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Supporting Information

for

# Dry-vortex grinding facilitates a [2 + 2] cycloaddition reaction that triggers a cascade-like reaction that improves the yield under substoichiometric conditions

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1. Materials, General Methods, and Synthesis of the Solids	Page 2
2. Powder X-ray Diffraction Diffractograms	Page 3-12
3. <sup>1</sup> H NMR Spectroscopic Data	Page 13-16
4. Pictures of the Experimental Setup for the Dry-Vortex Grinding	Page 17

#### 1. Materials, General Methods, and Synthesis of the Solids

#### Materials

The reactant *trans*-1,2-bis(2-pyridyl)ethylene (**2,2-BPE**) along with the template 2,4,6-trifluorophenol ( $C_6H_2F_3OH$ ) were both purchased from Sigma-Aldrich Chemical (St. Louis, MO, USA) and used as received.

### **General Methods**

Photoreactions were conducted using UV-radiation from a 450 W medium-pressure mercury lamp in an ACE Glass photochemistry cabinet. The ground solid that contains the cocrystal  $2(C_6H_2F_3OH) \cdot (2,2-BPE)$  was placed between a pair of Pyrex glass plates for irradiation. The photoreactivity of the resulting solid was determined by using <sup>1</sup>H NMR spectroscopy. <sup>1</sup>H NMR spectrum was collected using a Bruker Avance 400 MHz spectrometer using DMSO- $d_6$  as a solvent. The dry-vortex grinding occurred within a clear 30 mL SmartSnap Grinding Jar along with 2 ball bearings (5 mm diameter) using a VWR Vortex Genie 2.

### Synthesis of the Stoichiometric Co-crystal (2:1 Molar Ratio)

The solid containing a stoichiometric amount of the template was synthesized by dryvortex grinding 81.4 mg of  $C_6H_2F_3OH$  along with 50.0 mg of **2,2-BPE** in a 30 mL SmartSnap Grinding Jar along with 2 ball bearings (5 mm diameter) at a 2:1 molar ratio, respectively. The molecular components were dry-vortex ground for 30 minutes where at both the 10 and 20 minute marks the resulting solid was scraped from the edges before continuing grinding.

### Synthesis of the Substoichiometric Co-crystal (1:1 Molar Ratio)

The solid containing a substoichiometric amount of the template was synthesized by dryvortex grinding 40.7 mg of  $C_6H_2F_3OH$  along with 50.0 mg of **2,2-BPE** in a 30 mL SmartSnap Grinding Jar along with 2 ball bearings (5 mm diameter) at a 1:1 molar ratio, respectively. The molecular components were dry-vortex ground for 30 minutes where at both the 10 and 20 minute marks the resulting solid was scraped from the edges before continuing grinding.

### Synthesis of the Substoichiometric Co-crystal (0.5:1 Molar Ratio)

The solid containing a substoichiometric amount of the template was synthesized by dryvortex grinding 20.3 mg of  $C_6H_2F_3OH$  along with 50.0 mg of **2,2-BPE** in a 30 mL SmartSnap Grinding Jar along with 2 ball bearings (5 mm diameter) at a 0.5:1 molar ratio, respectively. The molecular components were dry-vortex ground for 30 minutes where at both the 10 and 20 minute marks the resulting solid was scraped from the edges before continuing grinding.

2. Powder X-ray Diffraction Diffractogram



**Figure S1.** Powder X-ray diffraction data for stoichiometric (2:1 molar ratio) co-crystal sample after a grinding experiment and before photoreaction for the resulting solid (blue) along with the theoretical pattern for  $2(C_6H_2F_3OH)\cdot(2,2-BPE)$  (orange) and 2,2-BPE (green).



**Figure S2.** Powder X-ray diffraction data for stoichiometric (2:1 molar ratio) co-crystal sample after a grinding experiment and after photoreaction for the resulting solid (blue) along with the theoretical pattern for  $2(C_6H_2F_3OH) \cdot (2,2-BPE)$  (orange).



**Figure S3.** Powder X-ray diffraction data for stoichiometric (2:1 molar ratio) co-crystal sample after a grinding experiment and after photoreaction for the resulting solid (blue) along with the theoretical pattern for **2,2-TPCB** (orange).



**Figure S4.** Powder X-ray diffraction data for substoichiometric (1:1 molar ratio) co-crystal sample after a grinding experiment and before photoreaction for the resulting solid (blue) along with the theoretical pattern for  $2(C_6H_2F_3OH) \cdot (2,2-BPE)$  (orange) and 2,2-BPE (green).



**Figure S5.** Powder X-ray diffraction data for substoichiometric (1:1 molar ratio) co-crystal sample after a grinding experiment and after photoreaction for the resulting solid (blue) along with the theoretical pattern for  $2(C_6H_2F_3OH) \cdot (2,2-BPE)$  (orange).



**Figure S6.** Powder X-ray diffraction data for substoichiometric (1:1 molar ratio) co-crystal sample after a grinding experiment and after photoreaction for the resulting solid (blue) along with the theoretical pattern for **2,2-TPCB** (orange).



**Figure S7.** Powder X-ray diffraction data for substoichiometric (0.5:1 molar ratio) co-crystal sample after a grinding experiment and before photoreaction for the resulting solid (blue) along with the theoretical pattern for  $2(C_6H_2F_3OH) \cdot (2,2-BPE)$  (orange) and 2,2-BPE (green).



**Figure S8.** Powder X-ray diffraction data for substoichiometric (0.5:1 molar ratio) co-crystal sample after a grinding experiment and after photoreaction for the resulting solid (blue) along with the theoretical pattern for  $2(C_6H_2F_3OH) \cdot (2,2-BPE)$  (orange).



**Figure S9.** Powder X-ray diffraction data for substoichiometric (0.5:1 molar ratio) co-crystal sample after a grinding experiment and after photoreaction for the resulting solid (blue) along with the theoretical pattern for **2,2-TPCB** (orange).

#### TriFOH 22BPE 100% 30min

Scan ID: TriFOH 22BPE 100percent 30 min.raw • TriFOH 22BPE 100% 30min

Scan Parameters: 3.0°/50.014°/0.01978°/114.6(s), I(p)=48520/1039, Cu(40kV,40mA), Wednesday, October 30, 2024, 8:32 AM Control File: \\VPR-MATFAB-012\data\unruh\Groeneman\20241030\TriFOH 22BPE 100percent 30 min.wrk.xml

<ul> <li>Zero Offset = 0.2189 (0.2237)</li> <li>Kα2 Peaks Present</li> </ul>	<ul> <li>Displacement = -0.2102 (0.2198)</li> <li>Kα2/Kα1 Ratio = 0.5</li> </ul>		Distance Slack = 0.0 X-Ray Polarization = 1.0			
Geometry: Diffractometer Lp	Fitted-Range: 5.0° - 50.0°	BG-Model:	Polynomial (7)	λ: 1.54	059Å (Cu)	
PSF: pseudo-Voigt Broade	ening: Individual FWHM Curve	Instrument:	LaB6 (Martin2023	3)		
Phase ID (2)	Chemical Formula	PDF-#	Wt% (	(o) DD%	6 (σ) RIR	μ
C24H16F6N2O2 (PO)	C24H16F6N2O2	C6H2F3OH_22	BPE.cif 96.4 (	0.7) 90.4	(2.0) 0.47	11.8
trans-1,2-bis((2-Pyridyl)ethylene (	C12H10N2	22-BPE.c	if 3.6 (	0.2) 9.6	(0.7) 2.37	12.1
			X	RF(Wt%): N2	0=9.7%, CO2=	223.3%

Refinement Converged (R/E=6.1), + Round=4, Iter=6, P=63, R=10.8% (E=1.77%, EPS=0.5)



Figure S10: Powder X-ray diffraction Rietveld refinement (Whole Pattern Fitting) within Jade Pro to determine the amount of the co-crystal  $2(C_6H_2F_3OH) \cdot (2,2-BPE)$  and 2,2-BPE in the diffractogram.

## 3. <sup>1</sup>H NMR Spectroscopic Data



**Figure S11.** <sup>1</sup>H NMR spectrum of the co-crystal  $2(C_6H_2F_3OH) \cdot (2,2-BPE)$  before the [2 + 2] cycloaddition reaction (400 MHz, DMSO-*d*<sub>6</sub>).



**Figure S12.** <sup>1</sup>H NMR spectrum of the stoichiometric (2:1 molar ratio) solid after dry-vortex grinding along with 50 hours of UV exposure resulting in a 97% yield for the [2 + 2] cycloaddition reaction (400 MHz, DMSO- $d_6$ ).



**Figure S13.** <sup>1</sup>H NMR spectrum of the substoichiometric (1:1 molar ratio) solid after dry-vortex grinding along with 75 hours of UV exposure resulting in a 98% yield for the [2 + 2] cycloaddition reaction (400 MHz, DMSO- $d_6$ ).



**Figure S14.** <sup>1</sup>H NMR spectrum of the substoichiometric (0.5:1 molar ratio) solid after dry-vortex grinding along with 40 hours of UV exposure resulting in a 97% yield for the [2 + 2] cycloaddition reaction (400 MHz, DMSO- $d_6$ ).

4. Pictures of the Experimental Setup for the Dry-Vortex Grinding



Figure 15. Picture of the 30 mL SmartSnap Grinding Jar.



Figure 16. Picture of the glass plates for UV exposure.



Figure 17. Picture of the dry-vortex grinding of the components.