Experimental and database studies of three-centered halogen bonds with bifurcated acceptors present in molecular crystals, cocrystals and salts

Supplementary Information

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Experimental

Mechanosynthesis

All starting materials were purchased from Sigma-Aldrich Chemical Co. and were used without further purification. Mechanochemical reactions were performed by using 200 mg of the mixture of solid reactants. For LAG experiments additional 50 μL of ethanol, nitromethane or acetonitrile were added. The reaction mixture was placed in a 10 mL stainless steel jar and ground either using a pair of 7 mm diameter stainless steel balls (each ball weighing 1.4 g). The mixture was then ground for 30 min in a Retsch MM200 grinder mill operating at 30 Hz. The temperature of the grinding jar increased by no more than 4 ^{o}C during grinding, as monitored via thermocouples embedded in the walls of the jar.

Powder X-ray diffraction

PXRD data was collected on a laboratory Philips X'Pert Pro diffractometer, equipped with an X'celerator RTMS detector, using Ni-filtered CuKα radiation, using a flat plate configuration. Data were typically collected in the 2θ range 5-40^{o}.

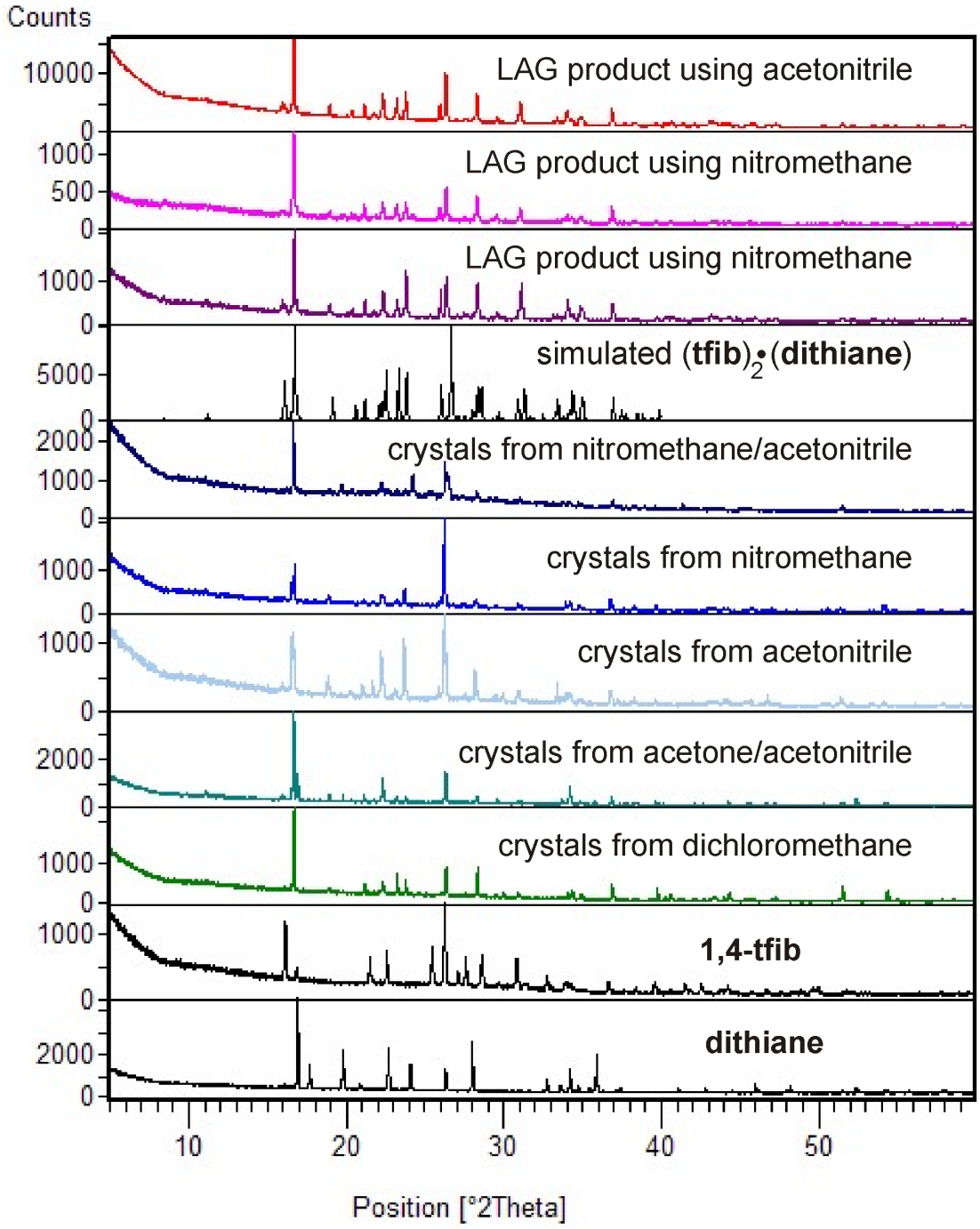

Figure S1. PXRD patterns for (top to bottom): LAG product of **1,4-tfib** and **dithiane** in 1:1 ratio, using acetonitrile as the grinding liquid; LAG product of **1,4-tfib** and **dithiane** in 1:1 ratio, using nitromethane as the grinding liquid; LAG product of **1,4-tfib** and **dithiane** in 2:1 ratio, using nitromethane as the grinding liquid; simulated for (**1,4-tfib**)$_2$·(**dithiane**); crystals obtained by recrystallising a 1:1 mixture of **1,4-tfib** and **dithiane** from a mixture of nitromethane and acetonitrile; crystals obtained by recrystallising a 1:1 mixture of **1,4-tfib** and **dithiane** from nitromethane; crystals obtained by recrystallising a 1:1 mixture of **1,4-tfib** and **dithiane** from acetonitrile; crystals obtained by recrystallising a 1:1 mixture of **1,4-tfib** and **dithiane** from a mixture of acetone and acetonitrile; crystals obtained by recrystallising a 1:1 mixture of **1,4-tfib** and **dithiane** from dichloromethane; commercial sample of **1,4-tfib** and commercial sample of **dithiane**.

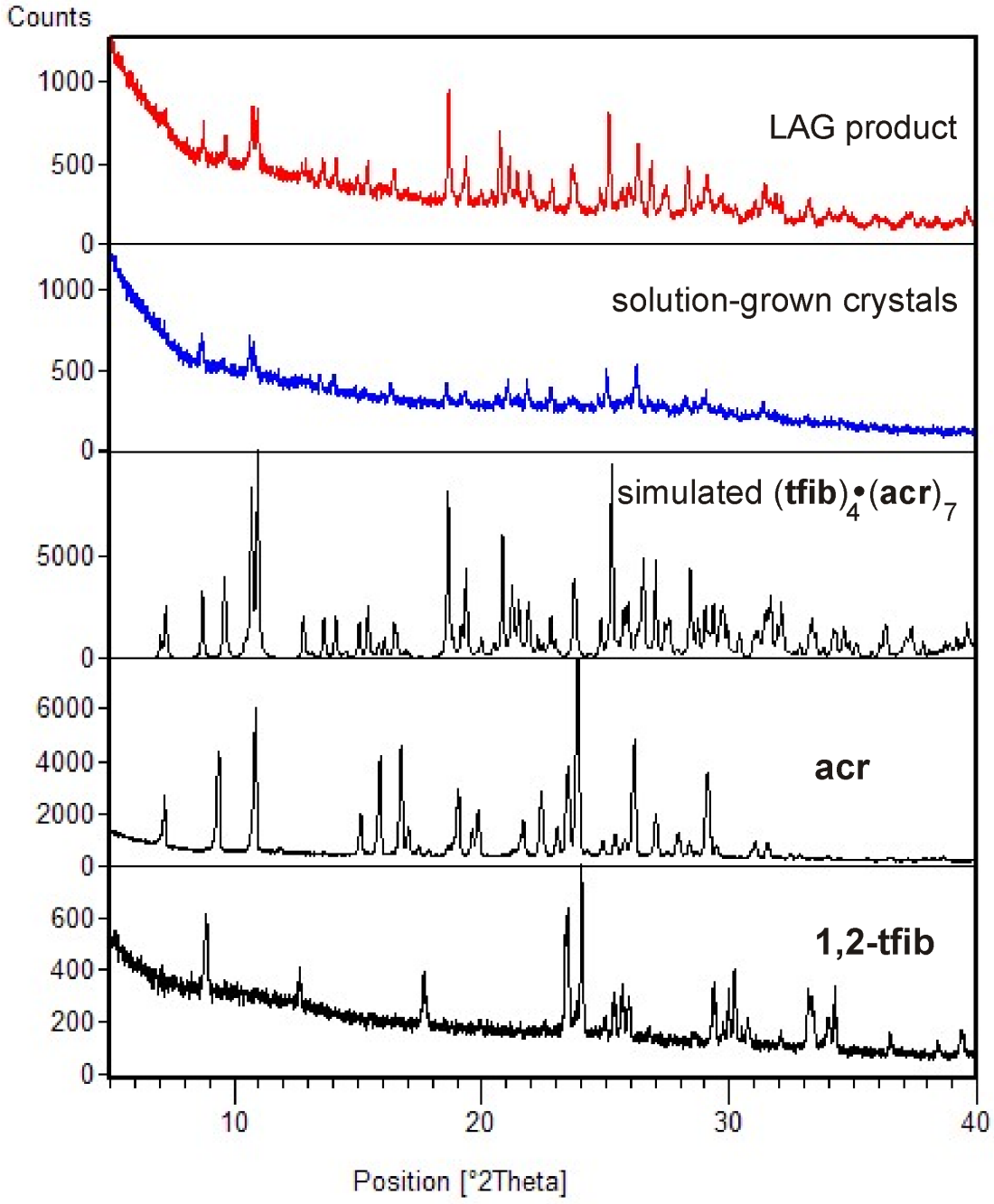

Figure S2. PXRD patterns for (top to bottom): LAG product of **1,2-tfib** and **acr** in 1:2 ratio, using nitromethane as the grinding liquid; crystals obtained by recrystallising a 1:2 mixture of **1,2-tfib** and **acr** from nitromethane; simulated for the cocrystal (**1,2-tfib**)$_4$·(**acr**)$_7$; commercial **acr** and commercial **1,2-tfib**.

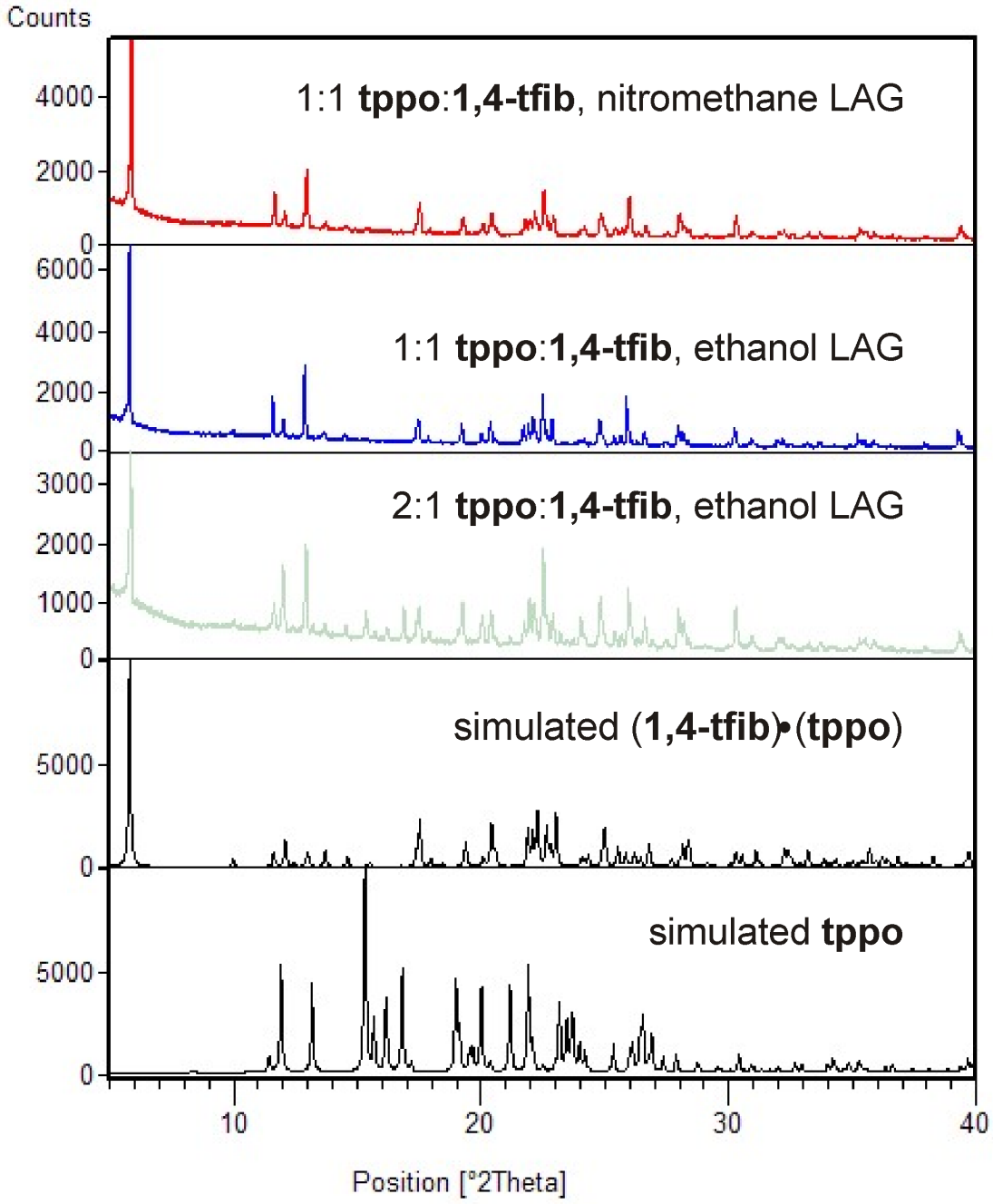

Figure S3. PXRD patterns for (top to bottom): LAG product of **1,4-tfib** and **tppo** in 1:1 ratio, using nitromethane as the grinding liquid; LAG product of **1,4-tfib** and **tppo** in 1:1 ratio, using ethanol as the grinding liquid; LAG product of **1,4-tfib** and **tppo** in 1:2 ratio, using ethanol as the grinding liquid; simulated for the cocrystal (**1,4-tfib**)·(**tppo**); simulated or **tppo** (CCDC code TPEPHO10).