

Supporting Information

## Synthesis, structure determination, and formation of a theobromine:oxalic acid 2:1 cocrystal

Franziska Fischer<sup>a,b</sup>, Gudrun Scholz<sup>b</sup>, Lisa Batzdorf<sup>a,b</sup>, Manuel Wilke<sup>a,b</sup>, Franziska Emmerling<sup>a,\*</sup>

<sup>a</sup> BAM Federal Institute for Materials Research and Testing, Richard-Willstaetter-Strasse 11, 12489 Berlin, Germany. Fax:030/8104-1139; Tel:030/8104-1133

<sup>b</sup> Department of Chemistry, Humboldt-Universität zu Berlin, Brook-Taylor-Str. 2, 12489 Berlin, Germany.

E-mail\*: franziska.emmerling@bam.de

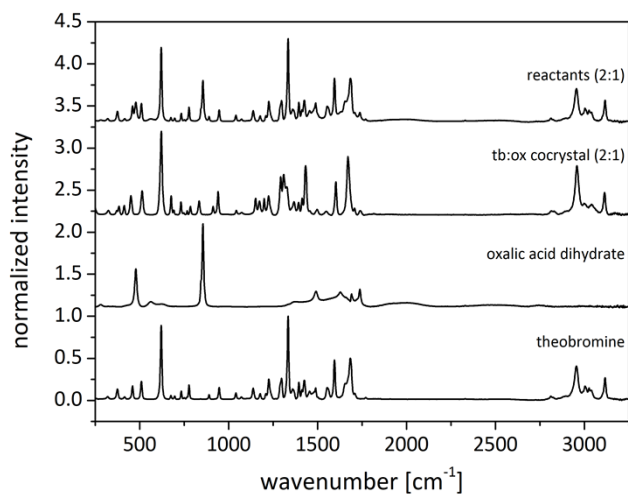


Fig. S1 Raman spectra of the tb:ox cocrystal, tb, ox dehydrate, and the Raman spectra of the mixed reactants in a 2:1 ratio.

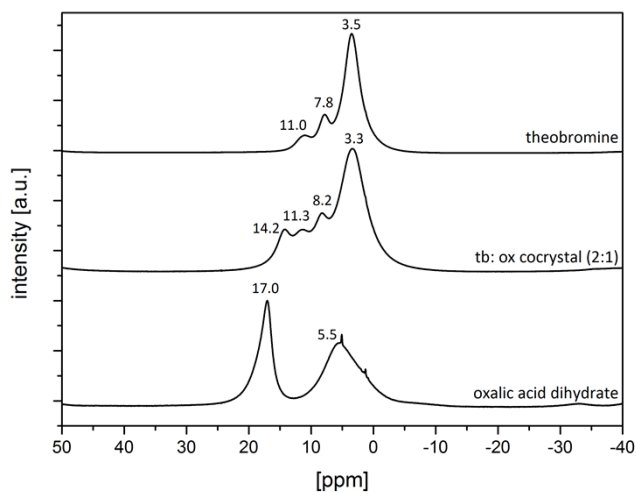
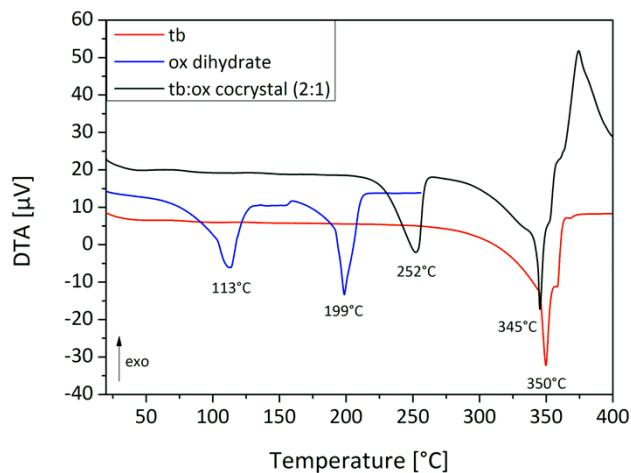
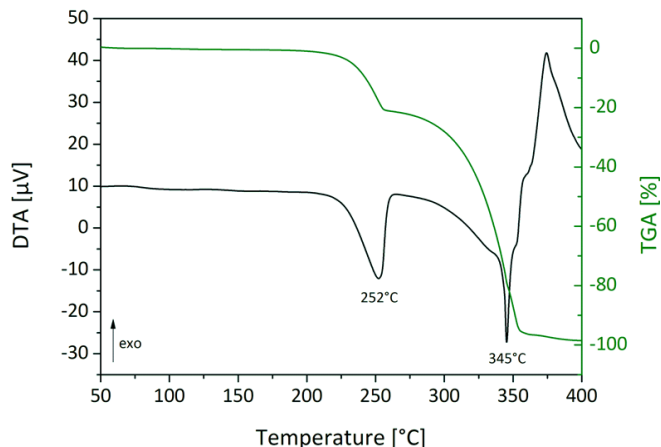


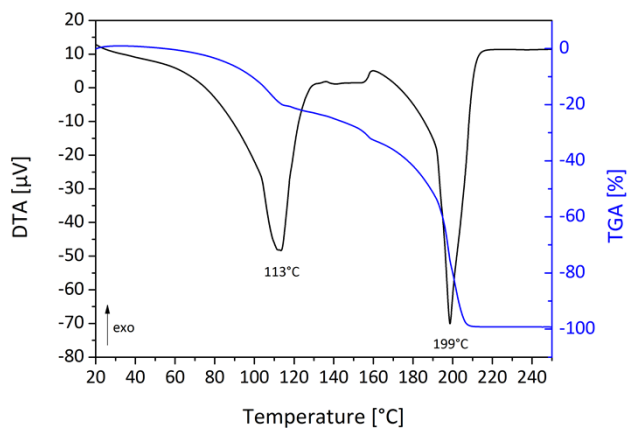
Fig. S2 <sup>1</sup>H MAS NMR spectra of the tb:ox cocrystal (center), tb (top) and ox dihydrate (bottom) without the spinning sidebands.



**Fig. S3** DTA measurements of the tb:ox cocystal (black), tb (red) and ox dihydrate (blue) (the DTA curves are shown with an offset): Pure ox dihydrate shows the first signal at 113 °C. The TGA measurement reveals that the mass of the ox dihydrate decreases at this temperature (Figure S5). It can be assumed that the melting point of the sample is in this temperature range and that the water molecules in the crystal structure are released.<sup>47</sup> The second DTA signal of ox at 199 °C refers to the complete decomposition of the ox molecules. Tb shows one DTA signal at 350 °C, evoked by the decomposition of the tb molecules (Figure S6).



**Fig. S4** DTA-TGA measurements of the tb:ox cocystal: The first DTA signal of the cocystal arises at a temperature of 252 °C. At this temperature, a mass loss of approximately 20% can be observed in the TGA measurements, which corresponds to the content of ox in the cocystal (Figure 6, right). Since the MS signals show the composition products of ox: water and carbon dioxide at that temperature (Figure S7), a decomposition of all ox molecules at 252 °C can be deduced. The second DTA signal of the cocystal is related to the decomposition of tb.



**Fig. S5** DTA-TGA measurements of oxalic acid dihydrate.

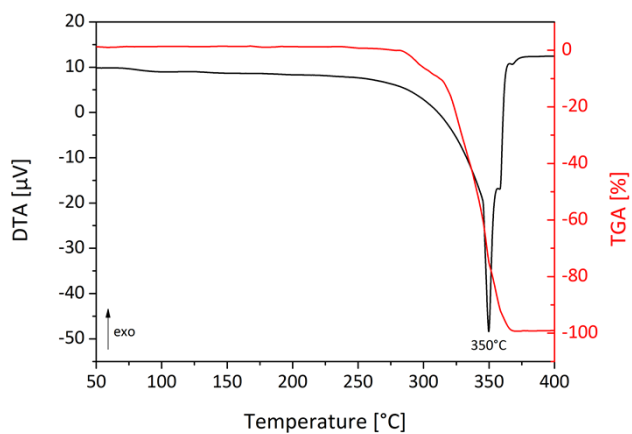


Fig. S6 DTA-TGA measurements of theobromine.

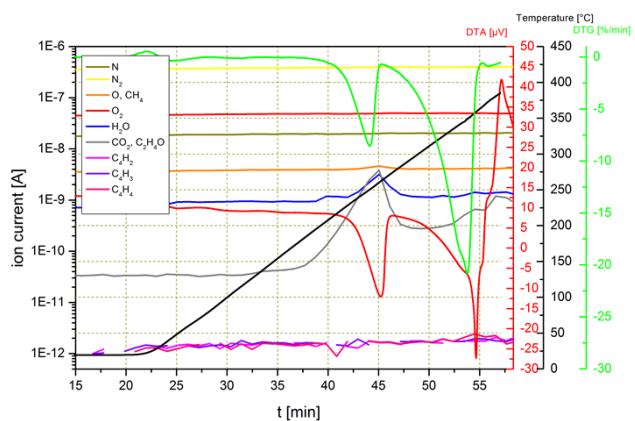


Fig. S7 Mass spectrometric measurements of the theobromine:oxalic acid cocrystal during the DTA-TGA investigations.

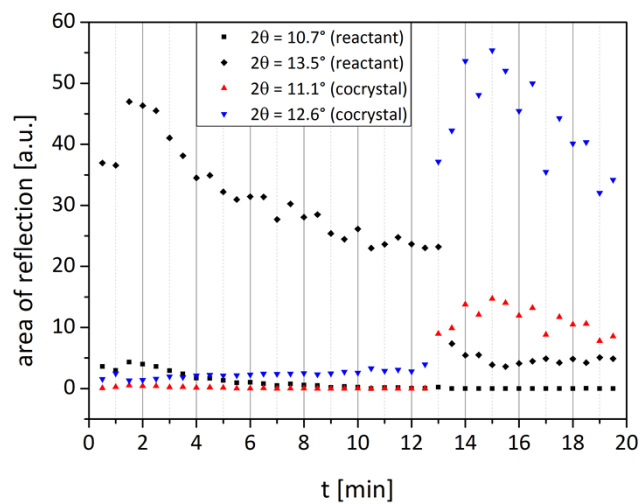


Fig. S8 Integrated areas of reflections of the reactants and the cocrystal during the milling synthesis process.