Mechanochemical Synthesis of Pyrazine:Dicarboxylic Acid Cocrystals and the study of their Dissociation by Quantitative Phase Analysis

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Supplementary Information
Table S1. Theoretical and experimental weight loss determined by TGA of the pyrazine cocrystals.

<table>
<thead>
<tr>
<th>Cocrystal</th>
<th>Weight loss (experimental) / %</th>
<th>Weight loss (theoretical) / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>pyrazine:terephthalic</td>
<td>30.0</td>
<td>32.5</td>
</tr>
<tr>
<td>pyrazine:phthalic</td>
<td>31.4</td>
<td>32.5</td>
</tr>
<tr>
<td>pyrazine:succinic</td>
<td>40.0</td>
<td>40.4</td>
</tr>
<tr>
<td>pyrazine:fumaric</td>
<td>39.6</td>
<td>40.8</td>
</tr>
</tbody>
</table>

Figure S1. Close contact between atoms H10 and O1 (x, 3/2-y, ½+z) in the pyr:pht crystal structure.
Figure S2. Molecular arrangements of the pyr:fum crystal faces. Faces (001) and (100) display hydrophilic character while faces (011) and (102) are mostly hydrophobic.

Figure S3. Molecular arrangements of the pyr:succ crystal faces. Faces (101) and (002) are hydrophilic.
Figure S4. Molecular arrangements of the pyr:ter crystal faces. (001) face is hydrophilic while (011) and (10\(\bar{1}\)) faces are mostly hydrophobic.

Figure S5. TGA of pyrazine:terephthalic acid cocrystal
Figure S6. TGA of pyrazine:phthalic acid cocrystal

Figure S7. TGA of pyrazine:fumaric acid cocrystal
Figure S8. TGA of pyrazine:succinic acid cocrystal

Figure S9. DSC of pyrazine:terephthalic acid cocrystal
Figure S10. DSC of pyrazine:phthalic acid cocrystal

Figure S11. DSC of pyrazine:fumaric acid cocrystal
Figure S12. DSC of pyrazine:succinic acid cocrystal

Figure S13. IR spectrum of pyrazine:terephthalic acid cocrystal
Figure S14. IR spectrum of pyrazine: phthalic acid cocrystal

Figure S15. IR spectrum of pyrazine:fumaric acid cocrystal
Figure S16. IR spectrum of pyrazine:succinic acid cocrystal

Figure S17. PXRD pattern of pyrazine:terephthalic acid cocrystal
Figure S18. Rietveld refinement of the pyrazine:terephthalic acid cocrystal. The blue outline shows the experimentally observed diffracted pattern, the red curve shows the Rietveld fit and the grey outline marks the difference between the calculated fit and the experimental pattern. Quantitative phase analysis suggests the presence of 3% of terephthalic acid form II (refcode TEPTH12) impurity.

Figure S19. PXRD pattern of pyrazine: phthalic acid cocrystal
Figure S20. Rietveld refinement of the pyrazine:phthalic acid cocrystal.

Figure S21. PXRD pattern of pyrazine:fumaric acid cocrystal
Figure S22. PXRD pattern of pyrazine:succinic acid cocrystal

Figure S23. Example of Rietveld refinement of a PXRD pattern recorded on a sample of pyrazine:phthalic acid cocrystal recorded during the kinetics measurement. Refinement of the scale factors of mixture components allows to calculate their corresponding mass fractions (shown in the top right corner).
Figure S24. X-ray powder patterns showing the conversion of pyr:pht cocrystal into phthalic acid. The patterns were recorded at 25°C temperature and room humidity. The most prominent peaks corresponding to the cocrystal are at 2θ 14.5°, 19.6°, 25.3° and 29.9°. The major peaks corresponding to phthalic acid are at 2θ 15.1°, 18.2°, 26.6° and 30.2°.

Figure S25. Arrhenius plot describing the dependence of pyr:pht cocrystal dissociation rate on temperature