Electronic Supplementary Material (ESI) for CrystEngComm
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Supporting information for

# Improved solid-state stability of salts by cocrystallization between conjugate acid – base pairs

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## S1. EXPERIMENTAL SECTION

### S1(a). Materials

Benzoic acid (99.5 % purity), sodium benzoate (99 % purity), potassium benzoate (99 % purity), and ammonium benzoate (98 % purity) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Phenoxy acetic acid (98 % purity) was purchased from TCI America (Portland, OR, USA). All chemicals were used as received without further purification.

In the presence of equal or excessive amount of strong base, most acid molecules in solution deprotonate. Consequently, the usual salt crystallizes out. For a CAB cocrystal to grow there should be sufficient amount of both components of the CAB in crystallization medium. This condition can be achieved by starting a crystallization experiment using the two CAB components instead of adding strong base solutions to the solution of the acid. Either monosalt or CAB cocrystals were prepared accordingly in this work when they are not commercially available to us. Sodium 2-phenoxyacetate was synthesized by reacting equimolar amount of 2-phenoxy acetic acid and sodium bicarbonate in aqueous solution, followed by slow evaporation of solvent. Ammonium hydrogen bis(benzoate), sodium dihydrogen tris(benzoate), potassium hydrogen bis(benzoate) and sodium hydrogen bis(2-phenoxyacetate) were synthesized by cocrystallizing acid and its salt at equi-molar concentration from water by slow evaporation for single crystals and slurry for bulk powders.

Single crystal structures of ammonium benzoate, ammonium hydrogen bis(benzoate), sodium dihydrogen tris(benzoate) and potassium hydrogen bis(benzoate)

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were determined at 173 K using single crystal X-ray diffraction (CDCC numbers 918822 - 918825). Powder X-ray diffraction (PXRD) was also used to confirm phase identification of prepared powders (see Figures S4 to S10).

**S1(b). Methods**

**Water Sorption and Desorption**

Water sorption and desorption profiles of the materials at 25 $^{o}$C were obtained by using an automated vapor sorption analyzer (DVS 1000, Surface Measurement Systems Ltd., Alperton, Middlesex, UK). The nitrogen flow rate was 15 mL/min. The sample was equilibrated at each step with the equilibration criteria of either rate of mass change (dm/dt) $\leq$ 0.0001 or maximum equilibration time of 2 hr. Once one of the criteria was met, the RH was changed to the next target value at either 3% or 5% RH step size.

**X-Ray Diffraction**

Powder X-ray diffraction (PXRD) patterns were obtained on a wide-angle diffractometer (D5005, Brucker AXS) using CuK$\alpha$ radiation (45 kV and 40 mA). Each pattern was collected with a step size of 0.02$^{o}$ in the two theta range of 5-35$^{o}$ and a dwell time of 0.5 sec. PXRD data analyses were performed using JADE software (Materials Data Inc., Livermore, CA).

Single crystal X-ray diffraction (SCXD) was carried out on a Bruker Apex CCD area detector diffractometer for data collec-tion using MoK$\alpha$ radiation (graphite monochromator)[1] at 173 K. The SAINT program was used for data processing. The structure was solved using Bruker SHELXTL and refined us-ing Bruker SHELXTL.[2] A direct-methods solution was calcu-lated, which provided most non-hydrogen atoms from

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the E-map. Full-matrix least squares/difference Fourier cycles were performed, which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic dis-placement parameters. All hydrogen atoms were located from the difference Fourier map and allowed to ride on their parent atoms in the refinement cycles.

**Thermogravimetric Analysis (TGA)**

In a thermogravimetric analyzer (Model Q50 TGA, TA In-struments, New Castle, DE), ~ 3 mg of sample was heated in an open aluminum pan from RT to 200 at 10 $^{o}$C/min under dry nitrogen purge (75 mL/min). The TGA data were analyzed using commercial software (Universal Analysis 2000, TA Instruments, New Castle, DE).

**Differential Scanning Calorimetry (DSC)**

A differential scanning calorimeter (DSC, Q1000, TA Instruments, New Castle, DE) equipped with a refrigerated cooling system was used to record thermograms of crystals at a heating rate of 10 $^{o}$C/min. The DSC cell was purged with nitrogen at a rate of 50 mL/min.

**Microscopy**

Crystals were observed under a polarized light microscopy (Nikon Eclipse e200, Japan) equipped with a DS-Fi1 microscope digital camera for capturing digital images. Hot-stage microscopy (HSM) experiment was performed, with a heating rate of 5 $^{o}$C/min, on a Linkam hot stage with heating controller (Linksys 32, V. 2.2.0, Linkam Scientific Instruments, Ltd., Waterfield, UK) mounted on the microscope.

Dinolite digital microscope (AnMo Electronics Corporation, Hsinchu 300, Taiwan) was used to record the deliquescence behaviour of powders.

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**Table S1.** Crystallographic details for all the **1, 2, 4** and **6** complexes.

| | **1** | **2** | **4** | **6** |
|---|---|---|---|---|
| CCDC deposition number | **918823** | **918824** | **918825** | **918822** |
| Empirical formula | $C_7H_9N_1O_2$ | $C_{14}H_{15}N_1O_4$ | $C_{21}H_{17}Na_1O_6$ | $C_{14}H_{11}K_1O_4$ |
| Formula wt. | 139.15 | 261.27 | 388.34 | 282.33 |
| Crystal system | Orthorhombic | Monoclinic | Monoclinic | Monoclinic |
| Space group | Pbca | C2/c | P21/c | C2/c |
| $a$ [Å] | 6.8750(11) | 29.234(10) | 5.8207(11) | 29.585(13) |
| $b$ [Å] | 6.9872(11) | 3.8543(13) | 14.460(3) | 3.8211(18) |
| $c$ [Å] | 30.188(5) | 11.408(4) | 22.090(4) | 11.156(5) |
| $\alpha$ [deg] | 90 | 90 | 90 | 90 |
| $\beta$ [deg] | 90 | 94.455(5) | 97.084(3) | 97.327(5) |
| $\gamma$ [deg] | 90 | 90 | 90 | 90 |
| $Z$ | 8 | 4 | 4 | 4 |
| Volume [Å$^3$] | 1450.2(4) | 1281.5(8) | 1845.0(6) | 1250.8(10) |
| $D_{calc}$ [g/cm$^3$] | 1.275 | 1.354 | 1.398 | 1.499 |
| $F$ (000) | 592 | 552 | 808 | 584 |
| $\mu$ [mm$^{-1}$] | 0.094 | 0.100 | 0.122 | 0.431 |
| $2\theta_{max.}$ | 25.04 | 25.05 | 25.08 | 25.07 |
| Range h | -8<=h<=8 | -34<=h<=34 | -6<=h<=6 | -34<=h<=34 |
| Range k | -8<=k<=8 | -4<=k<=4 | -17<=k<=17 | -4<=k<=4 |
| Range l | -35<=l<=35 | -13<=l<=13 | -26<=l<=26 | -13<=l<=13 |
| N-total | 12652 | 5543 | 17738 | 5513 |
| N-independent | 1288 | 1143 | 3266 | 1112 |
| N-observed | 1076 | 841 | 2511 | 992 |
| $R_1$ [I>2σ(I)] | 0.0428 | 0.0616 | 0.0437 | 0.0494 |
| $wR_2$ | 0.0916 | 0.1545 | 0.1159 | 0.1357 |
| GOF | 1.094 | 1.080 | 1.031 | 1.122 |

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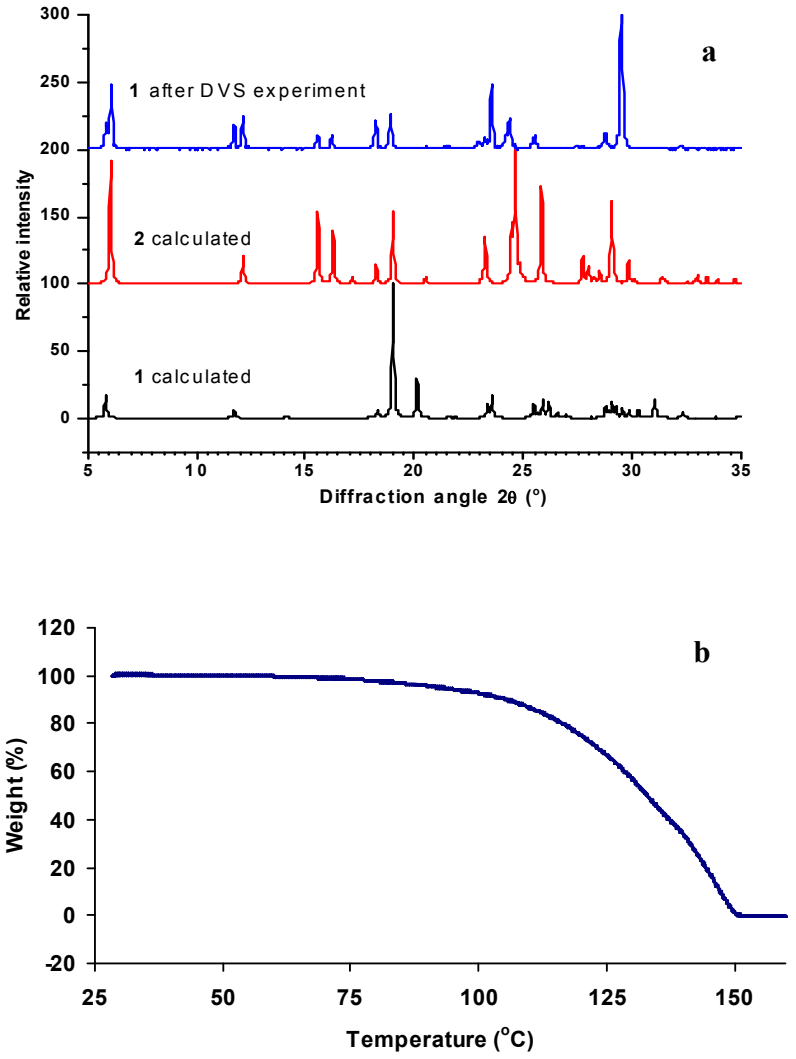


**Figure S1.** (a) PXRD patterns of **1** calculated, **2** calculated, and **1** after DVS experiment; (b) TGA thermogram of **1**.

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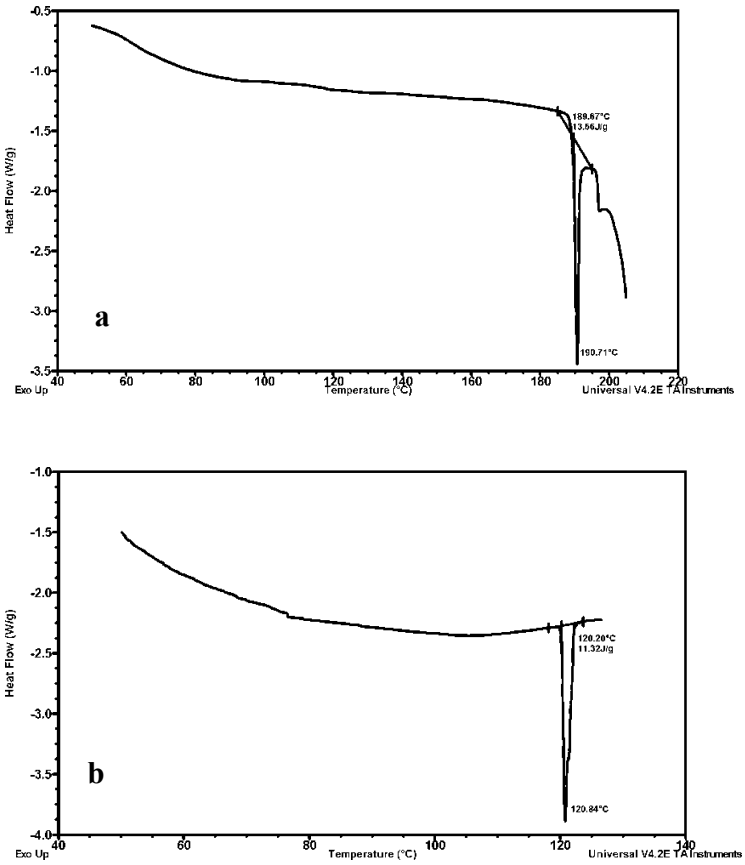


**Figure S2.** DSC thermograms of **1** and **2** in hermetically sealed pans. a) ammonia gas released during the initial degradation of **1** leads to an elevated pressure, under which **1** is physically stable. The endotherm at 191 $^{o}$C accompanied by degradation is attributed to the melting of **1** under elevated atmospheric pressure. b) initial sublimation of **2** leads to an elevated pressure, under which a melting event at 121 $^{o}$C is observed.

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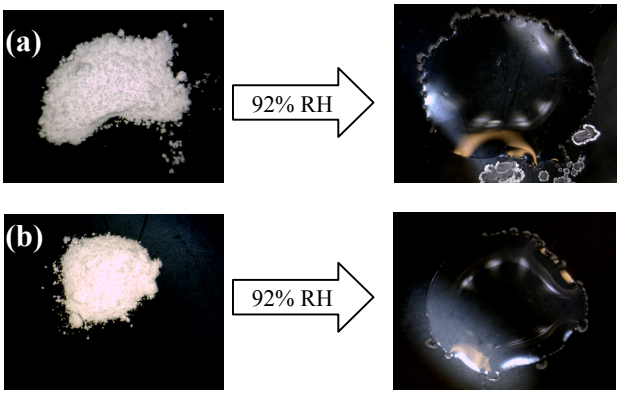


**Figure S3.** Deliquescence of a) sodium benzoate (mono salt), **3**, and b) potassium benzoate (mono salt), **5**, at 92 % RH.

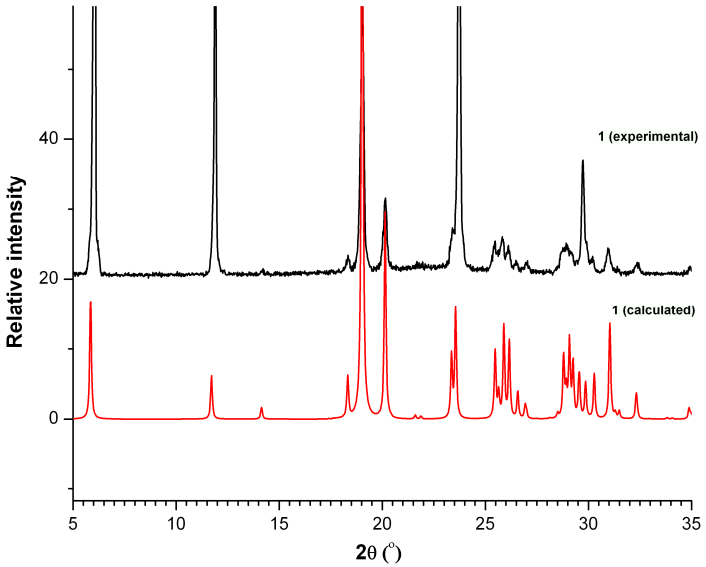


**Figure S4.** Comparison of experimental and calculated powder patterns of Ammonium benzoate, **1**.

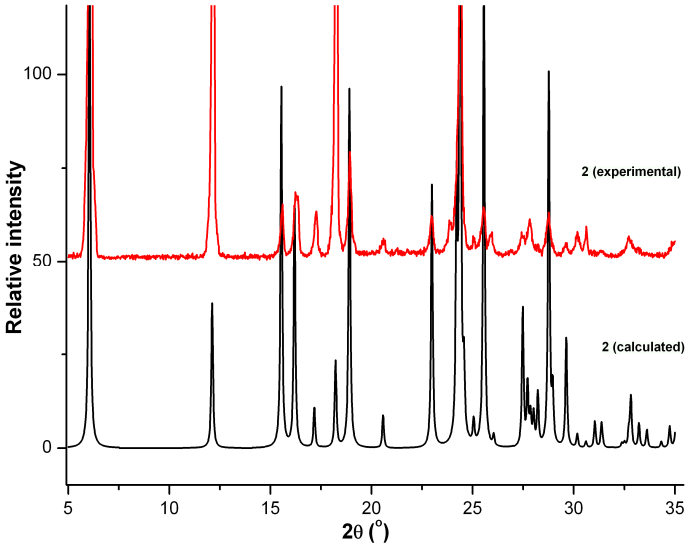


**Figure S5.** Comparison of experimental and calculated powder patterns of ammonium hydrogen bis (benzoate), **2**.

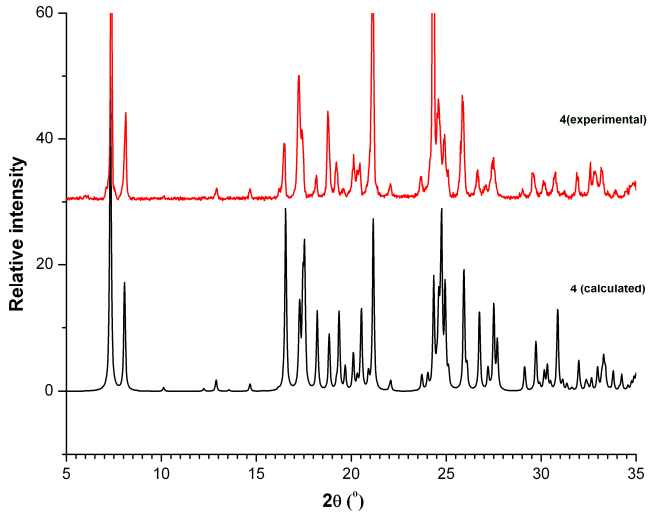


**Figure S6.** Comparison of experimental and calculated powder patterns of sodium dihydrogen tris (benzoate), **4**.

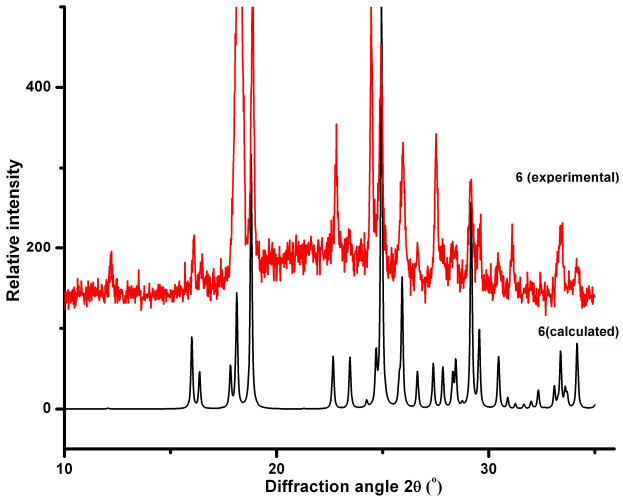


**Figure S7.** Comparison of experimental and calculated powder patterns of potassium hydrogen bis (benzoate), **6**.

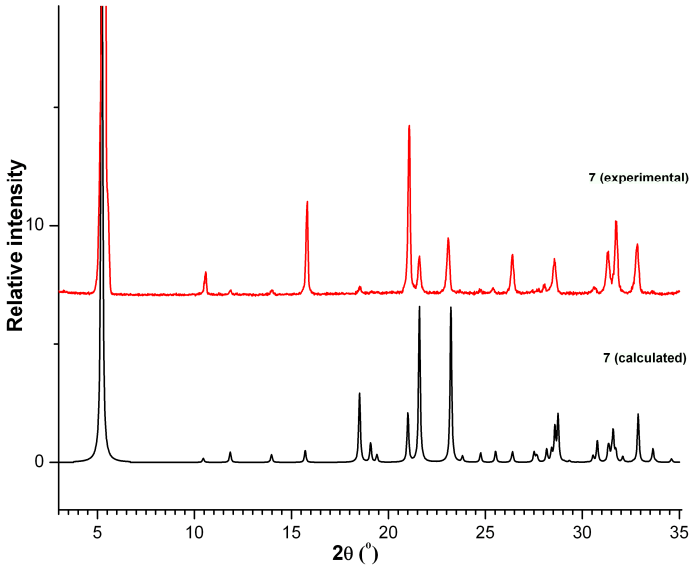


**Figure S8.** Comparison of experimental and calculated powder patterns of sodium phenoxy acetate hemihydrate, **7**.

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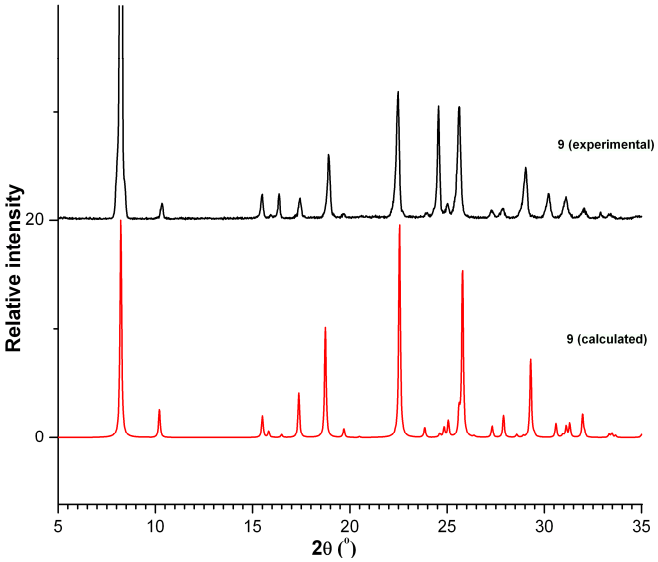


**Figure S9.** Comparison of experimental and calculated powder patterns of sodium hydrogen bis(phenoxy acetate), **9**.

## References

1. Bruker (2007). APEX, SADABS and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.
2. G. Sheldrick, *Acta Cryst*, 2008, **A64**, 112-122.