Supporting Information

Efficient Solvent-Controlled Crystallization of Pure Polymorphs of 1-Nitro-4-(4-nitrophenylmethylthio)benzene

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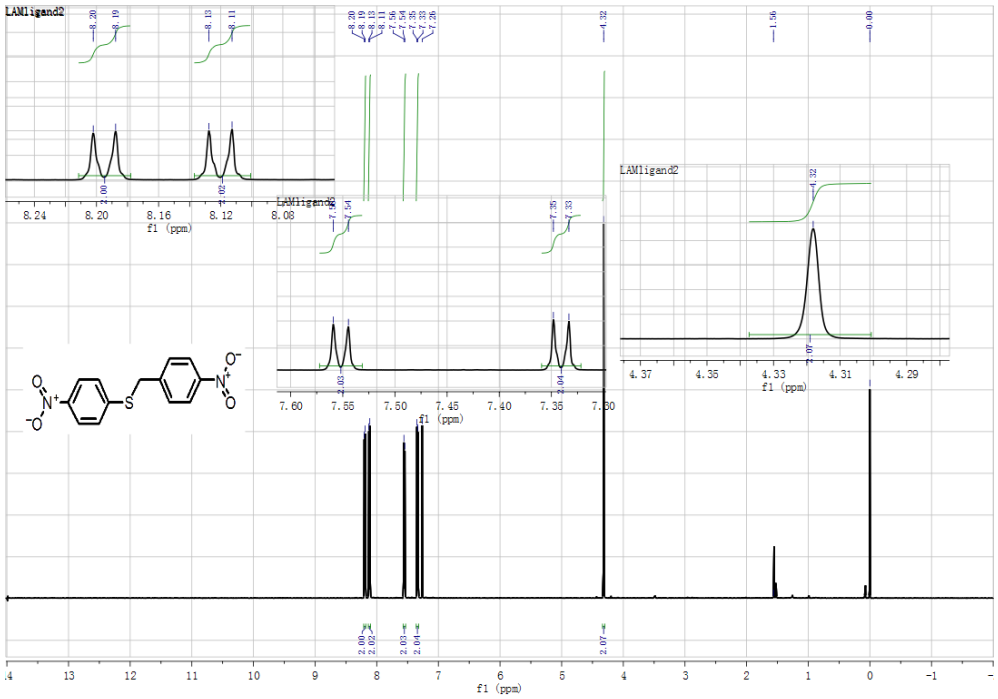


Figure S1. ^{1}H-NMR spectrum of **NNB**.

Table S1. Summary of crystallization methods for **I-IV** and the monohydrate of NNB.

Solvent	Volume ratio	Procedure	Product
H_2O (*protic polar*)	1	Cooling the hot solution to room temperature and slow evaporation the solvent	Form **I**
CH_3OH (*protic polar*)	1	As above	Form **I**
CH_3CH_2OH (*protic polar)*	1	As above	Form **I**
1-Butanol (*protic polar)*	1	As above	Form **I**
CH_2Cl_2 (*aprotic polar*)/CH_3OH (*protic polar)*	3:1	Slow evaporation of a mixed solvent at room temperature	Form **I**
CH_2Cl_2 (*aprotic polar*)/Ethyl acetate (*aprotic polar*)	3:1	As above	Form **I**
Ethyl acetate (*aprotic polar*)	1	Slow evaporation of a neat solvent at room temperature	Form **I**
Acetone (*aprotic polar*)	1	As above	Form **I**
Toluene (*non-polar*)	1	As above	Form **II**
THF (*aprotic polar*)	1	As above	Form **III**
CH_2Cl_2 (*aprotic polar*)	1	As above	Form **III**
$CHCl_3$ (*aprotic polar*)	1	As above	Form **III**
Acetonitrile (*aprotic polar*)	1	As above	Form **III**

1,4-Dioxane (*non-polar*)	1	As above	Form **III**
n-Hexane (*non-polar*)	1	Cooling the hot solution to room temperature and slow evaporation of the solvent	Form **III**
Benzene (*Nonpolar*)	1	As above	Form **III**
CH_2Cl_2 (*aprotic polar*)/Acetone (*polar aprotic*)	3:1	Dissolving NNB in the mixed solvent sealed in a Teflon-lined reactor, and heating at 80℃ for 7 days, then cooling at a rate of 10℃/h to room temperature	Form **IV**
DMF (*aprotic polar*)	1	Slow evaporation of a solution at room temperature for about three weeks	Hydrate

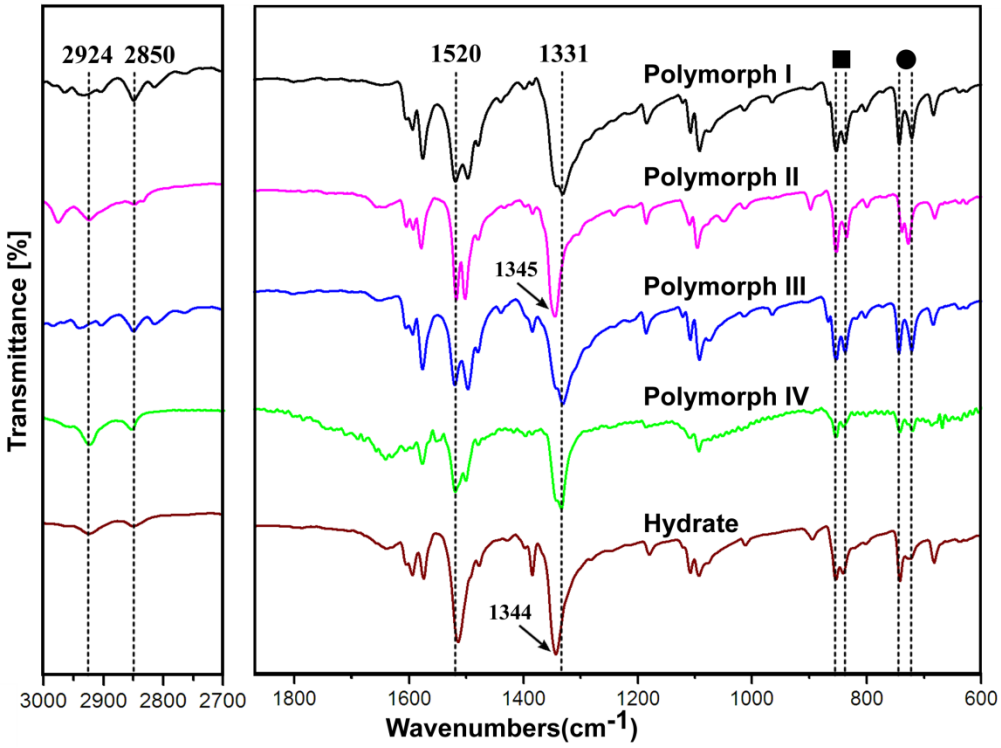
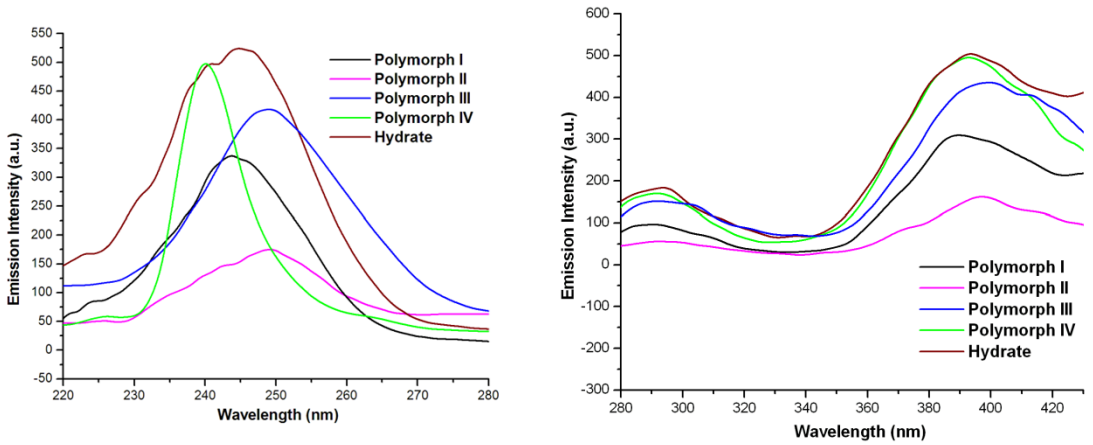


Figure S2 FT-IR spectra of **I-IV** and the monohydrate forms. ●and ■ indicate the double bands of 835~853 cm^{-1} and 721~742 cm^{-1} ranges, respectively.



(a) (b)

Figure S3 Fluorescence excitation (a) and emission spectra (b) of polymorph **I-IV** and the monohydrate.

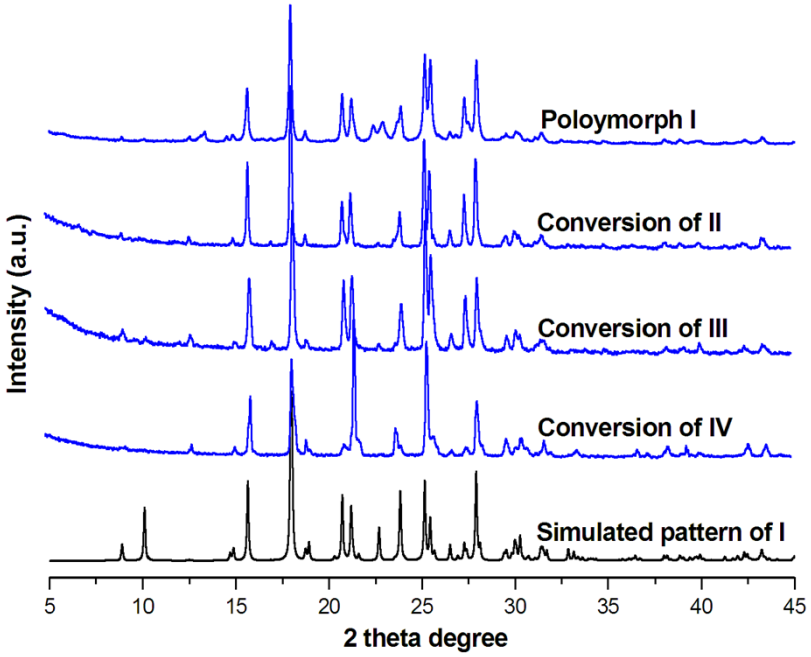


Figure S4 Powder X-ray diffraction measurements of the solid phase conversions of polymorphs **II-IV** (blue) after heated at 85°C for one day. The experimental and simulated patterns of form **I** were shown in comparison.

Table S2. Crystallographic data of polymorphs **I**–**IV** and monohydrate

Compound	**I**	**II**	**III**	**IV**	**Monohydrate**
Empirical formula	$C_{13}H_{10}N_2O_4S$	$C_{13}H_{10}N_2O_4S$	$C_{13}H_{10}N_2O_4S$	$C_{13}H_{10}N_2O_4S$	$C_{13}H_{12}N_2O_5S$
Formula weight	290.29	290.29	290.29	290.29	308.29
Crystal size	0.35×0.30×0.25	0.35×0.20×0.15	0.35×0.30×0.25	0.25×0.20×0.15	0.35×0.30×0.25
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	*P*2$_1$/*c (No. 14)*	*P*2$_1$/*c (No. 14)*	*C2/c (No. 15)*	*P-1 (No. 2)*	*P*2$_1$/*c (No. 14)*
a (Å)	6.1653(7)	4.0558(3)	24.4212(6)	13.1030(7)	3.9606(3)
b (Å)	17.4934(18)	20.4472(16)	8.3161(2)	13.8660(8)	12.1751(8)
c (Å)	12.4757(13)	16.1833(12)	13.2973(4)	15.6862(10)	31.027(2)
α (°)	90.00	90.00	90.00	81.809(4)	90.00
β (°)	104.928(7)	102.878(5)	92.341(2)	71.861(3)	93.629(3)
γ (°)	90.00	90.00	90.00	79.628(3)	90.00
V (Å^3)	1300.1(2)	1308.32(17)	2698.28(12)	2652.7(3)	1493.14(18)
Z′, *Z*	1, 4	1, 4	1, 8	4, 8	1, 4
D_{calc} (g/cm^3)	1.483	1.474	1.429	1.454	1.363
μ(Mo-Kα) (mm^{-1})	0.264	0.262	0.254	0.258	0.238
F(000)	600	600	1200	1200	632
Reflections collected	29694	9404	11775	24715	8925
Independent reflections	3098(0.0305)	2296 (0.0359)	3224(0.0303)	9332(0.1028)	2591 (0.0225)
Parameters	200	181	181	722	201
Goodness-of-fit	1.095	1.078	1.000	0.987	1.064
R_1 [$I > 2\sigma(I)$][a]	0.0788	0.0489	0.0461	0.0877	0.0576
wR_2 (all data)[b]	0.2695	0.1365	0.1494	0.2893	0.1888

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.