

**Supporting information for:**

**Role of 4-nitrobenzoic acid polymorphs in the crystallization process of the organic acid-base multicomponent system**

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**Experimental**

Table S1. Crystal data and structure refinement for 4NBH\*

Compound	4NBH*
Empirical formula	C <sub>7</sub> H <sub>5</sub> N <sub>1</sub> O <sub>4</sub>
Formula weight	167.12
T	293(2) K
Wavelength	0.71073
Crystal system	Monoclinic
Space group	C2/c
Z	8
a(Å)	21.297(6)
b(Å)	5.0396(12)
c(Å)	12.909(3)
β(°)	96.66(2)
V(Å <sup>3</sup> )	1376.2(6)
Dcalc(mg cm <sup>-3</sup> )	1.613
μ (mm <sup>-1</sup> )	0.136
F(000)	688
Reflections collected/unique	2261
Parameters	110
GOF on F <sup>2</sup>	0.994
R <sub>1</sub> , wR <sub>2</sub> [I>2σ(I)]	0.0643, 0.1140
R <sub>1</sub> , wR <sub>2</sub> (all data)	0.1447, 0.1568

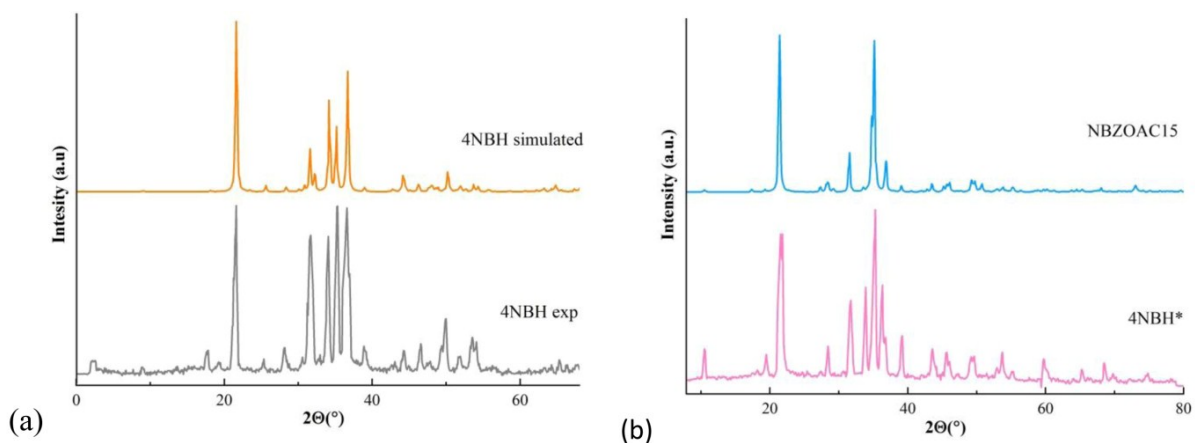


Figure S1. (a) XRPD overlay of experimental and theoretical patterns of 4NBH; (b) XRPD overlay of experimental 4NBH\* and NBZOAC-15 from CSD.

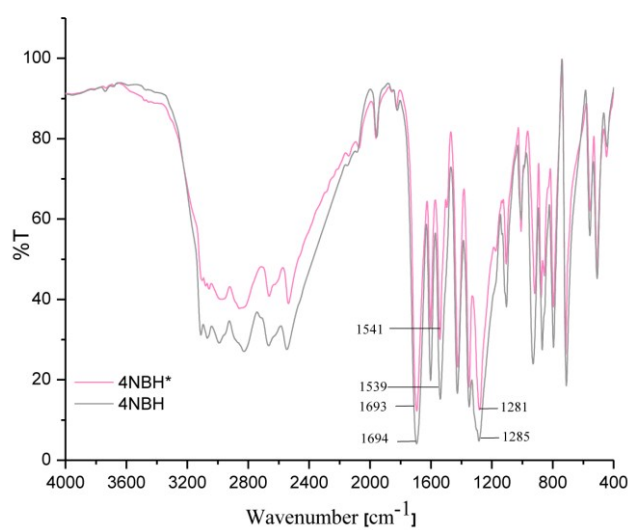


Figure S2. FTIR spectra comparison of 4NBH\* and 4NBH polymorphs

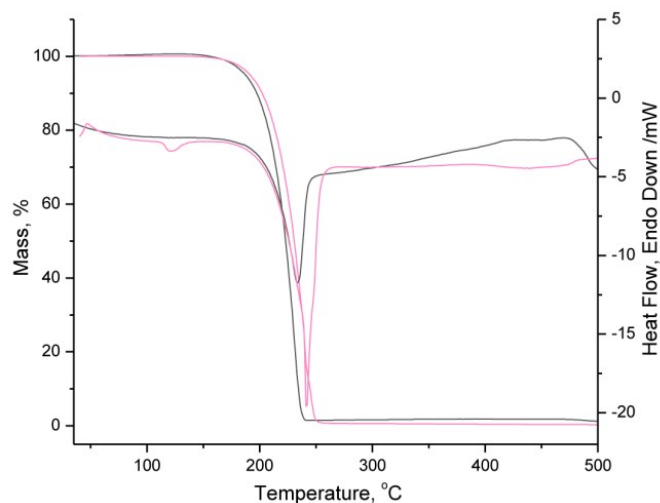


Figure S3. Thermogravimetric curves of 4NBH\* (pink) and 4NBH (grey) polymorphs

## Results and discussion

Table S2. Bond lengths [Å] and angles [°] for DMEA4NB

N(1)-C(4)	1.475(3)	C(1)-C(2)	1.517(3)
N(1)-C(1)	1.482(3)	C(5)-C(10)	1.385(3)
N(1)-C(3)	1.485(3)	C(5)-C(6)	1.391(3)
N(2)-C(8)	1.465(2)	C(5)-C(11)	1.505(3)
O(1)-C(2)	1.406(3)	C(6)-C(7)	1.377(3)
O(2)-C(11)	1.246(2)	C(7)-C(8)	1.378(3)
O(3)-C(11)	1.250(2)	C(8)-C(9)	1.382(3)
O(4)-N(2)	1.222(2)	C(9)-C(10)	1.379(3)
O(5)-N(2)	1.225(2)		
C(4)-N(1)-C(1)	112.90(19)	C(6)-C(5)-C(11)	120.09(16)
C(4)-N(1)-C(3)	109.2(2)	C(7)-C(6)-C(5)	121.11(17)
C(1)-N(1)-C(3)	111.11(18)	C(6)-C(7)-C(8)	118.37(17)
O(4)-N(2)-O(5)	123.02(17)	C(7)-C(8)-C(9)	122.22(17)
O(4)-N(2)-C(8)	118.56(17)	C(7)-C(8)-N(2)	118.58(16)
O(5)-N(2)-C(8)	118.41(16)	C(9)-C(8)-N(2)	119.20(17)
N(1)-C(1)-C(2)	113.12(19)	C(10)-C(9)-C(8)	118.29(17)
O(1)-C(2)-C(1)	112.2(2)	C(9)-C(10)-C(5)	121.13(17)
C(10)-C(5)-C(6)	118.87(17)	O(2)-C(11)-O(3)	124.99(19)
C(10)-C(5)-C(11)	121.02(16)	O(2)-C(11)-C(5)	117.59(17)
		O(3)-C(11)-C(5)	117.42(17)

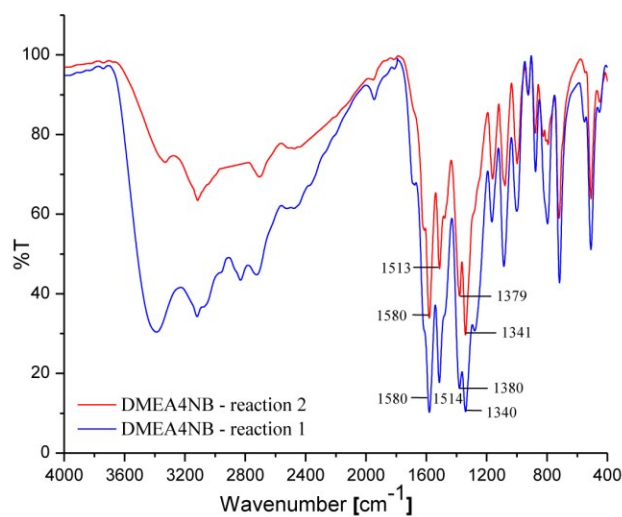


Figure S4. FT-IR spectra of DMEA4NB single crystals (reactions 1 and 2).

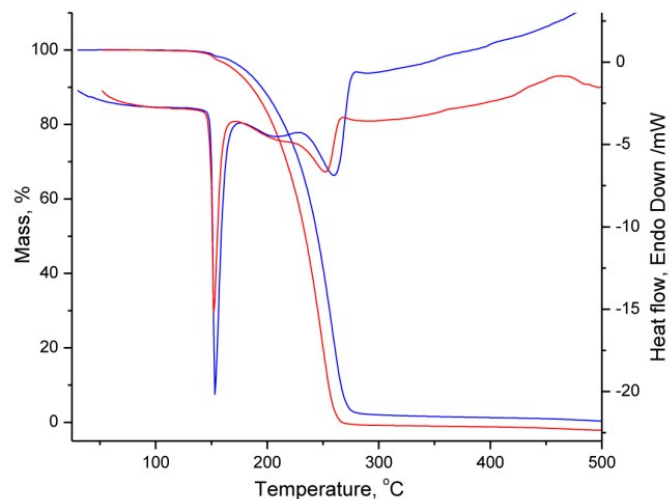


Figure S5. Thermogravimetric curves (TG and heat flow) of DMEA4NB single crystals (reactions 1- blue and reaction 2 - red) at a heating rate of  $10\text{ }^{\circ}\text{C min}^{-1}$ , in the air.

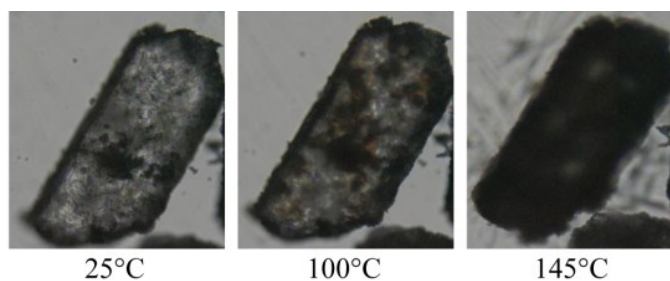


Figure S6. Optical micrographs of DMEA4NB collected at different heating temperatures.