Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

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

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Supplementary information

A

B

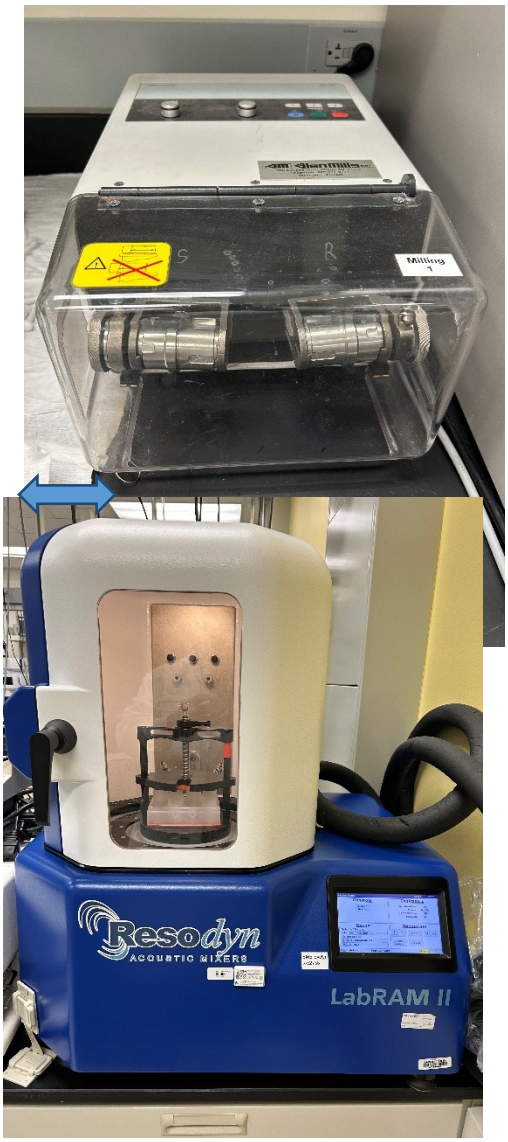

Figure S1. **A**: Retsch Ball Mill model #MM301. **B**: LabRAM II. The blue arrows indicate the direction of motion of the mixing vessels.

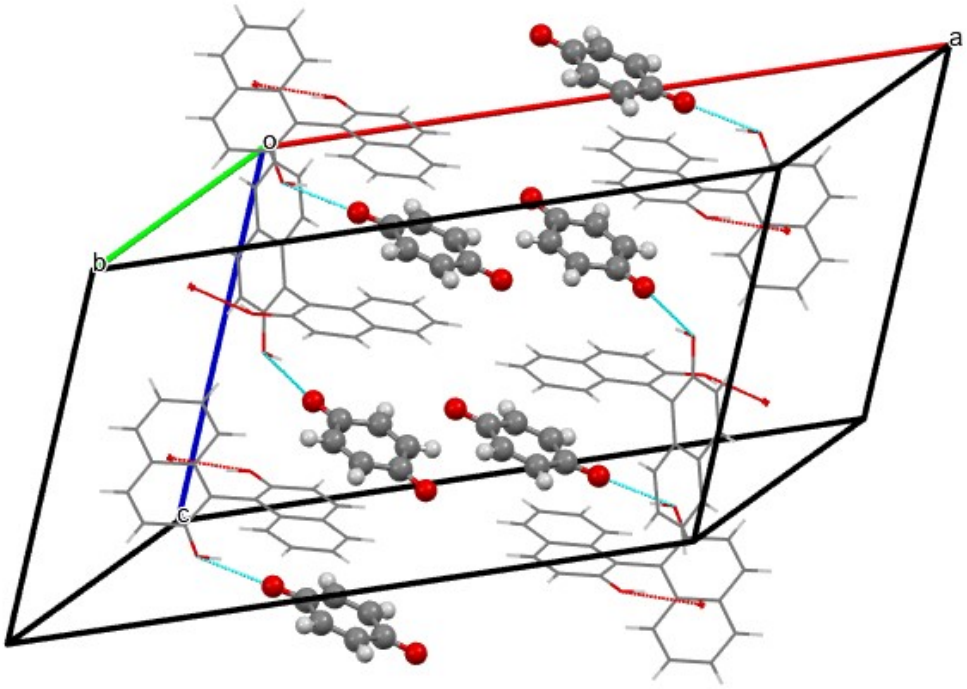

Figure S2: Stereo view of the molecular packing of Cocrystal I. The rBN molecules are represented as wireframes while the BQ molecule is represented using a ball and stick model. The blue lines indicate hydrogen bonds. **C**ocrystal **I** crystallizes in a monoclinic space group C2/*c* and has a 1: 1.5 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.[1]

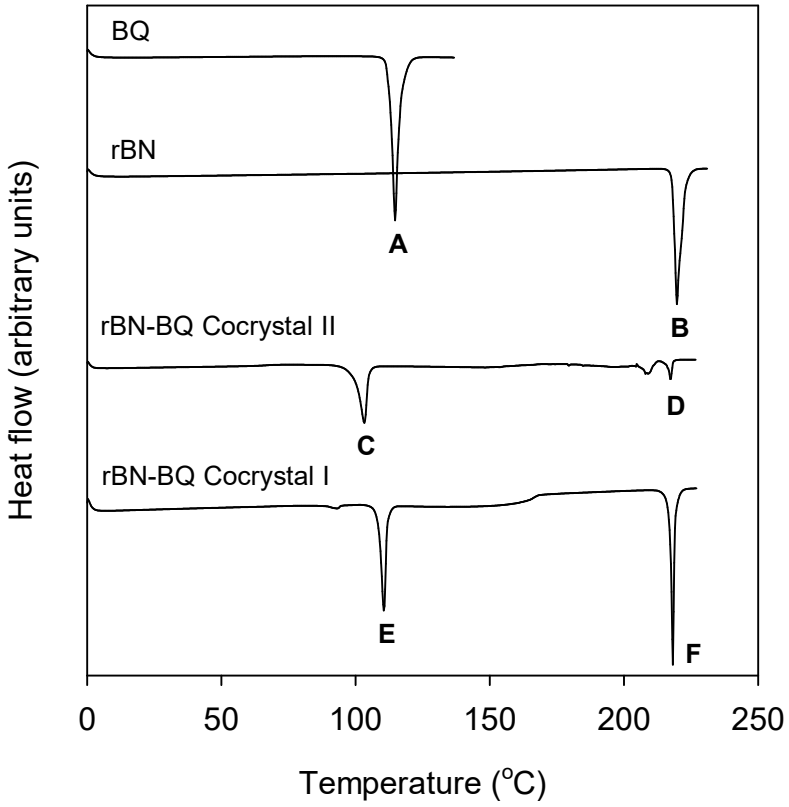

Figure S3: DSC thermograms of Benzoquinone (BQ), Racemic bi-Naphtol (rBN), Cocrystal II (1:1), and Cocrystal I (1:1.5). **A**: Melting endotherm of BQ, onset temperature = 112.5 °C and Heat of fusion = 163.2 J/g, **B**: Melting endotherm of BQ, onset temperature = 218.5 °C and Heat of fusion = 118. J/g, **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.

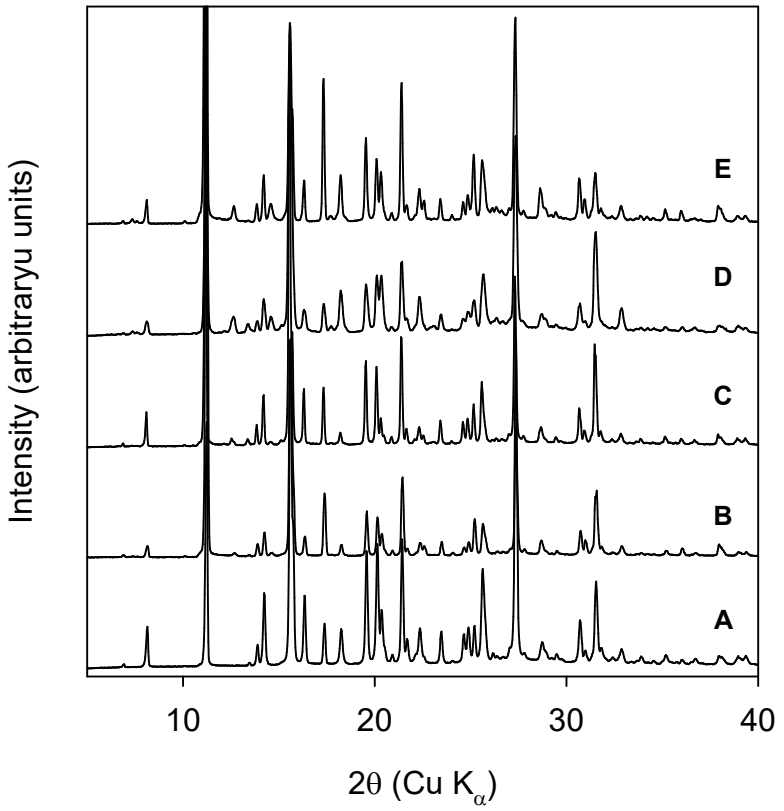

Figure S4. XRPD data of rBN/BQ samples subjected to RAM. **A**: Physical mixture of rBN and BQ, **B**: 1:1 rBN:BQ RAM at 75 Hz for 90 minutes, **C**: 1:1.5 rBN:BQ RAM at 75 Hz for 90 minutes, **D**: 1:2.5 rBN:BQ RAM at 90 Hz for 180 minutes, and **E**: 1:2.5 rBN:BQ RAM at 90 Hz for 540 minutes.

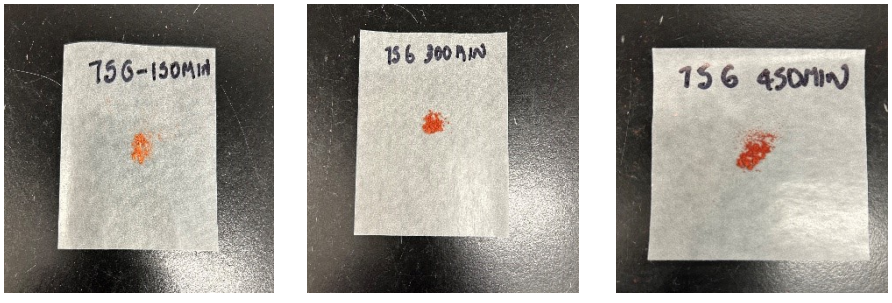

Figure S5. Color of samples of rBn/BQ at a 1:2.5 mole ratio after being subjected to RAM at 75 Hz for time periods ranging from 150 to 450 minutes.

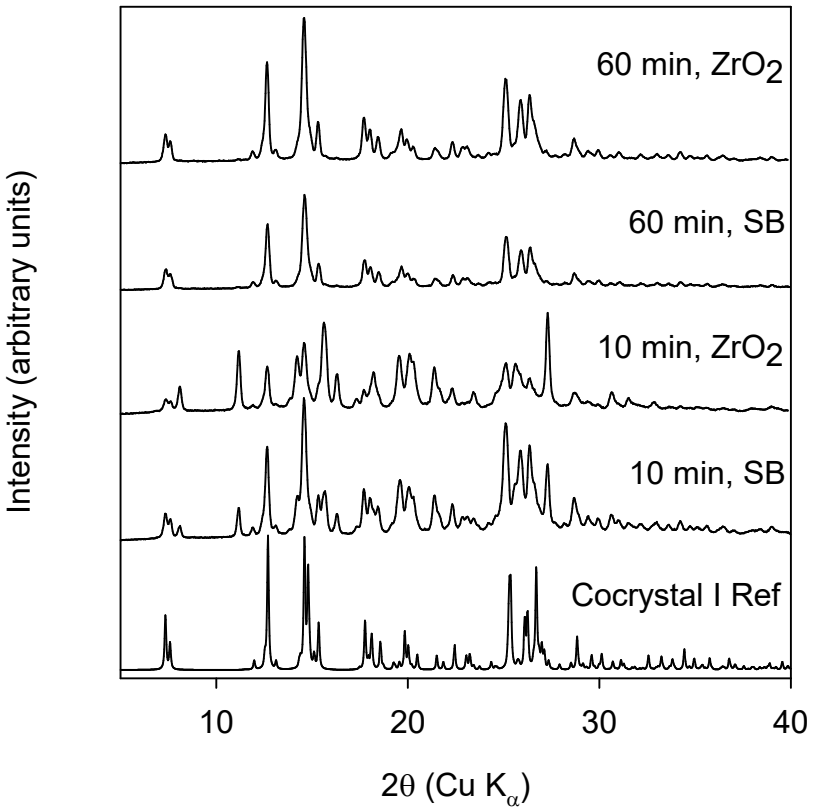

Figure S6. XRPD data of rBN/BQ at a 1:1.5 mole ratio samples subjected to BM with steel balls and ZrO_2 balls shown in comparison with the calculated powder data for Cocrystal I.

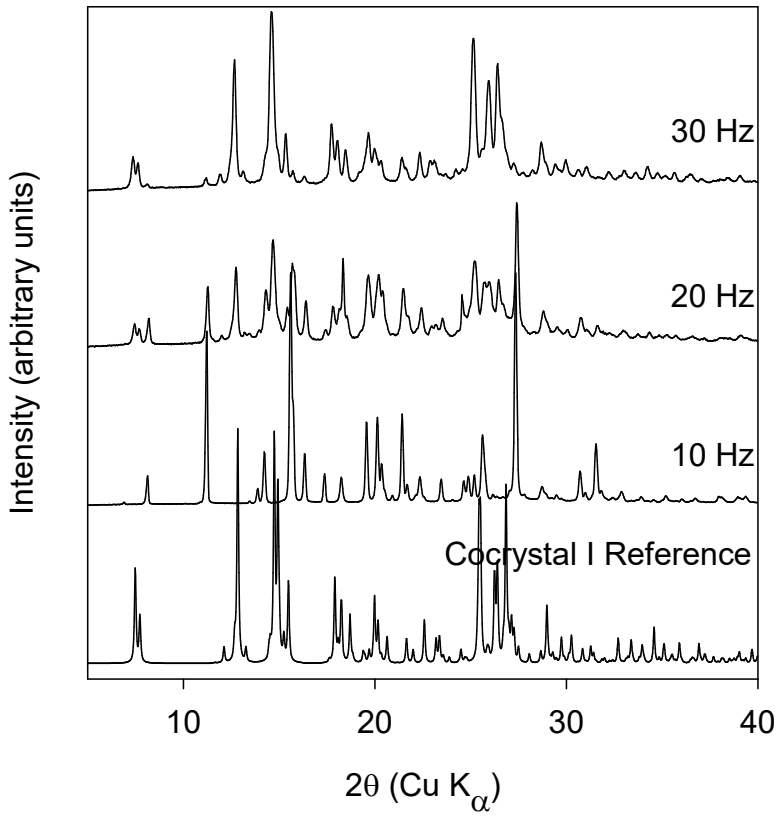

Figure S7. XRPD data of rBN/BQ at a 1:2 mole ratio samples subjected to BM shown in comparison with the calculated powder data for Cocrystal I.

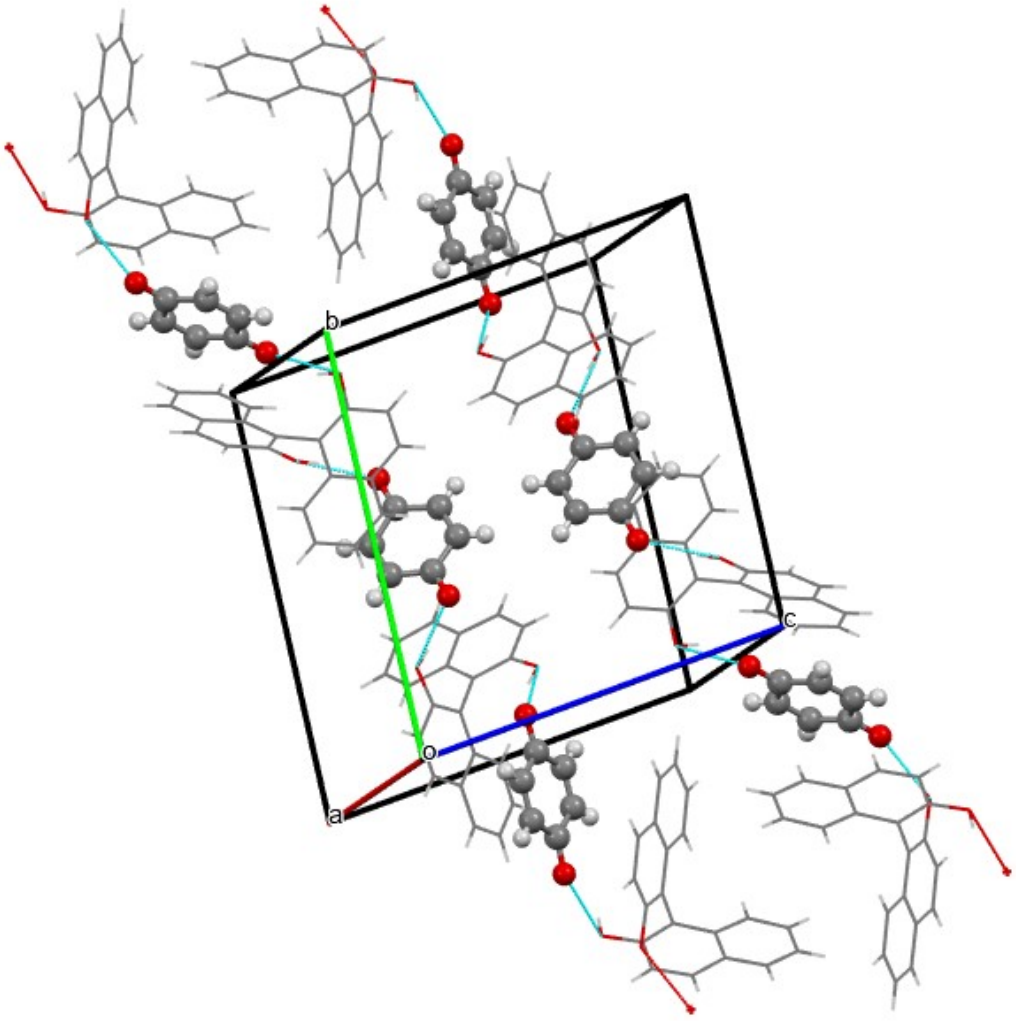

Figure S8: Stereo view of the molecular packing of Cocrystal II. The rBN molecules are represented as wireframes while the BQ molecule is represented using a ball and stick model. **C**ocrystal **II** crystallizes in a triclinic space group P1 with a mole ratio of 1:1 mole ratio of rBN:BQ. The BQ molecules 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]

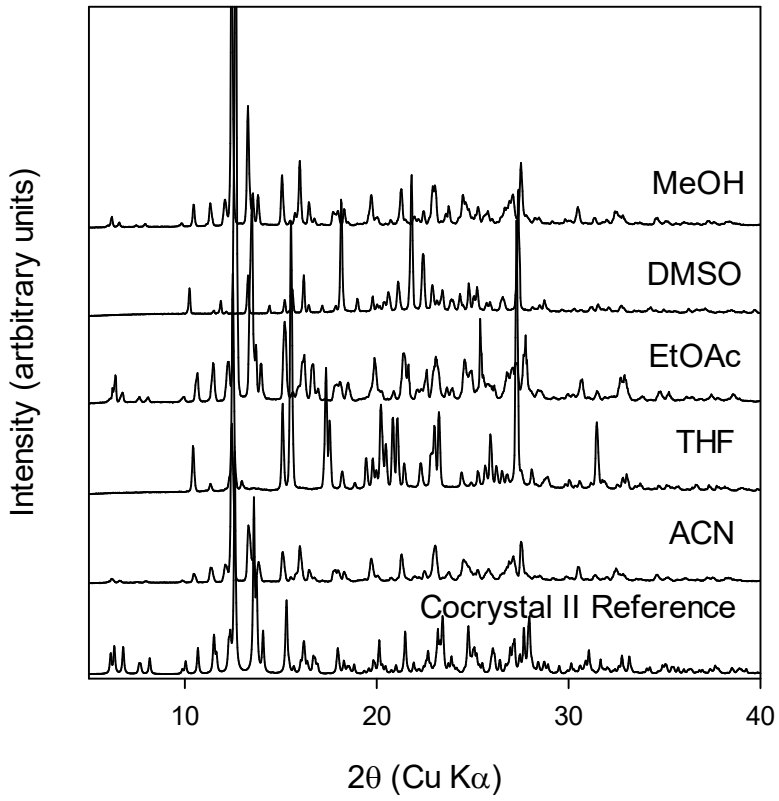

Figure S9. XRPD data of rBN/BQ at a 1:1 mole ratio samples subjected to RAM in the presence of liquid additives at a η of 0.5 shown in comparison with the calculated powder data for Cocrystal II.

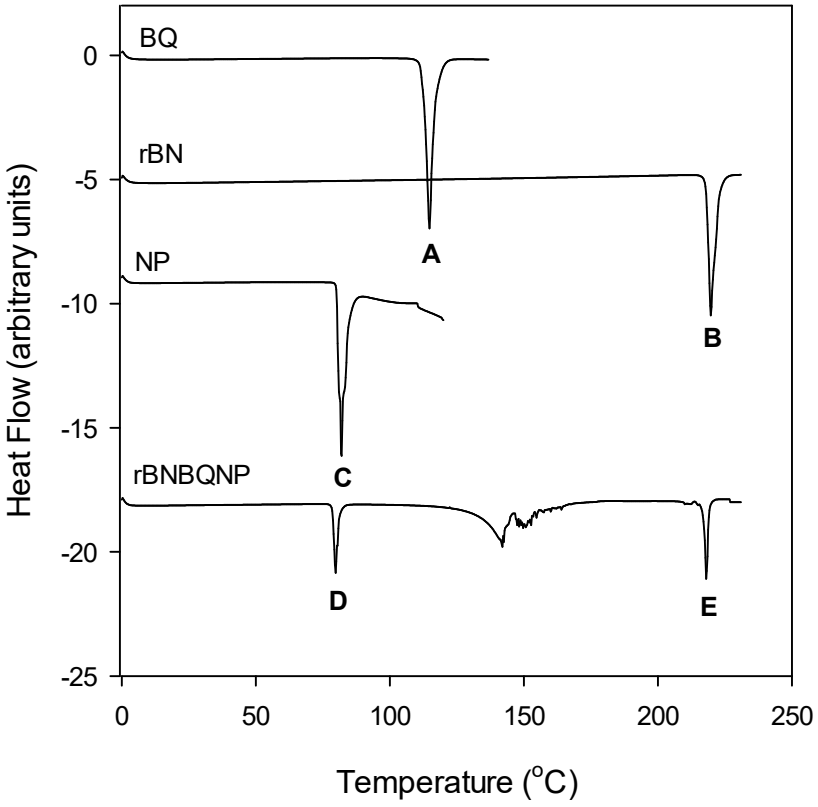

Figure S10: DSC thermograms of Benzoquinone (BQ), Racemic bi-Naphtol (rBN), Naphthalene (NP), and the ternary cocrystal rBNBQNP (2:1:2). **A**: Melting endotherm of BQ, onset temperature = 112.5 °C and Heat of fusion = 163.2 J/g, **B**: Melting endotherm of BQ, onset temperature = 218.5 °C and Heat of 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.

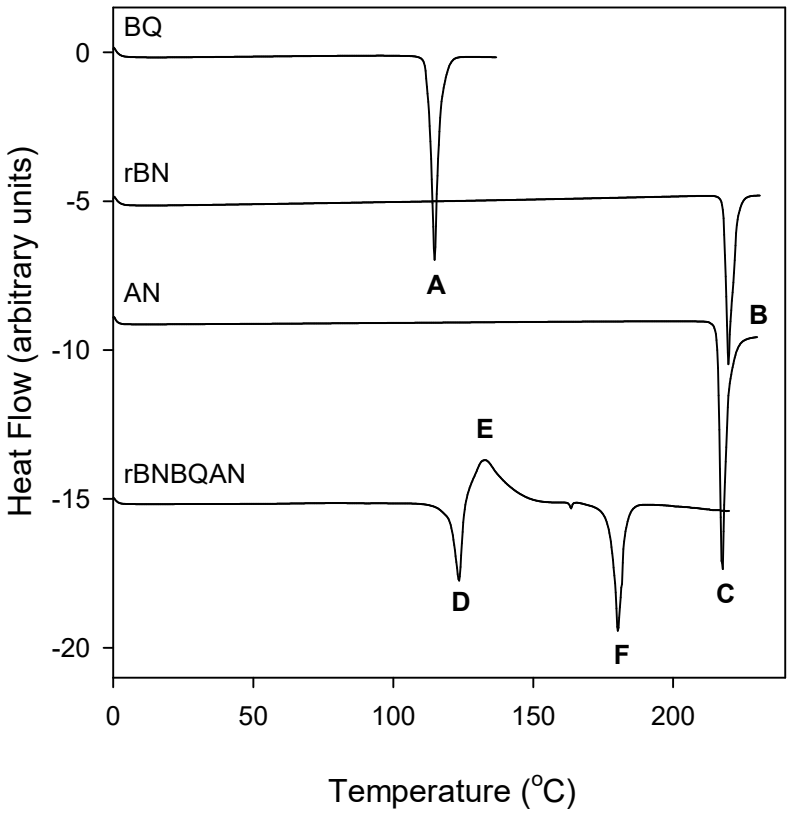

Figure S11: DSC thermograms of Benzoquinone (BQ), Racemic bi-Naphtol (rBN), Naphthalene (NP), and the ternary cocrystal rBNBQAN (2:2:1). **A**: Melting endotherm of BQ, onset temperature = 112.5 °C and Heat of fusion = 163.2 J/g, **B**: Melting endotherm of BQ, onset temperature = 218.5 °C and Heat of 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

1. R. Kuroda, Y. Imai and N. Tajima, *Chemical Communications*, 2002, DOI: 10.1039/B207417F, 2848-2849.