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Photomechanical Molecular Crystals and Nanowire Assemblies Based on the [2+2] Photodimerization of a Phenylbutadiene Derivative

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Methods

Single Crystal Structure Determination by X-Ray Diffraction (XRD)

(A) For (E)-4FCM monomer: Diffraction data were collected on a Bruker-AXS Apex II diffractometer with an Apex II CCD detector using Mo K_{α} radiation ($\lambda = 0.71073$ Å) from a fine-focus sealed tube source. Data were collected at 100 K by performing 0.5° ω -scans, integrated using SAINT, and absorption corrected using SADABS. The structure was solved by direct methods using SHELXT and refined against F^2 on all data by full-matrix least squares with SHELXL-2018/3 following established refinement strategies. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to. Crystal and data quality details, as well as a summary of the residual refinement values, are listed in the accompanying table. Compound cb77ft crystallizes in the triclinic centrosymmetric space group P-1 with one molecule of cb77ft per asymmetric unit.

Table S1. Crystal data and structure refinement for cb77ft.

Identification code	cb77ft			
Empirical formula	C12 H7 F N2			
Formula weight	198.20			
Temperature	100(2) K			
Wavelength	0.71073 Å			
Crystal system	Triclinic			
Space group	P-1			
Unit cell dimensions	a = 6.2669(4) Å	$= 96.746(3)^{\circ}.$		
	b = 8.0255(5) Å	$= 98.691(3)^{\circ}.$		
	c = 9.8682(6) Å	$=90.723(3)^{\circ}.$		
Volume	486.99(5) Å ³			
Z	2			
Density (calculated)	1.352 Mg/m ³			
Absorption coefficient	0.096 mm ⁻¹			
F(000)	204			
Crystal color	yellow			
Crystal size	0.234 x 0.189 x 0.110 n	0.234 x 0.189 x 0.110 mm ³		
Theta range for data collection	2.103 to 30.996°	2.103 to 30.996°		
Index ranges	$-9 \le h \le 9, -11 \le k \le 9$	$-9 \le h \le 9, -11 \le k \le 11, -14 \le l \le 14$		

Reflections collected	15064
Independent reflections	3100 [R(int) = 0.0290]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3100 / 0 / 136
Goodness-of-fit on F ²	1.048
Final R indices [I>2sigma(I) = 2415 data]	R1 = 0.0423, wR2 = 0.1115
R indices (all data, ? Å)	R1 = 0.0593, wR2 = 0.1240
Extinction coefficient	n/a
Largest diff. peak and hole	0.448 and -0.193 e.Å ⁻³

(B) For photodimer: Diffraction data were collected on a Bruker-AXS Apex II diffractometer with an Apex II CCD detector using Mo K_{α} radiation ($\lambda = 0.71073$ Å) from a fine-focus sealed tube source. Data were collected at 100 K by performing 0.5° @-scans, integrated using SAINT, and absorption corrected using SADABS. The structure was solved by direct methods using SHELXT and refined against F^2 on all data by full-matrix least squares with SHELXL-2018/3 following established refinement strategies. All nonhydrogen atoms were refined anisotropically. All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups). Crystal and data quality details, as well as a summary of the residual refinement values, are listed in the accompanying table. Compound cb79ft crystallizes in the monoclinic centrosymmetric space group $P2_1/c$ with half of one molecule of cb79ft per asymmetric unit. The para-fluorophenyl group exhibited disorder that was modeled over two positions; the disorder ratio was refined freely and converged at 84:16. This disorder was refined with the help of similarity restraints on 1,2- and 1,3- distances; similarity and rigid-bond restraints on anisotropic displacement parameters; and flatness restraints on the aromatic rings. The anisotropic displacement parameters of the ipso- and ortho- carbons were constrained to be equivalent.

Table S2. Crystal data and structure refinement for cb79ft.

Identification code	cb79ft
Empirical formula	C24 H14 F2 N4
Formula weight	396.39
Temperature	100(2) K

Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 7.4702(2) Å	= 90°.
	b = 13.0779(4) Å	= 96.4927(17)°.
	c = 10.3353(3) Å	= 90°.
Volume	1003.23(5) Å ³	
Ζ	2	
Density (calculated)	1.312 Mg/m ³	
Absorption coefficient	0.093 mm ⁻¹	
F(000)	408	
Crystal color	colourless	
Crystal size	0.255 x 0.103 x 0.037 mm ³	
Theta range for data collection	2.522 to 30.505°	
Index ranges	-10 <= <i>h</i> <= 10, -18 <= <i>k</i> <= 18, -14 <= <i>l</i> <= 14	
Reflections collected	19369	
Independent reflections	3067 [R(int) = 0.0328]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3067 / 317 / 182	
Goodness-of-fit on F ²	1.024	
Final R indices [I>2sigma(I) = 2415 data]	R1 = 0.0398, wR2 = 0.1009	
R indices (all data, 0.70 Å)	R1 = 0.0557, wR2 = 0.1097	
Largest diff. peak and hole	0.391 and -0.188 e.Å ⁻³	

(C) Calculation of positions of diffraction spots for 4FCM nanowires in AAO template

We first define a Cartesian coordinate system, wherein the z-axis is parallel to the incident X-rays, and the y-axis represents the sample rotation axis, such that the x-y plane is parallel to the detector. Considering first the case that $\Phi = 0$, then the y-z plane represents the sample surface, while the xaxis points along the sample surface normal. We then define the direction of the unit normal to a given crystallographic plane as $\mathbf{n}_0 = [\sin\sigma, \cos\sigma\cos\alpha, \cos\sigma\sin\alpha]$, where σ is the elevation angle of **n** from the sample plane, and α the azimuthal orientation. Since nanowires have a strongly preferred out-of-plane orientation, this defines a unique choice of σ for a given crystal plane and choice of crystal orientation direction. However, different nanowires may take on different values of α . As the sample is rotated by an angle Φ in the counterclockwise direction around the y-axis, **n** is transformed using a rotation matrix as

$$\mathbf{n} = \begin{bmatrix} \cos\Phi & 0 & \sin\Phi \\ 0 & 1 & 0 \\ -\sin\Phi & 0 & \cos\Phi \end{bmatrix} \mathbf{n}_0.$$

For a given value of Φ (here, 2°), a crystal plane satisfies the Bragg equation only when $\cos^{-1}(\mathbf{n}\cdot\mathbf{z}) = 90^{\circ} - \theta$, with θ representing half of the total scattering angle 2 θ . Solving for α , and then calculating its projection onto the x-y plane yields the expected orientation of the diffraction spot relative to the film plane on the 2D WAXS pattern. If there is no solution for α for a given crystal plane, there will be no corresponding reflection on the detector.



Fig. S1. IR spectrum of (*E*)-**4FCM**. IR (KBr): $v^{\sim} = 2227$ (m), 1599 (s), 1586, 1560, 1510, 1240, 1163, 980, 827, 523 cm⁻¹.



Fig. S2. ¹H-NMR spectrum of (*E*)-**4FCM**, DMSO-6d as solvent. The insert shows the magnified region from 7.2 ppm to 8.3 ppm. The multiple peaks at 2.5 ppm are due to DMSO-6d, and the large multiple peaks at around 3.33 ppm are due to water.



Fig. S3. ¹³C-NMR spectrum of (*E*)-4FCM, DMSO-6d as solvent, the DMSO-6d solvent peaks at 39.52 ppm are not shown here for clarity.



Fig. S4. IR spectrum of **4FCM** photodimer. IR (KBr): $v^{\sim} = 2236$ (m), 1604, 1511, 1225, 1164, cm⁻¹.



Fig. S5. ¹H-NMR spectrum of **4FCM** photodimer, acetone-6d as solvent. The insert shows the magnified region from 4.4 ppm to 8.5 ppm. The multiple peaks at 2.05 ppm are due to acetone-6d, and the double peaks at around 2.85 ppm are due to water.



Fig. S6. ¹³C-NMR spectrum of **4FCM** photodimer, acetone-6d as solvent, the multiple peaks at 29.84 and 206.26 ppm are due to acetone-6d solvent peaks.



Fig. S7. Snapshots of solid-state polycrystalline thin film of (*E*)-**4FCM** before (left) and after full UV light irradiation (right). Scale bar: 1 cm.



Fig. S8. (a)-(d) Sequential optical microscope images of a (E)-**4FCM** bulk crystal showing photosalient motion under visible light irradiation. The red arrows indicate the jump directions during the light irradiation.



Fig. S9. Optical microscope images to show size changing and shattering of *E*-**4FCM** bulk crystals (a) before and (b) after irradiation. The red dash lines describe the original size of this (*E*)-**4FCM** bulk crystal. Scale bar: 100 μ m.



Fig. S10. Optical microscope images to show expansion along short axis of an (*E*)-**4FCM** ribbon shape crystal (a) before and (b) after visible light irradiation. The red dash arrows describe the original width of this (*E*)-**4FCM** bulk ribbon crystal. The horizontal expansion is about 15%. Scale bar: 100 μ m.



Fig. S11. Azimuthal intensity profiles from figure 3b for (a) (100) plane, (b) (10-1) plane, (c) (11-1) plane and (d) (02-2) plane. Their corresponding full-widths-at-half-maximum (FWHM) indicates a similar level of out-of-plane orientation.



Fig. S12. Optical microscope images of an (*E*)-4FCM individual nanowire that coils up under weak UV light irradiation ($I \sim 4.0 \text{ mW/cm}^2$). Scale bar: 20 µm.



Fig. S13. Sequential optical microscope images of an (*E*)-4FCM nanowire bundle that coils up gradually under weak UV light irradiation. Scale bar: $20 \mu m$.



Fig. S14. Optical microscope images of a (*E*)-**4FCM** nanowire bundle showing exploding motion under intense UV light irradiation.



Fig. S15. SEM images of **4FCM** nanowires before (a) and after (b) full light irradiation with diameter measured by instrument ruler in SEM NN450 program.



Fig. S16. (a)-(c) Sequential microscope images of the (*E*)-**4FCM** nanowire bundle curling and coiling under weak UV light irradiation. (d)- (f) Associated cross-polarized microscope images of the bundle losing birefringence gradually under extended UV light irradiation. The crossed arrows show the directions of polarizers and the scale bar: 50μ m.



Fig. S17. GI-WAXS patterns for (*E*)-**4FCM** filled AAO templates, after UV light exposure (405 nm, $I \sim 5$ mw/cm²) for (a) 3 minutes and (b) 1 hour. After 1 hour the distinct peaks are broadened and an amorphous background has appeared.



Fig. S18. (a)-(c) Snapshot of AAO template containing (*E*)-4FCM nanowires showing bending motion under UV light irradiation. Half of the template was clamped between two opaque glass-slides. Scale bar: 2 mm. (d) A brief cartoon to show the AAO template bending under light.

R: Radius of curvature of the bending template after light irradiation. The R can reach as large as 77 mm and the bending curvature can be obtained by 1/R=1/77 mm = 12.99 m⁻¹ and the Δh is around 0.92 mm. (r: Radius of AAO template, which is 12.7 mm. Δh : Height increased by bending.)



Fig. S19. Powder x-ray diffraction patterns of (a) calculated (*E*)-**4FCM** monomer, (b) (*E*)-**4FCM** nanowires vertical inside AAO template before light exposure with the (02-2) Miller plane, (c) **4FCM** nanowires vertical inside AAO template after full UV light irradiation, and (d) calculated **4FCM** dimer.



Fig. S20. Schematic outline of laser deflection setup.