Comparison of mechanochemical methods in the synthesis of Binaphtol-Benzoquinone based cocrystals

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Supplementary information

\textbf{Figure S1}. A: Retsch Ball Mill model #MM301. B: LabRAM II. The blue arrows indicate the direction of motion of the mixing vessels.
Figure S2: Stereo view of the molecular packing of Cocrystal I. The rBN molecules are represented as wireframes while the BQ molecule is represented using a ball and stick model. The blue lines indicate hydrogen bonds. Cocrystal I crystallizes in a monoclinic space group C2/c and has a 1:1.5 mole ratio of rBN:BQ. The BQ molecules are sandwiched between R- and S-BN molecules. The view was modeled using Mercury® (version 4.2) software based on crystal structure determined by Kuroda et al.\textsuperscript{1}
Figure S3: DSC thermograms of Benzoquinone (BQ), Racemic bi-Naphtol (rBN), Cocrystal II (1:1), and Cocrystal I (1:1.5). A: Melting endotherm of BQ, onset temperature = 112.5 °C and Heat of fusion = 163.2 J/g, B: Melting endotherm of BQ, onset temperature = 218.5 °C and Heat of fusion = 118 J/g, C: Melting endotherm of Cocrystal II, onset temperature = 99.7 °C and Heat of fusion = 58.9 J/g, D: Minor endotherm associated with the melting of residual rBN (onset and heat of fusion values not reported due to baseline interference), E: Melting endotherm of Cocrystal I, onset temperature = 108.6 °C and Heat of fusion = 68.2 J/g, F: Endotherm associated with the melting of residual rBN, onset temperature = 217.4 °C and Heat of fusion = 82.1 J/g.
Figure S4. XRPD data of rBN/BQ samples subjected to RAM. A: Physical mixture of rBN and BQ, B: 1:1 rBN:BQ RAM at 75 Hz for 90 minutes, C: 1:1.5 rBN:BQ RAM at 75 Hz for 90 minutes, D: 1:2.5 rBN:BQ RAM at 90 Hz for 180 minutes, and E: 1:2.5 rBN:BQ RAM at 90 Hz for 540 minutes.

Figure S5. Color of samples of rBn/BQ at a 1:2.5 mole ratio after being subjected to RAM at 75 Hz for time periods ranging from 150 to 450 minutes.
Figure S6. XRPD data of rBN/BQ at a 1:1.5 mole ratio samples subjected to BM with steel balls and ZrO₂ balls shown in comparison with the calculated powder data for Cocrystal I.
Figure S7. XRPD data of rBN/BQ at a 1:2 mole ratio samples subjected to BM shown in comparison with the calculated powder data for Cocrystal I.
Figure S8: Stereo view of the molecular packing of Cocrystal II. The rBN molecules are represented as wireframes while the BQ molecule is represented using a ball and stick model. Cocrystal II crystallizes in a triclinic space group P1 with a mole ratio of 1:1 mole ratio of rBN:BQ. The BQ molecules are sandwiched between homochiral BN molecules. The view was modeled using Mercury® (version 4.2) software based on crystal structure determined by Kuroda et al.¹
Figure S9. XRPD data of rBN/BQ at a 1:1 mole ratio samples subjected to RAM in the presence of liquid additives at a $\eta$ of 0.5 shown in comparison with the calculated powder data for Cocrystal II.
**Figure S10:** DSC thermograms of Benzoquinone (BQ), Racemic bi-Naphtol (rBN), Naphthalene (NP), and the ternary cocrystal rBNBQNP (2:1:2). **A:** Melting endotherm of BQ, onset temperature = 112.5 °C and Heat of fusion = 163.2 J/g, **B:** Melting endotherm of BQ, onset temperature = 218.5 °C and Heat of fusion = 118. J/g, **C:** Melting endotherm of NP, onset temperature = 80.1 °C and Heat of fusion = 136.3 J/g, **D:** Melting endotherm of ternary cocrystal, onset temperature = 78.6 °C and Heat of fusion = 31.5 J/g, **E:** Endotherm associated with the melting of residual rBN, onset temperature = 217.3 °C and Heat of fusion = 32.9 J/g.
Figure S11: DSC thermograms of Benzoquinone (BQ), Racemic bi-Naphtol (rBN), Naphthalene (NP), and the ternary cocrystal rBNBQAN (2:2:1). A: Melting endotherm of BQ, onset temperature = 112.5 °C and Heat of fusion = 163.2 J/g, B: Melting endotherm of BQ, onset temperature = 218.5 °C and Heat of fusion = 118. J/g, C: Melting endotherm of AN, onset temperature = 216.0 °C and Heat of fusion = 185.5 J/g, D: Melting endotherm of ternary cocrystal, onset temperature = 120.0 °C (Heat of fusion could not be calculated due to interference from exotherm E), E: Exotherm likely associated crystallization of a new phase, peak temperature = 132.4 °C (heat associated with the exotherm could not be calculated due to interference from endotherm E), and F: Endotherm likely associated with the melting of the new phase produced by crystallization event E, onset temperature = 178.6 °C and Heat of fusion = 111.6 J/g.
References