.65(2)	x,y,z
	iii	0.894(2)	2.670(2)	1.784(2)	170.19(2)	x,y,z

Table S2 Crystallography data for seven salts.

	form 1a	form 1b	form 1c
Empirical formula	C ₁₃ H ₁₄ N ₂ O ₈ S	C ₁₃ H ₁₄ N ₂ O ₈ S	C ₁₃ H ₁₄ N ₂ O ₈ S
Formula weight	358.32	358.32	358.32
Crystal temperature (K)	298	298	298
Crystal system	Orthorhombic	Monoclinic	<i>Monoclinic</i>
Space group	<i>Pbca</i>	<i>Cc</i>	<i>P2₁</i>
Z	8	4	2
a(Å)	13.5387(9)	7.0166(6)	6.6646(4)
b(Å)	12.9149(8)	17.0455(14)	13.3543(8)
c(Å)	16.7636(10)	13.0055(11)	8.4280(5)
α(deg)	90.00	90.00	90.00
β(deg)	90.00	103.212(3)	101.223(2)
γ(deg)	90.00	90.00	90.00
V(Å ³)	2931.1(3)	1514.3(2)	735.76(8)
D _x (Mg.cm ⁻³)	1.624	1.572	1.617
μ(mm ⁻¹)	0.270	0.261	0.269
F(000)	1488	744	372
R _{int}	0.0243	0.0192	0.0140
No.of collected data(unique)	46949	13127	12479
No.of data with I>2σ(I)	3295	3621	3474
No.of parameters varied	238	245	245
s	1.073	1.058	1.058
Rf/wRf	0.0394/0.1002	0.0247/0.0636	0.0257/0.0674
All data Rf/wRf	0.0431/0.1038	0.0256/0.0645	0.0260/0.0678
CCDCnumber	1964236	1964237	1964238

	(5-SSA-2H) ₂ ⁻ ·(INA-H) ₂ ⁺ (2)	(5-SSA-2H) ⁻ ·(INA-H) ⁺ ·MeOH (3)	(5-SSA-2H) ₂ ⁻ ·(INA-H) ₂ ⁺ ·H ₂ O·MeOH (4)	(5-SSA-2H) ⁻ ·(INA-H) ⁺ ·(I NA) (5)
Empirical formula	C ₁₃ H ₁₂ N ₂ O ₇ S	C ₁₄ H ₁₆ N ₂ O ₈ S	C ₂₇ H ₃₀ N ₄ O ₁₆ S ₂	C ₁₉ H ₁₈ N ₄ O ₈ S
Formula weight	340.31	372.35	730.67	462.43
Crystal temperature (K)	296	296	296(2)	293
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2/ <i>c</i>
Z	8	4	4	8
a(Å)	13.7162(10)	8.669(4)	14.4333(18)	15.9529(17)
b(Å)	15.8548(11)	17.187(8)	16.943(2)	10.2279(11)
c(Å)	14.2306(10)	10.895(5)	13.5818(16)	25.638(3)
α(deg)	90.00	90.00	90.00	90.00
β(deg)	117.171(2)	94.057(12)	111.633(4)	102.346
γ(deg)	90.00	90.00	90.00	90.00
V(Å ³)	2753.2(3)	1619.2(13)	3087.4(6)	4086.5(7)
D _x (Mg·cm ⁻³)	1.642	1.527	1.572	1.503
μ(mm ⁻¹)	0.278	0.248	0.258	0.215
F(000)	1408	776	1520	1920.0
R _{int}	0.0246	0.0188	0.0256	0.0265
No. of collected data(unique)	22644	14559	19462	17429
No. of data with I>2σ(I)	5730	3999	4696	4415
No. of parameters varied	420	234	492	290
s	1.105	1.039	1.073	1.093
R _f /wR _f	0.0454/0.1102	0.0397/0.1064	0.0386/0.0941	0.0402/0.1018
All data R _f /wR _f	0.0544/0.1172	0.0470/0.1131	0.0446/0.0998	0.0467/0.1067
CCDC number	1964242	1964239	1964240	1964241

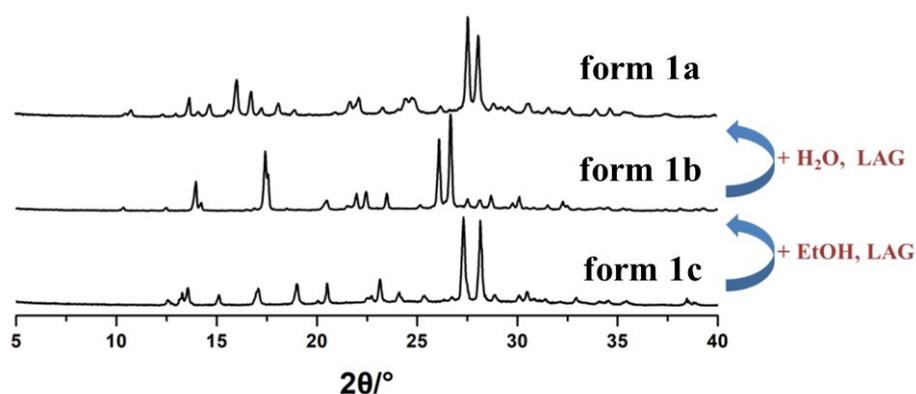


Fig. S1 Transformation between form 1a, form 1b and form 1c.

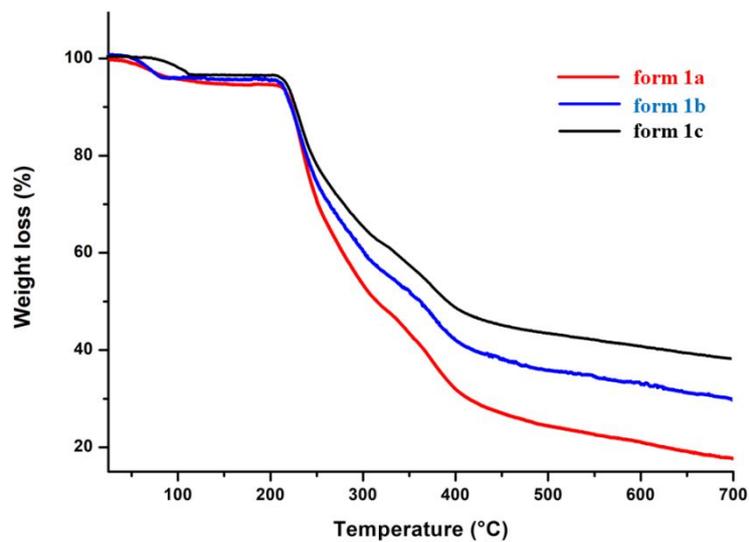
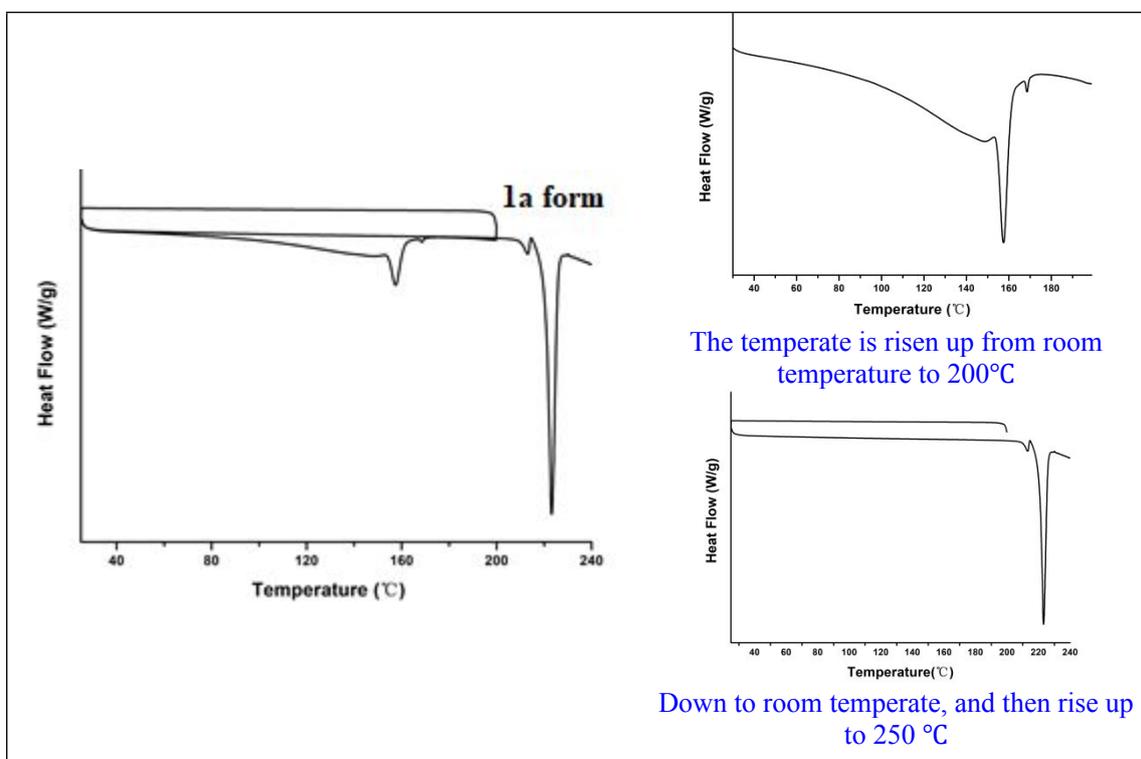


Fig. S2 TG curve of three polymorphs of $(5\text{-SSA-2H})^{\cdot-} \cdot (\text{INA-H})^{\cdot+} \cdot \text{H}_2\text{O}$ (1).



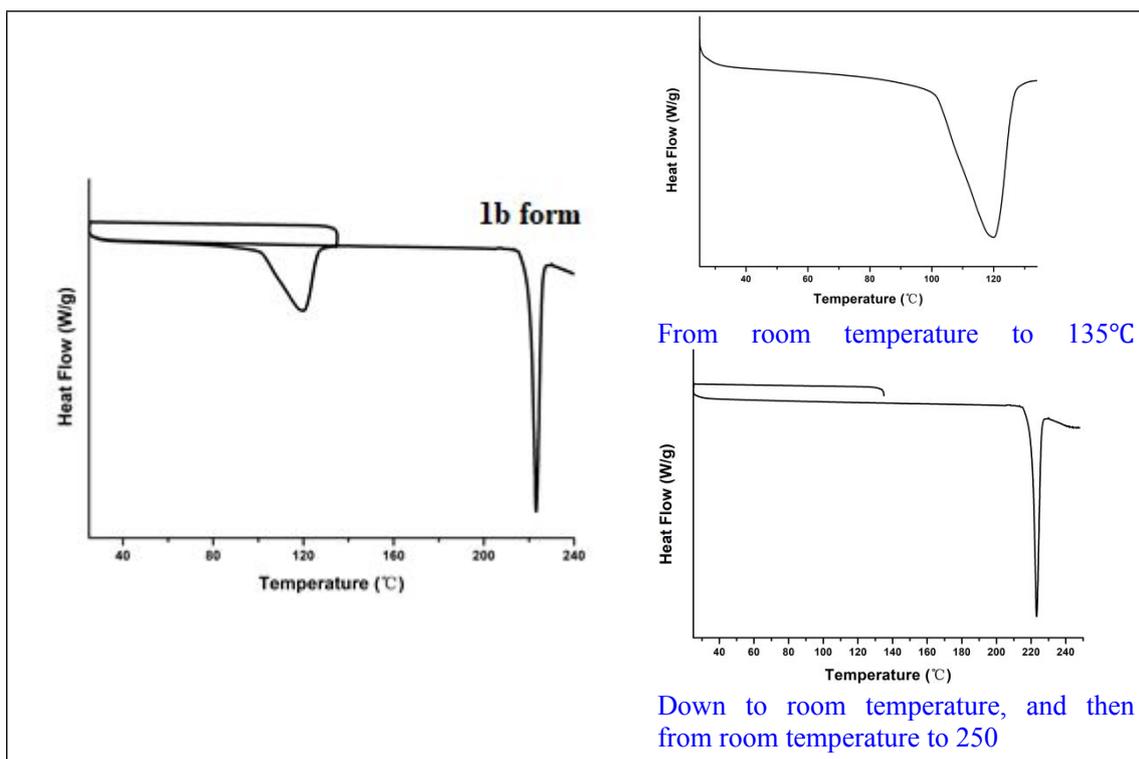
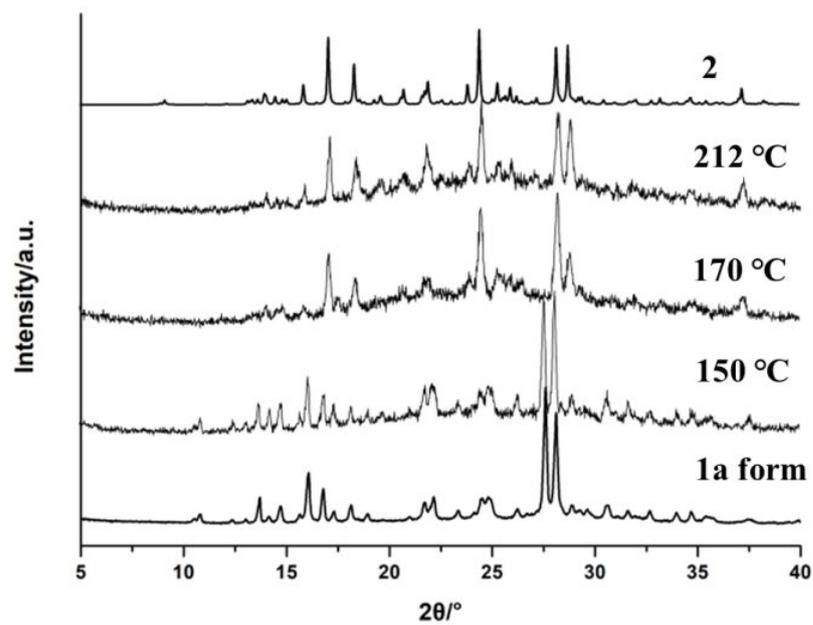


Fig. S3 The DSC ramp experiments for phase **1a** and **1b**.

form 1a



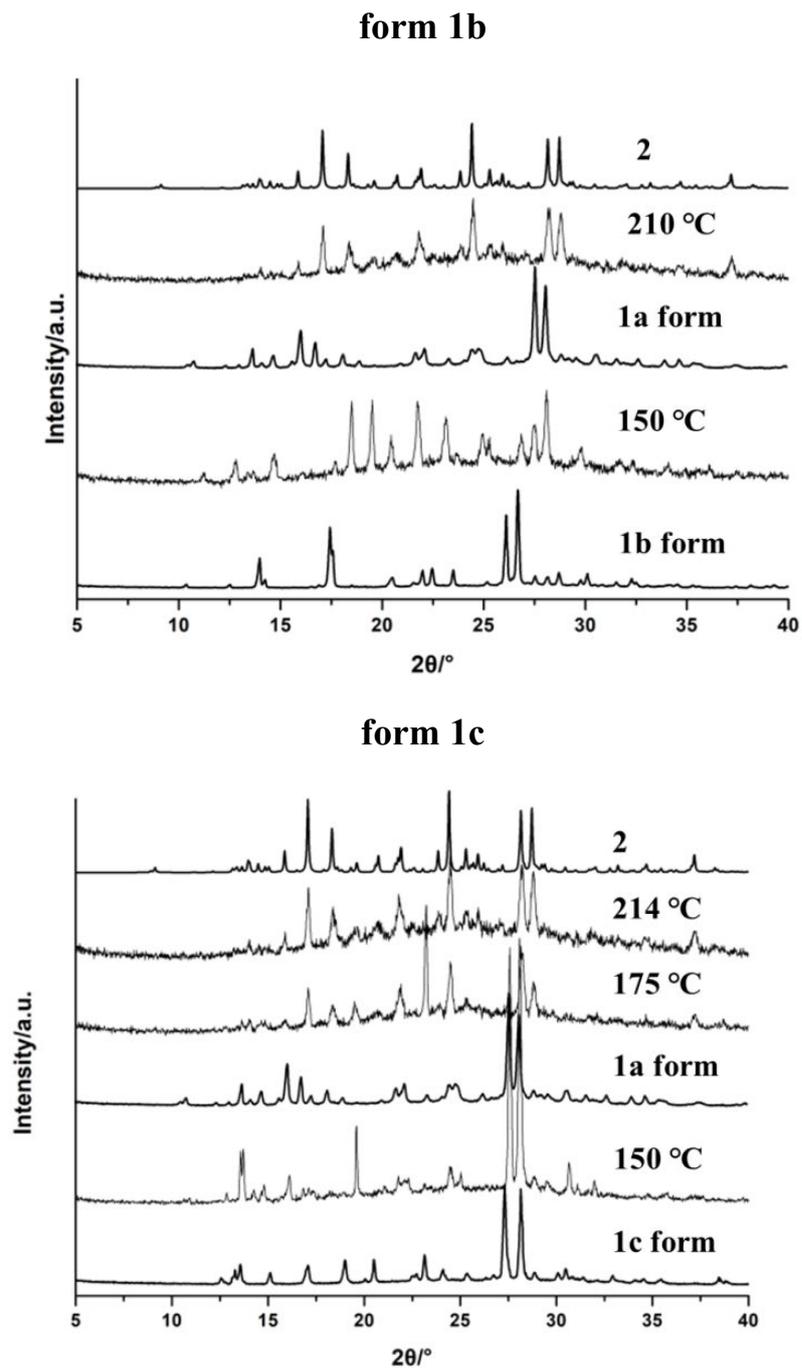


Fig. S4 Dehydration of three polymorph of $(5\text{-SSA-2H})\cdot(\text{INA-H})^+\cdot\text{H}_2\text{O}$ (1).

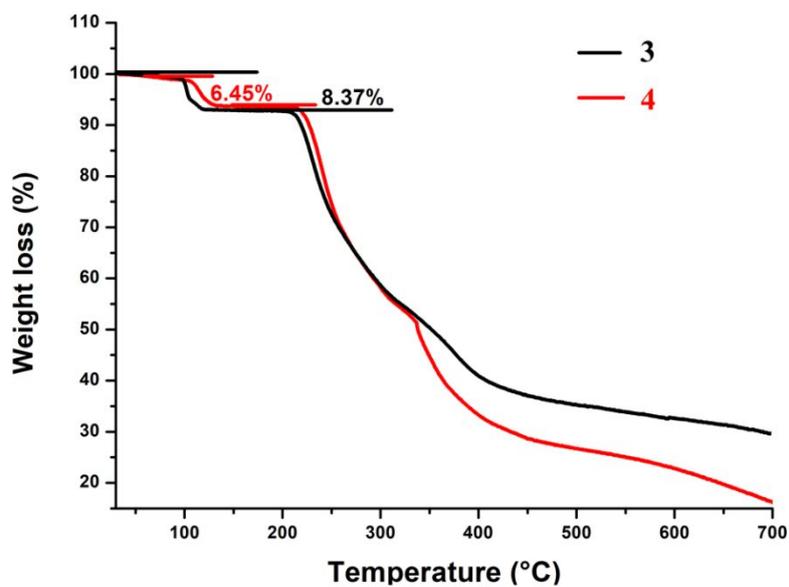


Fig. S5 TG curve of 3 and 4.

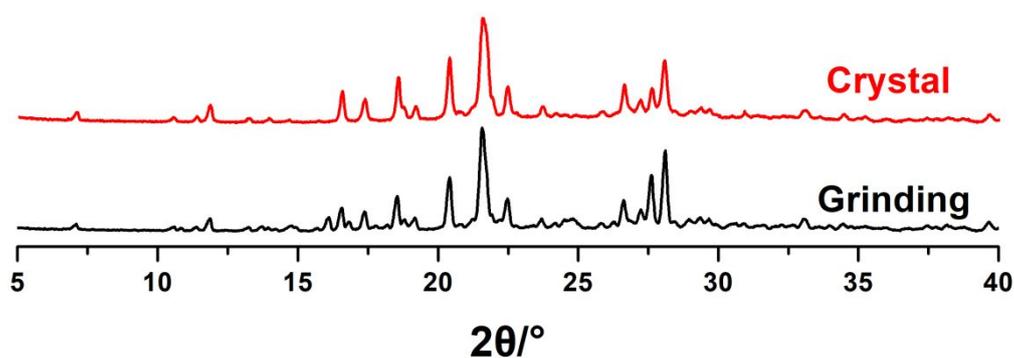


Fig. S6 Crystallization product from ethanol (red) and Grinding product (black) of 5-SSA·2H₂O and INA in 1:2 molar ratio gave rise to 5.

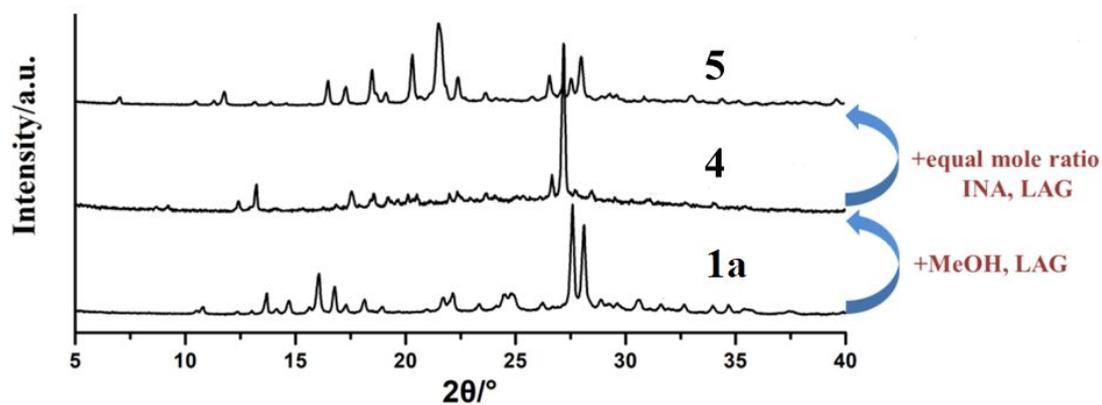


Fig. S7 Transformation of 1a, 4, and 5 in the solid state.

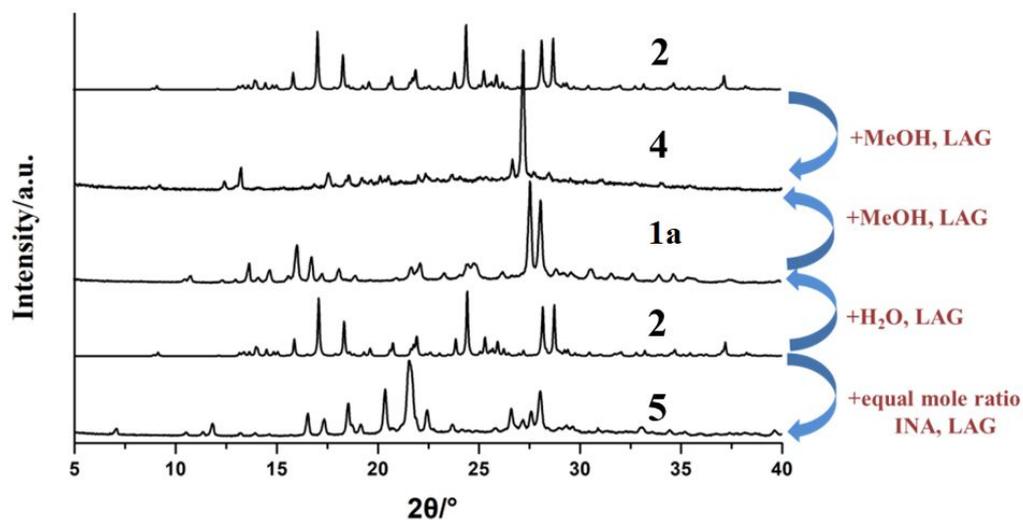


Fig. S8 Transformation of 1a, 4, 2 and 5 in the solid state.

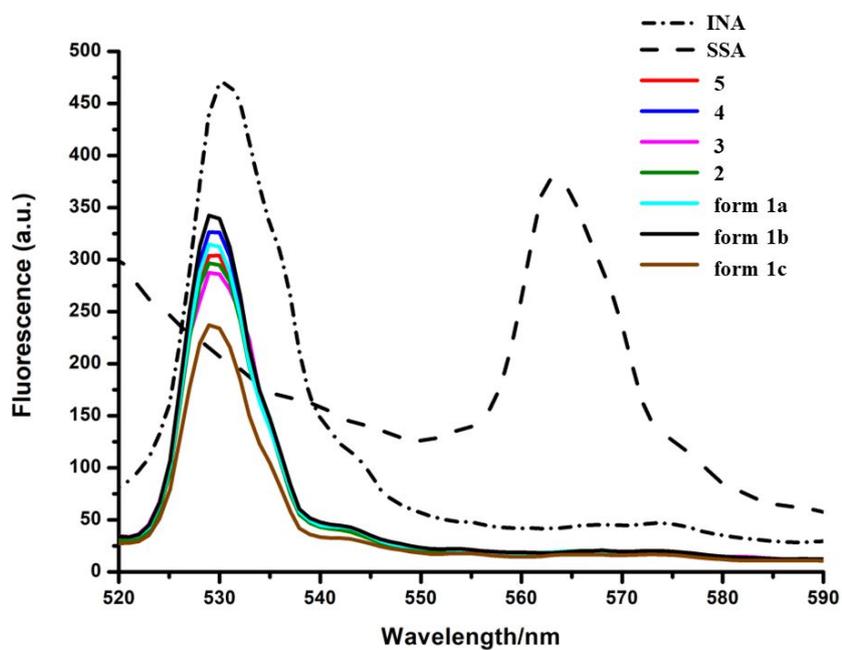


Fig. S9 Solid state fluorescence emissions of crystals.