'Sacrificial' Supramolecular Assembly and Pressure-Induced Polymerization:

Toward Sequence-Defined Functionalized Nanothreads

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Supporting Information

Materials and Methods

1. Co-Crystal Synthesis and Structure Characterization

Phenol (\geq 99%, reagent grade, solid) and pentafluorophenol (\geq 99%, reagent grade, low-melting solid) were purchased from Sigma-Aldrich and used as distributed for co-crystal growth. Phenol and pentafluorophenol were added in equimolar amounts to a glass vial with room temperature 95% hexanes (ethanol also acted as an appropriate solvent for co-crystal formation; we report herein the structure solved with hexanes). The solvent was slowly evaporated to grow solid, white crystal tendrils. During co-crystal formation, an N95 mask was used to avoid excessive inhalation of phenol. No unexpected hazards occurred in the handling of the co-crystal. X-Ray Diffraction (XRD) was performed to confirm co-crystal formation.

The ambient pressure co-crystal structure was solved using XRD at ambient pressure with a Rigaku Microfocus Micromax 007 X-Ray Generator and Saturn 944+ CCD Detector at 293 K using graphitemonochromated Mo K α 1 radiation (λ =0.71073 \dot{A}) with specified parameters for data collection illustrated in Table S1. Structure solution and refinement were completed using ShelXT¹ using intrinsic phasing and ShelXL,² respectively, in the Olex2 graphical user interface.³ All non-hydrogen atoms were identified from the difference Fourier map and refined anisotropically. All hydrogen atoms were placed in calculated positions and refined using isotropic thermal parameters.¹⁻³ The co-crystal illustrated a monoclinic crystal structure with unit cell parameters that do not match the constraints of the reported crystal structures of phenol or pentafluorophenol.^{4,5} π - π stacking distances dominate the structure as held with hydrogen bonded distances as noted in Table S2 and S3. The ORTEP structure with 50% thermal ellipsoids is in Figure S1.

CCDC Code	1980178
Empirical Formula	$C_{36}H_{21}F_{15}O_6$
Formula Weight	834.53
Temperature (K)	298.15
Crystal System	Monoclinic
Space Group	Cc
a/Å	7.4348(6)
b/Å	23.1324(18)
c/Å	20.2671(16)
α/°90	90
β/°90	90.3770(10)
γ/°90	90
Volume/Å ³	3485.6(5)
Ζ	4
$\rho_{calc}g/cm^3$	1.590
μ/mm ⁻¹	0.160
Radiation MoK _α	$(\lambda = 0.71073)$
2 θ range for data collection/°	3.522 to 49.998
Reflections collected	12695
Independent reflections	$[R_{int} = 0.0235, R_{sigma} = 0.0360]$
Data/restraints/parameters	6051/2/521
Goodness-of-fit on F ²	1.028
Final R indexes	$[I \ge 2\sigma(I)]$ R1 = 0.0333, wR2 = 0.0800
Final R indexes	[all data] $R1 = 0.0446$, $wR2 = 0.0876$

Table S1. Crystallographic Data Collection Parameters of Phenol:Pentafluorophenol Co-Crystal

Table S2. $\pi - \pi$ Stacking Distances within Phenol:Pentafluorophenol Co-Crystal

Centroid #	Centroid Atom Labels	$\pi - \pi$ Stacking Distance, Centroid to Centroid (Å)
1:2	O1:O2 (C1-6:C19-24)	3.729
2:1	O2:O1 (C19-24:C1-6)	3.735
3:5	O3:O5 (C7-12:C25-30)	3.664
5:3	O5:O3 (C25-30:C7-12)	3.790
4:6	O4:O6 (C13-18:C31-36)	3.672
6:4	O6:O4 (C31-36:C13-18)	3.801

Oxygen Labels	H-Bonding Distances
	(Å)
01-06	2.846
01-05	2.775
02-03	2.756
02-04	2.787
03-06	2.731
04-05	2.801

Table S3. H-Bonding Distances within Phenol:Pentafluorophenol Co-Crystal



Figure S1. ORTEP with thermal ellipsoids set at 50% for 1:1 phenol:pentafluorophenol co-crystal.

2. Compression of Co-Crystal C₆H₅OH:C₆F₅OH using *in situ* Raman Spectroscopy

High-pressure experimentation was facilitated using *in situ* Raman in a diamond anvil cell (DAC) to jointly measure ruby fluorescence in conjunction to changes in chemical functionality throughout compression. All *in situ* high pressure work in addition to final product characterization in the gasket did not pose any unexpected safety concerns. To allow for *in situ* Raman, stainless steel gaskets were prepared for a symmetric DAC equipped with type IIA diamonds with a 400 μ m culet. The stainless-steel gaskets were pre-indented between 45-55 μ m and drilled to 100 μ m in diameter using an electric discharge machine (EDM) or laser drilling⁶ to serve as the sample chamber. To load the low-melting co-crystal in the DAC, the solid crystal was cooled in the fridge, ground using a mortar and pestle, and placed on the lower diamond within the gasket. A ruby chip was added to the sample chamber to monitor the pressure using fluorescence that indicated a quasi-hydrostatic pressure environment.⁷ The DAC was closed to form a powder sample appearance by applying 2.0 GPa of pressure.

All Raman spectra were acquired on a Renishaw inVia Raman spectrometer and microscope with a 633 nm laser excitation source of 1.34 mW of power. A 5 μ m pinhole was used to cut out excess light scattering from the mirrors and external cavities. A long-pass 20x objective of 0.35 NA was utilized in order to focus on the sample through the diamonds. For *in situ* experimentations, the DAC was equipped with a double-membrane gas controller in order to control the rate of slow compression. Compression proceeded over the course of 16 hours to a maximum pressure of 24 GPa. The compression rate slowed upon the incidence of a photoluminescent (PL) background at 11 GPa to 2-3 GPa/hour and again slowed above 17 GPa to less than 1 GPa/hour. The decompression rate progressed over the course of 16-18 hours with similar rates on the descent. *In situ* Raman spectroscopy is illustrated in Figure 2.

3. Compression of Individual Co-Crystal Components

Each individual co-crystal component was slowly compressed maintaining the rates and final pressures as utilized for the co-crystal compression. Pentafluorophenol illustrated a decrease in precursor Raman signal upon compression (Figure S2) and yielded few grains of solid stuck in the gasket with a large ruby crystal. Upon removal of the gasket, the crystallites sublimed to produce small unrecoverable amounts of solid, resulting in no data being collected to test for nanothread formation.

Phenol did illustrate some reactivity, but likely requires a higher pressure for nanothread formation as strong signals of precursor remained (Figure S2), and no new peaks emerged from the PL background (such as sp³ carbon). The sample changed to a yellow-clear solid upon compression indicative of partial reactivity at the pressure of 24 GPa. However, for phenol we have little evidence of any crystalline order to indicate a glassy/amorphous solid, even under slow compression. From both single component compressions, we do not observe nanothread formation from *in situ* Raman spectroscopy of the recovered sample. While

higher pressures and use of temperature might force a reaction to occur, the results suggest that co-crystal design can combat sluggish reactivity and more harsh conditions (e.g., higher pressure/temperature).



Figure S2. Raman spectra of phenol (black) and pentafluorophenol (red) during compression. The resultant products are indicated to the right; small crystallites are observed using pentafluorophenol as a reactant, while glassy amorphous striations result from phenol.

Table S4 compares the Raman mode peak assignments of the individual components to the co-crystal under pressure to illustrate the vibrational differences between components once introduced into a cocrystal. We note that many peaks for pentafluorophenol were covered by ruby signals or diamond, but we note that strong fluorine stretching serves the best purpose of arguing for a candidate co-crystal structure upon compression. For the individual components, each spectrum was compared to a known standard as compiled from BioRad's Raman spectral database.⁸ We note that in comparison to the individual components, our new co-crystal experiences new peaks in addition to shifts in wavelengths (energy) due to new vibrational allowances within the crystal lattice.⁹

Peak Assignments	5.0 GPa C₄H₅OH	5.0 GPa C₅F₅OH	5.0 GPa C ₆ H ₅ OH: C ₆ F ₅ OH
C–C aliphatic	247 m	283 vw	263 vw
C-F out-of-plane bending	N/A	411 m	393 m
C-C-C in-plane bending	451 vw, 507 w	465 m	457 m
Ring breathing	538 s	592 s	574 vs
C-C-C in-plane bending	622 s	619 vw	624 m
Intramolecular ring	N/A	N/A	713 vw
Hydrogen bonding	757 w, 816 s, 835 s	917, w, b	817 s
Ring breathing	1002 vs	924 w, b	1007 vs
C–H out of plane vibration	1029 vs	N/A	1037 m
C–H out of plane vibration	1074 w	N/A	1084 vw
Phenol O-H	1158 m	1172 w	1178 w
C-H in-plane bending	1171 w	N/A	1181w
C-H/C-F in-plane bending	1257 m	-	1227, 1266
C–O out of plane vibration	1481 m	-	1495 vw
C–O in-plane bending	1505 vw	-	1528 vw, 1568 vw
C–C stretching	1600 m	-	1607 w, 1678 w
O–H broad stretching	-	-	1800 vw, b
Diamond Absorbance	2189-2736, vvs	2189-2736, vvs	2189-2736, vvs
Doubly degen. C-H stretching	2997 w, 3026 w	-	-
Totally sym. C–H in phase	3189 s	-	3100 m
Doubly degen. O-H stretching	-	-	3206 vw
O-H stretching	-	-	3252 vw

Table S4. Raman Mode Peak Assignments of Individual Components and Co-Crystal

Note: - denotes a lack of anticipated vibrational stretching (signal covered by ruby or amorphous material) vs = very strong; s = strong; m = medium; w = weak; vw = very weak

4. Polarized Light Microscopy on Recovered Material

A compressed gasket of the 1:1 Ar/ArF polycrystalline co-crystal sample was analyzed under polarized light in order to analyze birefringence (Figure S3). An Olympus BX62 microscope was used, equipped with a blue-field correction plate and focused on samples with a 20x objective. Compressed powder samples witnessed a vague tan-orange color that interfered with birefringent image collection. A 530 nm half wave-plate was utilized in order to enhance the polarization images for a shifted viewing to more easily facilitate colors to the eye. The sample was turned to at a set angle to illustrate specific regions of brighter white/orange in the polarized light images and brighter blue/teal in the 530 nm filter images indicate greater crystalline order. As illustrated, multiple regions of the sample illustrate prominent birefringence due to

these colors and often appear brighter at one specific tilt angle, indicating axial crystalline order, as may be present in a hexagonally packed sample.



Figure S3. Polarized light images with and without a 530 nm waveplate of the Ar/ArF co-crystal after compression as adhered in a stainless-steel diamond anvil cell gasket. The gasket was tilted in order to illustrate the crystalline striations occurring across the sample and high birefringence at certain angles, supporting a hexagonally packed crystal as common for nanothreads.

5. Synchrotron X-ray Diffraction (XRD) on Recovered Sample

XRD utilizing synchrotron radiation was performed at the Advanced Photon Source (APS) in Argonne National Lab on a recovered polycrystalline sample from compressed co-crystal. A 30 keV 5x5 μ m focused beam was used at the 16-BM-D beamline for powder diffraction experiments with a MAR345 area detector. Three regions were probed in a recovered gasket sample by collecting wide-angle reflections of $\pm 32^{\circ}$ ω scans with 10 sec./deg. of exposure over a 75 μ m square area. Data interpretation was performed using the Dioptas software program with corrections from the absorptions of the diamonds and shadows from the gasket edge.¹⁰ The final hexagonally packed co-crystal pattern was achieved after slow compression and decompression to illustrate a highly crystalline product indicative of nanothread formation (Figure 4).

6. Infrared Spectroscopy (IR) of Co-crystal Precursor and Recovered Nanothread

An IR absorption spectrum for the co-crystal was calculated with density functional theory using the PBE exchange-correlation functional implemented in Quantum Espresso packages.^{11,12} The self-consistency threshold for the vibrational frequencies calculation was 10-16 Ry. The acoustic sum rules were imposed in order to correct the negative acoustic modes wing to finite plane-wave cutoff. A comparison of the experimental IR spectrum to the theoretical prediction (Figure S4) illustrates a close match, alluding to co-crystal formation.

Infrared spectroscopy (IR) was obtained using a Bruker Hyperion 3000 Microscope for samples in the gasket to achieve a diffraction limited spatial resolution of three 10 µm spots in each gasket. An MCT detector was used in order to acquire the transmission spectra images after focusing on a single point of interest. Attenuated Transmission (ATR) Spectroscopy was performed on the solid co-crystal sample using an FTIR Bruker Vertex V70 with an ATR attachment sampling accessory. The widths of the peaks after compression are broader indicating some possible amorphous character. The peak assignments are found in Table S5 to compare the co-crystal sample before and after compression.



Figure S4. Acquired co-crystal IR spectra (red) compared to calculated vibrational frequencies (black).

Before Compression	After Compression	Peak Assignment
-	3664	Free O–H
3446	3418	H-Bonded O-H Stretching
3205	3224 (shoulder)	Sp ² -hybridized C-H
-	2956 (shoulder)	Sp ³ -hybridized C-H
-	1717	C=O stretching
1599	1621 (shoulder)	C=C Bending
1520, 1476	1520, 1500	C-H bending
1373, 1346,	1318, 1360	C-F stretching
1245	1237	O-H bending
1209	-	C–F bending
1150	1158	Secondary C-(OH)
1076, 1011	-	C-O Alcohol Stretching
995, 976	998	Monosubstituted Alkene
894	914	Tertiary C-(OH)
809	-	C-H Disubstituted Bending
756, 691	759, 699	C=C Alkene Disubstituted (cis) Bending
612, 536, 506, 451	-	Benzene derivative/Fingerprint

Table S5. IR Spectral Peak Assignments of Co-Crystal Prior to and After Compression

7. X-ray Photoelectron Spectroscopy (XPS)

XPS was conducted using a Physical Electronics VersaProbe II on a gasket sample approximately 45 μ m in thickness. A monochromatic Al K X-ray source was used with a concentric hemispherical analyzer. Low-energy electrons of less than 5 eV and argon ions were utilized in order to neutralize charge. The measurements were made at a takeoff angle of 45 degrees to the sample surface to give a sampling depth of 3-6 nm with a standard quantification comparison to a poly(vinylpyrrolidone) reference. Some silicon was observed in the survey scan (<0.1%), corresponding to PDMS with a full-width-half-max (FWHM) of 1.45 at 102.02 eV, consistent with siloxanes from proximal sources in the laboratory (Figure S5).¹³



Figure S5. Survey scan XPS spectra to depict elemental composition of final compressed sample.¹⁶

A high F/C ratio of 1.0 and an O/C ratio of 0.4 is theorized if the nanothread comprises equal amounts of hydrogenated and fluorinated rings, while maintaining the hydroxyl groups (Table S6). However, a lower F/C content of 0.89 is observed in the survey scan, with a consistent O/C ratio of 0.41 indicative of preservation of O-atoms within the nanothread. The lower F/C content may indicate the loss of HF as observed in compression of the benzene/hexafluorobenzene co-crystal.^{14,15} Additionally, perfluorinated polymers can release HF overtime,¹⁷ which may occur at fragile breaking points of residual C=C moieties.

High-resolution spectra were collected of C 1s, F 1s, and O 1s (Figure S6) on the recovered gasket sample to determine relative stoichiometric amounts of each functionality. To acquire quantified data for the high-resolution C 1s spectra, a hydrocarbon peak (CH_x%) was fitted at 284.7 eV. In the spectra, a FWHM of 1.88 eV was set to be uniform for each component in order to quantify the functionality present in the broad spectra as common in polymeric samples.¹⁴ The percentages determined for hydrogenated carbon backbones (e.g., (CH_x), C–O, C=O/C–F, and O–C=O) are highlighted in Table S3. The CH_x is higher than anticipated at 58.8% rather than 41.6%, which can be explained by a skewed F 1s spectra, in which 9.1% of the fluorine is released from the backbone rather than remaining bound. The F 1s high-resolution spectra contains two peaks at 687.3 eV and 684.7 eV with a FWHM of 2.45 eV. As a result, fluoride ions were likely released during compression, which skews the anticipated C/F ratio for the thread.



Figure S6. High-resolution O1s, F1s, and C1s XPS spectra.

The O1s spectra were set to have an equal FWHM of 2.1 eV. The peak could be interpreted as only exhibiting a C–O peak with a FWHM of 2.6 eV, but theC 1s spectrum indicates there are most likely carbonyl groups present in the structure. Upon the addition of carbonyl peaks, the FWHM is reduced by nearly 0.5 eV and the following percentages were obtained (Table S6), with an 82.3% of C–O continually dominating the spectrum as expected. The presence of such a high ratio of carbonyl peaks attributed to fast keto-enol tautomerization (Figure S7).

Survey Scan	C1s%	F1s%	O1s%	
% Theory	41.6	41.6	16.8	
% Calc.	43.4	38.7	17.9	
C1s	CH _x %	С-О%	C-O/C-F%	O-C-O%
% Theory	41.6	16.6	16.8	0
% Calc.	58.8	12.4	25.6	3.3
eV	284.7	286.2	287.6	288.8
·		•	· ·	
O1s	C-0%	C=0%	O-C=0%	
% Theory	100	0	0	
% Calc.	82.3	4.2	13.5	
eV	532.8	532.2	532.1	
·		•		
F1s	C-F%	F-%		
% Theory	100	0		
% Calc.	90.9	9.1		
eV	687.3	684.7		

Table S6. Calculated and Observed Relative Percentages of Survey Scan and O1s, F1s, and C1s from XPS



Figure S7. Representative cycloadduct that can promote keto-enol tautomerization during nanothread formation. This is a key feature in the final nanothread product as illustrated by C=O and prominent C=C stretching in the IR spectrum.

8. Theoretical Investigation of [4+2] Cycloaddition Barriers

Geometries were optimized using density functional theory (DFT) with the B3LYP functional¹⁸ and the 6-31G(d) basis set.¹⁸⁻²¹ Harmonic vibrational analyses were performed at the same level of theory to verify the optimized structures being minima or transition states. Calculations were done with the Gaussian 09 suite²² of programs.

The onset pressure (Table S7) – indicated by a substantial increase in the Raman background fluorescence – for forming our Ar/ArF co-crystal nanothreads (12 GPa) is lower than that for benzene or hexafluorobenzene nanothreads (17 GPa and >25 GPa, respectively). One may argue that the alternating electron-rich and -poor Ar ring stacks in our co-crystal, as favored by the quadrupole-quadrupole-like interaction, decreases the separation between neighboring rings and may favor the initiation reaction (e.g., [4+2] cycloaddition) for the polymerization into nanothreads, resulting in a lower reaction pressure.

Precursor	Onset pressure (GPa)	1 atm [4+2] cycloaddition barrier (kcal/mol)
C_6H_6	17 ^a	68
$C_6H_6C_6F_6$	>25 ^b	58 and 60 ^{<i>c</i>}
C ₆ H ₅ OH ₂ C ₆ F ₅ OH	11	57–66 ^d

Table S7. Polymerization onset pressure and reaction barriers for different organic molecular precursors

^{a.} Li et. al. J. Am. Chem. Soc. 2017, 139, 16343.

^{b.} The co-crystal remains molecular (no polymerization) up to 25 GPa at room temperature; an amorphous material was formed above 25 GPa (*J. Phys. Chem. C* **2016**, *120*, 29510).

^{c.} Only two isomers of the transition state, 58 kcal/mol for ArF as diene, 60 kcal/mol for Ar as diene.

^d Many isomers of transition state, with energies ranging from 57 to 66 kcal/mol relative to isolated reactant molecules.

While the above argument seems reasonable for the hydroxy-substituted co-crystal, a benzenehexafluorobenzene co-crystal does not follow this trend. In addition, the benzene-hexafluorobenzene polymerizes at a higher pressure into a graphene-like product but with a lower calculated barrier than either of the two molecular components.

The computed geometries for the transition states of [4+2] cycloadditions between various Ar rings are shown in Figure S8.



Figure S8. Transition state structures and energies of [4+2] cycloadditions, computed at B3LYP/6-31G(d) level of theory.

To enumerate the transition state isomers of [4+2] cycloaddition between pentafluorophenol and phenol, we considered two cases corresponding to the ArF ring participating either as the diene or dienophile in the cycloaddition reaction. For each case, –OH groups were constructed to each fluorinated and nonfluorinated transition state (TS) for each enumerated possibility for a benzene:hexafluorobenzene co-crystal. For each ring, there are six positions on each ring to which the –OH group can be attached, enumerated to a total of 6*6 = 36 isomers of the TS. Since the parent, non-OH-substituted TS has a mirror plane symmetry, half the 36 isomers of the –OH-substituted TS are enantiomers to simplify the TS possibilities to only 18 diastereomers for each TS case of a ring acting as the diene or dienophile. Thus, in our calculations, 18 + 18 = 36 diastereomers of the TS were considered.



Figure S9. (Left) The [4+2] cycloaddition transition states of hexafluorobenzene with benzene, with the ring positions labeled. (Right) Two cycloaddition TSs of pentafluorophenol with phenol, constructed by -OH substitution at positions 1 and 1' of the corresponding TSs on left.

The computed energies of the 36 transition states ranged from 57 to 66 kcal/mol (Table S7). A histogram of the distribution of 36 TS energies is shown in Figure S10. The transition states in which ArF acts as dienophiles appear on the lower energy side, indicating that the [4+2] cycloaddition favors pentafluorophenol as dienophile and phenol as diene, which is consistent for conventional electron-demand of a Diels-Alder cycloaddition to favor for an electron-rich diene with an electron-poor dienophile.



TS energy (kcal/mol) histogram

Figure S10. Histogram of cycloaddition TS energies. 36 entries in total, bin size = 1 kcal/mol.

Inspection of the optimized transition state structures (the two lowest and highest energy structures are shown in Figure S11) confirms that favorable transition states serve for phenol to react as the diene and pentafluorophenol as the dienophile with the –OH substituted carbons not participating in bond formation. Highly unfavorable transition states have the phenol counterpart acting as the dienophile while additionally possessing –OH substitution within the formed bond.



Figure S11. The two lowest energy and highest energy [4+2] cycloaddition transition states of phenol with pentafluorophenol.

9. Theoretical Investigation of the Crystallographic Packing of Nanothreads

To obtain a crystal structure of packed co-crystal nanothreads, one needs to decide on (1) the thread type, such as polytwistane and thread (3,0), (2) the substitution pattern arrangement for the on a given thread skeleton, and (3) how individual threads pack in the crystal. Since each of the above three items can have infinite possibilities, we only considered a few representative ones for each item. The goal here is not to identify the exact structure and packing of the threads in the synthesized sample, but to obtain a representative set of structures and packings to compare to the simulated *d*-spacings in the diffraction pattern with experimental values. We aim to provide support for the suggestion that nanothreads were synthesized from the co-crystal.

One assumption here is that the Ar and ArF rings are always alternating along the threads owing to quadrupolar interactions and preorganization, as they are in the co-crystal stacks, thus prohibiting any adjacent Ar or ArF rings. A second assumption for our simulations is that the –OH groups remain intact after polymerization. Geometry relaxations of the crystal packings were performed using the plane-

wave/pseudopotential approach with the VASP program.²³ The PBE exchange-correlation functional, ^{24,25} and the projector-augmented wave method were used. ^{26,27} Dispersion correction was included by the Becke-Jonson damping DFT-D3(BJ) method of Grimme *et al.*^{28,29} The energy cutoff for the plane-wave basis was set to 600 eV. A 0.2 eV Gaussian smearing and a k point mesh of 0.5 Å⁻¹ were used.

To first consider the thread type and substitution pattern, two representative thread types, polytwistane and thread (3,0), were considered. As to the substitution pattern for the –OH groups, we considered one for the polytwistane type with a helical arrangement of the –OH groups and three for thread (3,0) containing eclipsing –OH groups, 60-degree zig-zag arrangement of the –OH groups, and multiple threads with different arrangements of the -OH groups (Figure S12).



Representative Crystallographic Packings

Figure S12: Representative crystallographic packings of the polytwistane and thread(3,0) packings simulated, with their respective unit cells and structured inter/intra-thread hydrogen-bonding.

The thread **polytwistane-1** has a helical arrangement of –OH groups, which forms a linear H-bond chain. The H-bond distances are 1.86 Å and 2.50 Å. The thread (3,0) structure with eclipsing –OH groups (**thread(3,0)-eclipsed**) has the strongest intrathread bonding, as reflected by the short O–H…H distances.

Note that the –OH groups are not in perfectly eclipsed form; they are apart by about 20 degrees. The oxygen lone-pair repulsion, although mitigated substantially by hydrogen bonding, is likely the cause for the non-perfect eclipse. In addition, the hydrogen bonds would be destabilizing if the OH groups were perfectly eclipsde. **Thread(3,0)-gauche** does not have intra-thread H-bond because the neighboring –OH groups are 60 degrees apart. Also notice in this thread structure, the –OH groups avoid being perfectly eclipsed with the –F substituents due to lone-pair repulsion.

Once we have the structures of individual threads, we then proceed to pack them into crystals. The choices needed to be made here are: (1) how many threads per unit cell, and (2) if multiple threads per unit cell, what are the *relative orientation angle* and *axial offset* (Figure S12). Consider the case of a two-thread unit cell, the relative orientation angle is the angle need to be rotated about the thread axis for the second thread to have the same orientation as the first thread. Axial shift measures the distance (relative to the unit cell length) shifted by the second thread along the thread direction relative to the first thread. In this particular case at bottom of Figure S13, an axial shift of 0.5 (meaning shifted by half unit cell) aligns the Ar rings in first thread with the ArF rings in the second thread, which may be favored electrostatically.



Figure S13. Relative orientation angle and axial offset within simulations.

Table S8 shows the six packings investigated for the two thread types. The relative orientation angle and axial shift listed in the table are the initial values for the initial geometry of the packing of threads in the crystal. Relaxation in calculation may result in small changes of these initial values.

Thread	-OH Substitution Pattern	Packing Details
		• One thread per unit cell
Polytwistane	helical arrangement	• Two threads per unit cell
		• Relative orientation angle =0
		• Axial shift = 0.5
		• Two threads per unit cell
		• Relative orientation angle = 180
		• Axial shift = 0.5
	eclipsing arrangement	• 3 x 2 = Six threads per unit cell
		• Relative orientation angles = 6- &
Thread(3,0)		120
		• Axial Shift = 0.5 & 0.5
		• Two threads per unit cell
-	gauche arrangement	• Relative orientation angle = 180
		• Axial shift = 0.5
		• Twelve threads per unit cell
	multiple arrangements	• Similar H-bond network as the
		precursor co-crystal

Table S8. Crystallographic Packing Details of the Thread Types Studied

The relaxed packing of the polytwistane-type threads (Figure S14) shows no inter-thread H-bond for the one-thread-per-unit-cell packing, and only one inter-thread H-bond between the two threads within the unit cell for the second packing. The H-bond in **polytwistane-1-pack-2** may not be obvious, but notice the hydrogens sticking out from the thread across the border of the unit cell where the H-bond is. The eclipsing arrangement of the –OH groups of the thread (3,0) type was intended to form dimer and trimer-like inter-thread H-bonding for the two packing by orienting the –OH groups towards each other (Figure S15). Only the dimer-like packing has inter-thread H-bonding after relaxation.







Figure S15. Two different packings for the thread (3,0) type threads with eclipsing –OH groups. Two views are shown.

For the gauche arrangement of the –OH groups of the thread(3,0) type, we intended to form dimer-like H-bonds between the two threads in the unit cell, but the relaxed structure shows weak inter-thread H-bonding with H–O…H distances of 2.3 and 2.7 Å (Figure S16).



Figure S16. One packing for the thread (3,0) type threads with gauche arrangement of the -OH groups. Two views are shown.

Thread(3,0) (from co-crystal) was constructed with the intention to preserve the same H-bonding network as in the precursor co-crystal. Thus, the –OH groups in individual threads are either eclipsing, gauche, or 120 degrees apart. The relaxed structure shows a very similar H-bonding network (Figure S17).



Figure S17. One packing for the thread (3,0) type threads with similar H-bond network as in the precursor cocrystal.

The above packings were simulated in the SingleCrystal software program as an odd-on feature to Crystal Maker. Simulations of the representative crystallographic packings were performed looking down the thread axis of the presumed Ar/ArF stacks with each *d*-spacing of the correlated reflection, with the wavelength set to 20 keV (Figure S18).



Representative Crystallographic Packings

Figure S18. Representative simulated diffractions of polytwistane and thread(3,0) packings, with the denoted hkl of the most intense reflections noted for each simulation.

To compare the *d*-spacings of the simulated diffraction spots for above packed threads with the experimental values (Figure 4), we accounted for 1-3% thermal contraction from two different sets of experimental *d*-spacings. The two sets of experimental *d*-spacings originated from a polycrystalline (six-fold diffraction spots/arcs) and a powder sample (diffraction ring). The experimental resulting ranges after 1-3% thermal contraction (the black bars in Figure) of the polycrystalline sample matches well the calculated *d*-spacings (at 0 K) for the **thread(3,0)-eclipsed-B** packing, and the ranges of the powder sample match closely to the two polytwistane packings and the thread (3,0) packing derived from precursor co-crystal. The *d*-spacings for other packings do not match the experimental ranges that well, but at least one of the three *d*-spacings falls in the experimental range.

Polytwistane and thread(3,0), two representative fully-saturated thread structures, with chosen packings can match in terms of the *d*-spacings to the experimental data. These packing calculations suggest that nanothreads have been synthesized from the current co-crystal. Other types of threads (e.g., zipper threads or degree-4 threads) may well be present, but the *d*-spacings for those threads are expected to be in similar range as the *d*-spacings for threads considered thus far. Other thread types are the subject of ongoing studies.

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