The Role of Co-crystals in Solid-State Synthesis: Co-crystal Controlled Solid-State Synthesis of Imides

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Supporting Information

Reaction 1: 2-Methyl-4-Nitroaniline (MNA) and 1,4,5,8-Naphthalenetetracarboxylic dianhydride (NTCDA)

Figure S1. The IR spectrum obtained from the DMF solvent drop grind of NTCDA and MNA (co-crystal 1, red) exhibits shifts in the carbonyl and primary amine region when compared to pure NTCDA (purple) and pure MNA (blue).

Figure S2. IR spectra of solvent drop grinds involving NTCDA and MNA with chloroform (red), cyclohexane (dark purple), DMSO (green), and DMF (light purple), all of which resulted in mixtures of NTCDA and MNA except for the DMF solvent drop grind, which afforded co-crystal 1.

Figure S3. IR spectra of solvent drop grinds of NTCDA and MNA with ethyl acetate (blue), methanol (green), toluene (yellow) and water (red). All solvent drop grinds resulted in mixtures of NTCDA and MNA.

Figure S4. IR spectrum of diimide 2 (red) generated from heating the DMF solvent drop grind of NTCDA and MNA for three hours at 180°C. 2 exhibits shifts in the carbonyl region consistent with imide formation and shows loss of NH2 peaks. NTCDA (purple) and pure MNA (blue) spectra are provided for comparison purposes.

Figure S5. IR spectra of solvent drop grinds involving NTCDA and MNA with chloroform (green), cyclohexane (light blue), DMSO (purple), and DMF (red) after heating for three hours at 180°C. All IR spectra are consistent with condensation to diimide 2.

Figure S6. IR spectra of solvent drop grinds of NTCDA and MNA with ethyl acetate (blue), methanol (green), toluene (yellow) and water (red) after heating for three hours at 180°C. All IR spectra are consistent with condensation to diimide 2.

Figure S7. X-ray powder diffraction (XPD) patterns of water (dark purple), toluene (dark blue), methanol (olive), ethyl acetate (yellow), DMSO (light purple),
cyclohexane (light blue) and chloroform (blue) solvent drop grinds with NTCDA and MNA are consistent with mixtures of NTCDA and MNA. XPD patterns of pure NTCDA (black) and pure MNA (red) are provided for comparison purposes. The XPD of the DMF solvent drop grind (dark green) and the heated methanol solvent drop grind (130°C, light green) are consistent with the simulated XPD pattern generated from the single crystal structure of co-crystal 1.  

**Figure S8.** X-ray powder diffraction (XPD) patterns of water (dark purple), toluene (dark blue), methanol (olive), ethyl acetate (yellow), DMSO (light purple), DMF (light blue), cyclohexane (blue) and chloroform (green) solvent drop grinds with NTCDA and MNA after heating for three hours at 180°C. The XPD patterns show formation of a new phase that is different from pure NTCDA (red), pure MNA (black) and the simulated XPD of the solvated forms of 2.

**Figure S9.** The UV-vis spectrum of co-crystal 1 (blue) exhibits a broad band at ca. 600nm which is indicative of charge transfer. The methanol solvent drop grind of NTCDA and MNA (black), pure NTCDA (red), and pure MNA (green) are shown for comparison purposes.

**Figure S10.** (a) DSC of methanol solvent drop grind exhibiting phase transitions at ca. 130°C and ca. 160°C. (b) DSC of DMF solvent drop grind exhibiting a phase transition at ca. 160°C. (c) The color changes observed as the methanol solvent drop grind and co-crystal 1 were heated correspond to the phase transitions seen in the DSC’s. The methanol solvent drop grind has phase transitions from a mixture to 1 at ca. 130°C (yellow to purple) and from 1 to diimide 2 at ca. 160°C (purple to orange). The DMF solvent drop grind has a phase transition from 1 to 2 at ca. 160°C (purple to orange).

**Figure S11.** Crystal packing of co-crystal 1. 1 obeys the topochemical postulate because the shortest distance between the nitrogen atoms of the amine moieties and the carbon atoms of the carbonyl moieties is 3.42Å.

**Figure S12.** (a) Molecular structure of diimide 2 as generated via recrystallization of 2 from DMSO. (b) Crystal packing of 2 DMSO solvate (3:2) obtained via recrystallization from DMSO.

**Figure S13.** (a) Molecular structure of diimide 2 as generated via recrystallization of 2 from DMF. (b) Crystal packing of 2·DMF solvate (3:2) of 2 formed via recrystallization from DMF.

**Reaction 2: 3-Aminobenzoic acid (ABA) and 1,4,5,8-Naphthalenetetracarboxylic dianhydride (NTCDA)**

**Figure S14.** The IR spectrum of the DMF solvent drop grind of NTCDA and ABA (purple) exhibits shifts in the carbonyl region. Pure NTCDA (green) and ABA (red) have been shown for comparison purposes.

**Figure S15.** IR spectra of chloroform (light blue), cyclohexane (green), DMSO (purple), and DMF (red) solvent drop grinds with NTCDA and ABA. The DMF
solvent drop grind of NTCDA and ABA (red) exhibits a shift in the carbonyl region with respect to pure NTCDA and pure ABA. Additional solvent drop grinds of NTCDA and ABA resulted in mixtures of NTCDA and ABA.

**Figure S16.** The IR spectra of ethyl acetate (dark blue), methanol (yellow), toluene (blue), and water (red) solvent drop grinds of NTCDA and ABA. All solvent drop grinds resulted in mixtures of NTCDA and ABA.

**Figure S17.** IR spectrum of diimide 4 (purple) generated from heating the solvent drop grinds of NTCDA (green) and ABA (red) for 14 hours at 150°C. 4 shows shifts in the carbonyl region consistent with imide formation. Pure NTCDA (green) and pure ABA (red) spectra are provided for comparison purposes.

**Figure S18.** IR spectra of NTCDA and ABA solvent drop grinds with chloroform (light blue), cyclohexane (purple), DMSO (blue), and DMF (red) after heating for 14 hours at 150°C. All IR spectra are consistent with condensation to diimide 4.

**Figure S19.** IR spectra of NTCDA and ABA solvent drop grinds with ethyl acetate (yellow), methanol (green), toluene (purple), and water (red) heated for 14 hours at 150°C. All IR spectra are consistent with condensation to diimide 4.

**Figure S20.** The IR spectrum of the 1,4-dioxane solvate of co-crystal 3 (purple) after heating for 24 hours at 250°C (blue) indicates conversion of 3 to diimide 4. The 1,4-dioxane solvate of the co-crystal (blue) and the IR spectrum of the NTCDA and ABA chloroform solvent drop grind after heating for 14 hours at 150°C (red) are shown for comparison purposes.

**Figure S21.** X-ray powder diffraction (XPD) patterns of water (dark purple), toluene (dark blue), methanol (olive), ethyl acetate (yellow), DMSO (light blue), cyclohexane (blue), and chloroform (green) solvent drop grinds with NTCDA and ABA are consistent with mixtures of NTCDA and ABA. The DMF solvent drop grind (purple) generates a unique XPD pattern that is different from the NTCDA (red) and ABA (black). XPD patterns of pure NTCDA (red) and pure ABA (black) are provided for comparison purposes.

**Figure S22.** X-ray powder diffraction (XPD) patterns of water (dark purple), toluene (dark blue), methanol (olive), ethyl acetate (yellow), DMF (light purple), DMSO (light blue), cyclohexane (blue), and chloroform (green) solvent drop grinds with NTCDA and ABA after heating for 14 hours at 150°C. The XPD patterns all show formation of a new phase that is different from pure NTCDA (red) and pure ABA (black) and the simulated XPD of the solvated form of 4.

**Figure S23.** The UV-vis spectrum of co-crystal 3 (black) exhibits a broad band at ca. 550nm which is indicative of charge transfer. The methanol solvent drop grind of NTCDA and ABA (green), pure NTCDA (blue), and pure ABA (light blue) are shown for comparison purposes.

**Figure S24.** DSC of the DMF solvent drop grind (purple) coupled with observation of color changes indicates that the phase transition at ca. 127°C can be attributed to the conversion of the DMF solvent drop grind to diimide 4 (gold).
**Figure S25.** The DSC of the methanol solvent drop grind of NTCDA and ABA exhibited two phase transitions at ca. 155°C and ca. 167°C resulting in the formation of diimide 4.

**Figure S26.** Crystal packing of co-crystal 3·1,4-dioxane. The shortest distance between the nitrogen atoms of the amine moieties and the carbon atoms of the carbonyl moieties was found to be 3.14Å therefore, 3 obeys the topochemical postulate.

**Figure S27.** Crystal packing of the pyridine solvate of the 1:2 complex of 4 with pyridine.
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