

Supporting Information

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**Two Isostructural Explosive Cocrystals with Significantly Different Thermodynamic Stabilities\*\***

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## SI 1. Experimental

**Caution:** *Although no unplanned detonation was encountered during this work, DADP, TCTNB and TBTNB are dangerous high power explosives. Proper safety practices and equipment must be used to prevent explosion due to friction, heat, static shock, or impact. Be aware that the potential for severe injury exists if these materials are improperly handled.*

Synthesis of diacetone diperoxide (DADP) was modified from the literature method.<sup>1</sup> Into a flask cooled by an ice bath, 1 mL of acetone (Fisher, Certified ACS) and 2 mL of 30% hydrogen peroxide (Fisher, Certified ACS) were added to 5 mL of dichloromethane (Fisher, stabilized HPLC Grade). Once cooled, 2 mL of 70% perchloric acid (B&A, Reagent ACS) were then added to the reaction drop-wise. The reaction stirred for one hour at 0 °C and then stood at room temperature for three days to ensure full conversion to DADP. The precipitate was filtered, washed with water and 5% NaHCO<sub>3</sub> to remove any residual acid, and then recrystallized from methanol to afford a colorless solid. The optimum yield after recrystallization was 54.4%, and <sup>1</sup>H NMR data were in accord with literature.<sup>2</sup>

Both 1,3,5-trichloro-2,4,6-trinitrobenzene (TCTNB) and 1,3,5-tribromo-2,4,6-trinitrobenzene (TBNTB) were synthesized by literature methods without modification.<sup>3</sup>

Cocrystals of DADP/TCTNB were obtained by solvent mediated transformation. A mixture of a 1:1 molar ratio of DADP and TCTNB were slurried at room temperature under acetonitrile (ACN, Fisher, HPLC Grade) to afford phase-pure cocrystal as colorless prisms.

Many conditions were tested for optimizing DADP/TBTNB cocrystal synthesis. Though the DADP/TBTNB cocrystal was first obtained by dissolving a 1:1 molar ratio of DADP (1.544 mg) and TBTNB (4.663 mg) in 0.1 mL ACN and evaporating the solution, the resulting cocrystal accounted for less than 10% of the solids obtained, as determined by optical microscopy and Raman spectroscopy. In attempts to scale up the original cocrystal growth condition larger quantities of both components were dissolved in ACN (14.299 mg of TBTNB with 4.738 mg of DADP dissolved in 0.3 mL of ACN, and 11.811 mg of TBTNB and 3.952 mg of DADP in 0.4 mL of ACN) and left to evaporate at room temperature, but little if any cocrystal was formed, indicating unpredictable formation of this cocrystal from these conditions. Other attempted methods included solvent inversion, solvent mediated transformation (slurrying), seeding, and recrystallization. Most methods failed to produce cocrystals. Solvent inversion, accomplished by dissolving a 1:1 mole ratio of DADP and TBTNB in ACN and then adding water produced no cocrystal.

Solvent mediated transformation in solutions co-saturated with DADP and TBTNB and containing both solid DADP and TBTNB were made with water, ethanol, methanol (Fisher, Certified ACS), ethyl acetate (Fisher, HPLC Grade), 1,4-dioxane (Fisher, Certified ACS), tetrahydrofuran (Fisher, Certified, dry), chloroform (Fisher, Certified ACS), *N,N*-dimethylformamide (Fisher, Sequencing Grade), cyclohexane (Aldrich, anhydrous), ACN, and diethyl ether (Fisher, Stabilized HPLC Grade) at room temperature. All room-temperature slurries produced no cocrystal. Another method attempted to form this cocrystal involved heating and then cooling solutions containing both cocrystal formers. In cases where one of the cocrystal formers was undersaturated, cocrystal

formation usually was not observed and only pure component solids were produced. Furthermore, saturating solutions of DADP and TBTNB in ACN, methanol, ethanol (Decon Laboratories, Inc., 200 proof), toluene, benzene, propyl alcohol, and isopropyl alcohol never produced cocrystals. Consistent cocrystal formation was only achieved by the rapid cooling of solutions supersaturated with both cocrystal formers in solvents that were poor for both cocrystal formers, such as cyclohexane and heptane.

Based on these results, a method to consistently form DADP/TBTNB was developed. To obtain larger quantities of the cocrystal, a supersaturated solution of both DADP and TBTNB was created in cyclohexane by heating to 80 °C. This solution was then hot-filtered into a clean vial and monitored with optical microscopy as the solution came to room temperature. Cocrystals formed concomitantly with pure TBTNB and/or DADP solids, which required manual separation. The optimized procedure employed 4.0 mg of TBTNB, 28 mg of DADP in 1.0 mL of cyclohexane, sonicated for 30 minutes and heated to in a sealed 4 mL vial at 80 °C for at 10 minutes. Cocrystals were stored by removing the solvent then sealing the material within the growth vial. Though pure DADP and TBTNB were also present in the storage vial, the cocrystal did not transform in the absence of a solvent. Furthermore, as DADP is a volatile solid and was observed to evaporate from the cocrystal, the presence of pure DADP in the DADP/TBTNB storage vial helped to saturate the atmosphere and stabilize the cocrystal.

Solvent mediated transformation could fail to produce a cocrystal if the kinetic potential energy barrier is too high. Thus, cocrystal seeds were introduced into these systems to reduce this barrier. Solutions co-saturated with DADP and TBTNB of either water, ethanol, methanol, ethyl acetate, 1,4-dioxane, tetrahydrofuran, chloroform, *N,N*-dimethylformamide, cyclohexane, ACN, or diethyl ether were added to DADP/TBTNB cocrystal seeds and their behavior was monitored by optical microscopy. In all cases the cocrystal (needle) became smaller, dissolved, and then completely disappeared while the pure solids DADP and TBTNB remained. This dissolution took less than 30 seconds in all solvents except for methanol, ethanol, cyclohexane and water. For these four solvents, the times to total cocrystal dissolution were 2 minutes, 5 minutes, 50 minutes and more than two weeks, respectively.

## SI 2. Crystallography of DADP/TCTNB and DADP/TBTNB

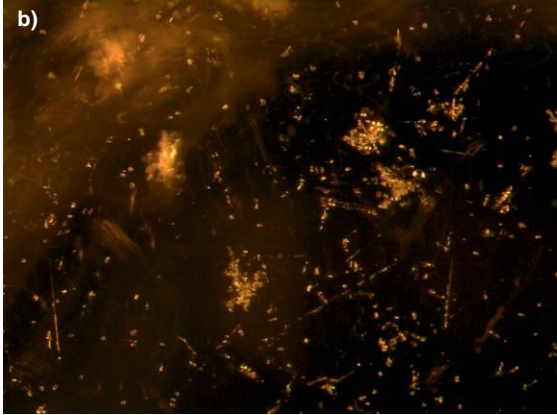
Single crystal X-ray diffraction data for DADP/TCTNB were obtained using a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a Micromax-007HF Cu-target microfocus rotating anode ( $\lambda = 1.54187 \text{ \AA}$ ) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at room temperature with the detector placed at a distance 42.00 mm from the crystal. The DADP/TCTNB cocrystal was mounted on a glass fiber.

Single crystal X-ray diffraction data for DADP/TBTNB were obtained using a Rigaku R-Axis Spider diffractometer with an image plate area detector using graphite monochromated Cu-K $\alpha$  radiation ( $\lambda = 1.54187 \text{ \AA}$ ) operated at 2.0 kW power (50 kV, 40 mA). The X-ray intensities were measured with the detector at a distance 127.00 mm from the crystals. The cocrystal was mounted in a 0.3 mm capillary loaded with DADP to make a DADP-saturated atmosphere to stabilize the cocrystal; some decay was observed.

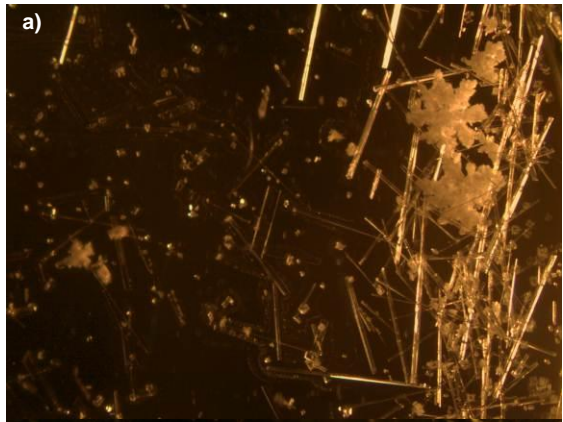
Diffraction data were collected at room temperature for both cocrystals because both exhibited transformations at lower temperatures. All data were processed with CrystalClear 2.0 (Rigaku) and corrected for absorption using an empirical absorption correction. Both structures were solved by direct methods<sup>4</sup> refined and expanded using the CrystalStructure 4.0<sup>5</sup> crystallographic software package (Rigaku). Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using the riding model. The final cycle of full-matrix least-squares refinement was made on  $F^2$ . An empirical absorption correction was applied to the structure.

## SI 3. Dissolution of the DADP/TBTNB Cocrystal into Saturated Solvents

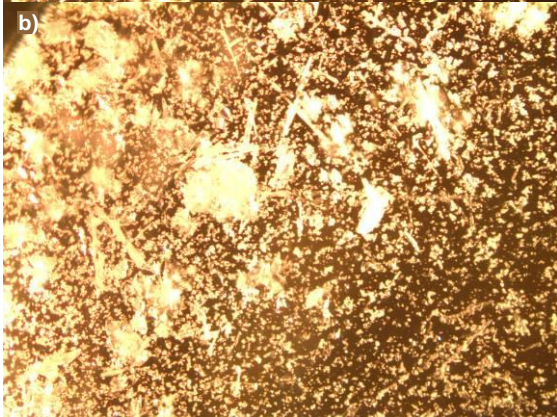
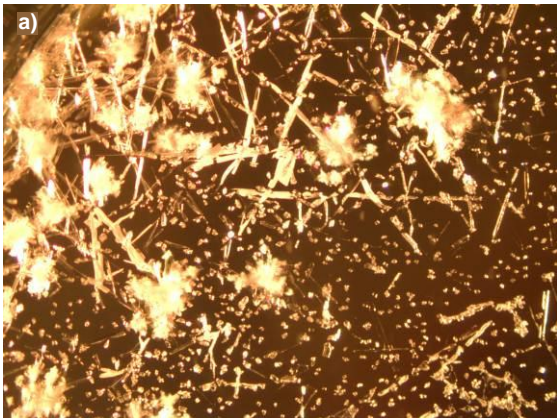
DADP/TBTNB was formed from evaporation of cyclohexane solution and isolated before transformation could occur. A photo was taken of the cocrystals before solvents co-saturated with both TBTNB and DADP were added. As soon as solvent was added pictures were taken at 0.5 second intervals. The pictures below show a) the initial picture and b) the time at which the cocrystal disappeared entirely from view of the camera. The results were repeatable allowing for the amount of cocrystal and the speed of mixing. All solvents except for methanol, ethanol, cyclohexane and water showed transformation in less than a thirty seconds (see above). Photos of these transitions are shown on the following pages.



1,4-dioxane a) before and b) 0.5 s after



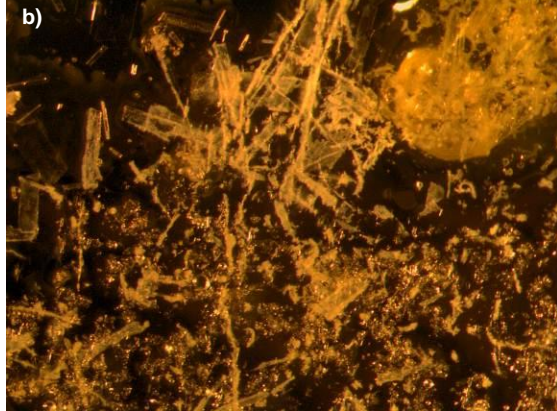
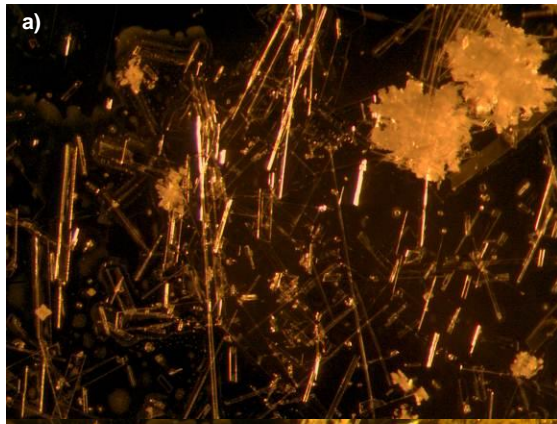
tetrahydrofuran a) before and b) 2 s after



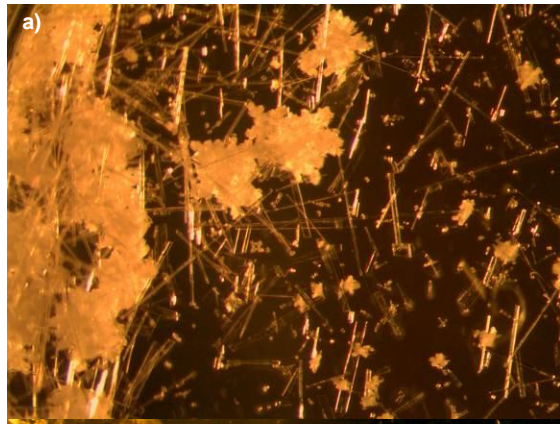
acetonitrile a) before and b) 6 s after



ethyl acetate a) before and b) 15 s after



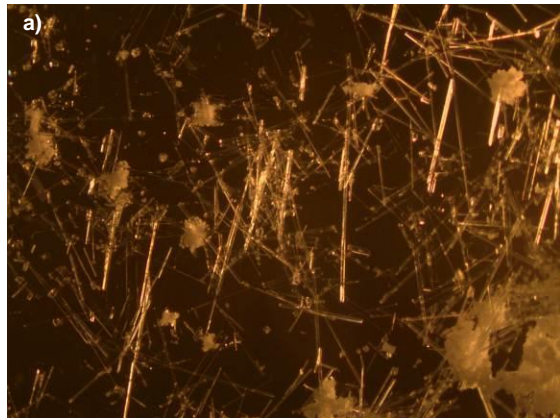
dimethylsulfoxide a) before and b) 8 s after



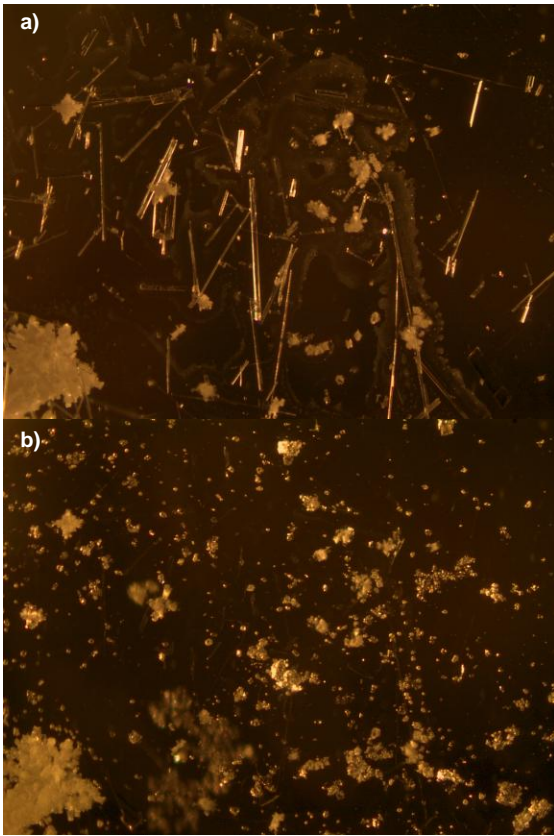
*N,N*-dimethylformamide a) before and b) 15 s after



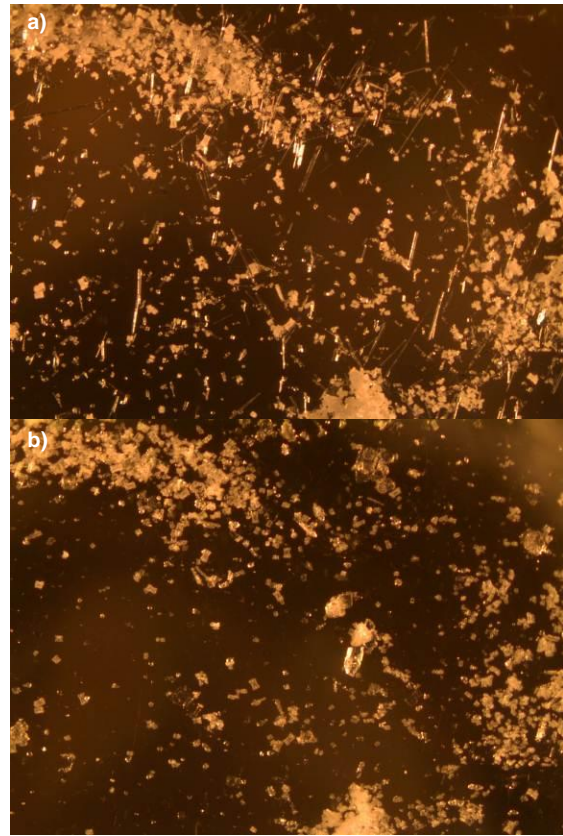
chloroform a) before and b) 30 s after



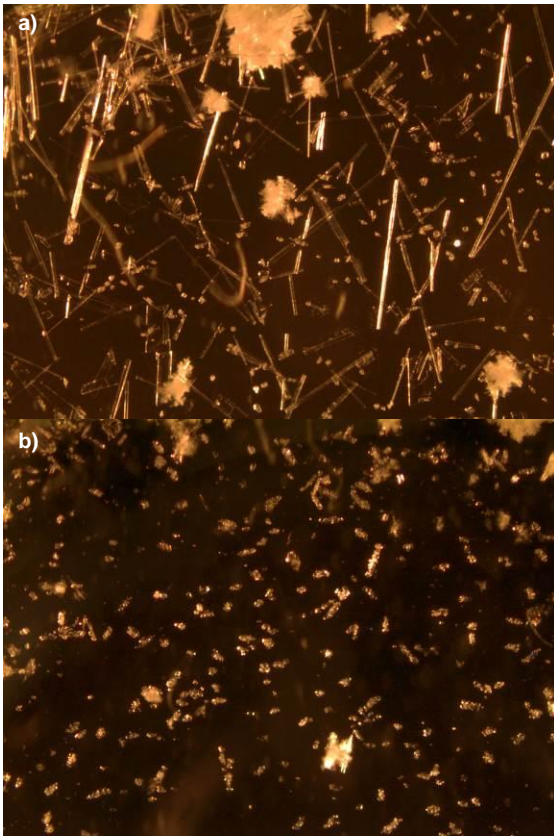
diethyl ether a) before and b) 30 s after



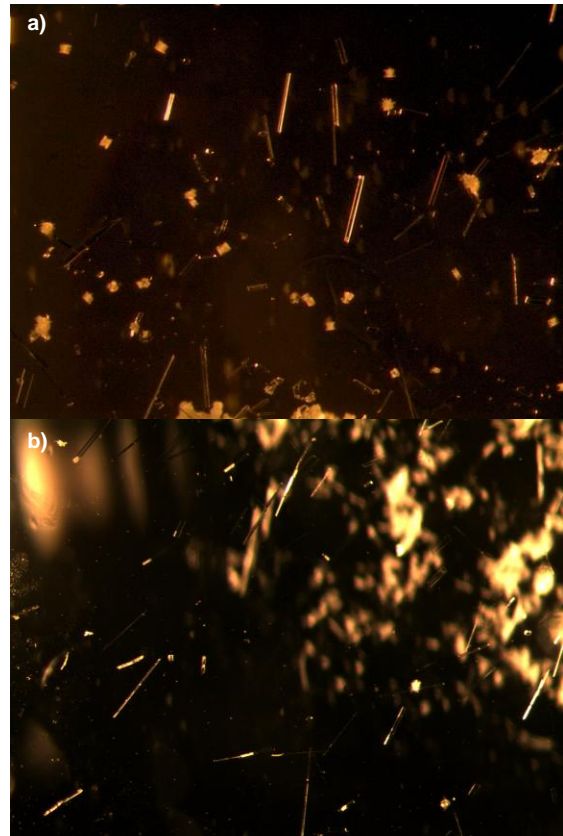
methanol a) before and b) 2 min after



ethanol a) before and b) 5 min after



cyclohexane a) before and b) 1 hr after



water a) before and b) 1 week after

#### SI 4. References

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