Supporting Information

Fast and Reversible Bidirectional Photomechanical Response Displayed by a Flexible Polycrystalline Aggregate of a Hydrazone

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5. Supporting Videos

Video S1: Photomechanical bending away from the light source.

Video S2: Photomechanical bending towards the light source.

1. Supporting methods:

1.1 Materials: 2,4-Dinitrophenylhydrazine (from SRL), hydrochloric acid (from SRL), 3,4-dimethoxybenzaldehyde (from Spectrochem) and methanol (from FINAR) were used without further purification.

1.2 Instrumentation

FT-IR spectroscopy: FT-IR spectra in UATR mode was recorded using the Perkin Elmer FT-IR spectrometer.

1H NMR: Solution NMR spectra were recorded on Bruker Avance 400 MHz spectrometer (Bruker-Biospin, Karlsruhe, Germany) in DMSO-D6 solvent.

Single crystal X-ray diffraction: Bruker D8 QUEST Eco CCD single crystal X-ray diffractometer with MoKα source ($\lambda = 0.71073$ Å) and a fine-focus sealed tube were used for structure determination. Apex II[S1] program was used to record diffraction frames and integrated with Bruker SAINT.[S2] SADABS was used for absorption correction.[S3] Crystal structure solution and refinement were carried out with the SHELX package.[S4–S6]

Powder X-ray Diffraction: Powder X-ray diffraction pattern of the compound **1** was recorded on Bruker D8 Advance diffractometer (Bruker-AXS, Karlsruhe, Germany) using Cu-Kα X-radiation ($\lambda = 1.5406$ Å) at 40 kV and 30 mA power, over the 2θ range 5–50° at a scan rate of 5°/min.

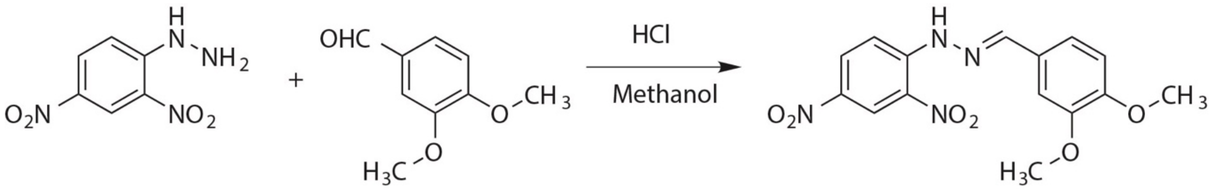
UV-Visible spectroscopy: Solution state UV-vis spectra was recorded using the Perkin Elmer UV-vis spectrometer (Lambda 35). The photoswitching behaviour of the synthesized compound was studied by irradiating the solutions with UV light originating from a mercury–xenon lamp (wavelength 365 nm, power density 361 mW cm^{-2})

Scanning electron microscope: Field emission scanning electron microscope (FE-SEM) images were obtained from a Carl Zeiss model Merlin compact microscope using a 30 keV electron beam. The sample was prepared on a cleaned glass substrate coated with a thin layer of gold to avoid charging.

Atomic Force Microscopy: Atomic force microscopy studies were carried out on NT-MDT Model Solver Pro M microscope using a class 2R laser of 650 nm wavelength having a maximum output of 1 mW. All calculations and image processing were carried out using NOVA 1.0.26.1443 software. The images were recorded in a semi-contact mode using a noncontact super sharp silicon cantilever (NSG 10_DLC) with a diamond-like carbon tip (NT-MDT, Moscow). The dimension of the tip is as follows: Cantilever length = 100 (±5) μm, Cantilever width 35 (±5) μm, and Cantilever thickness = 1.7-2.3 μm, Resonate frequency = 190-325 kHz, Force constant = 5.5-22.5 N/m, Chip size = 3.6×1.6×0.4 mm, Reflective side = Au, Tip height = 10-20 μm and DLC Tip curvature radius = 1-3 nm.

Mechanical effects: Experiments of Stress-induced mechanical effect and UV light induced mechanical effects of the polycrystalline aggregates were done using M80 Leica microscope attached to a MC170HD camera. LAS (ver. 4.9.0) software was used to analyse the recorded videos. Mercury-xenon UV lamp (model L9566-01A, LC8 UV spotlight source, Hamamatsu Photonics) equipped with a heat filter (model A9616-05, Hamamatsu Photonics, wavelength range 300–450 nm) was used as a light source (455 mW cm^{-2} power density) for the light-induced mechanical effects of the polycrystalline aggregates. The power density of the UV light was determined with the help of a precalibrated light power meter (model C6080-365-03, Hamamatsu).

1.3 Synthesis: Compound **1** was synthesised utilising a reported procedure.[S7] In a round-bottomed flask, a catalytic amount of HCl was added to a methanol solution of one equivalent of 2,4-Dinitrophenylhydrazine (2.52 mmol, 500 mg) and one equivalent of 3,4-dimethoxybenzaldehyde (2.52 mmol, 415 mg). The resulting solution was stirred for 30 minutes at room temperature and pressure, which afforded an orange-colored precipitate of the product with a yield of ~97%. The uncorrected melting point of the compound is 265-268 °C



Scheme S1. Synthetic scheme for compound **1**.

2. Supporting Figures

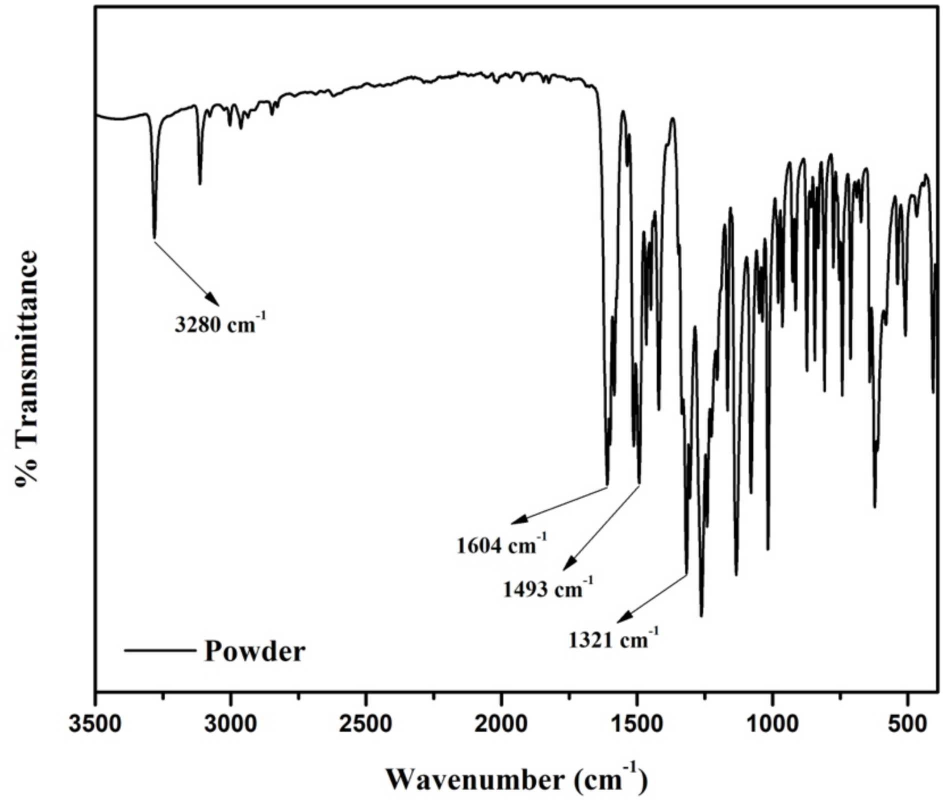


Figure S1. FT-IR spectra of compound **1** in powdered form.

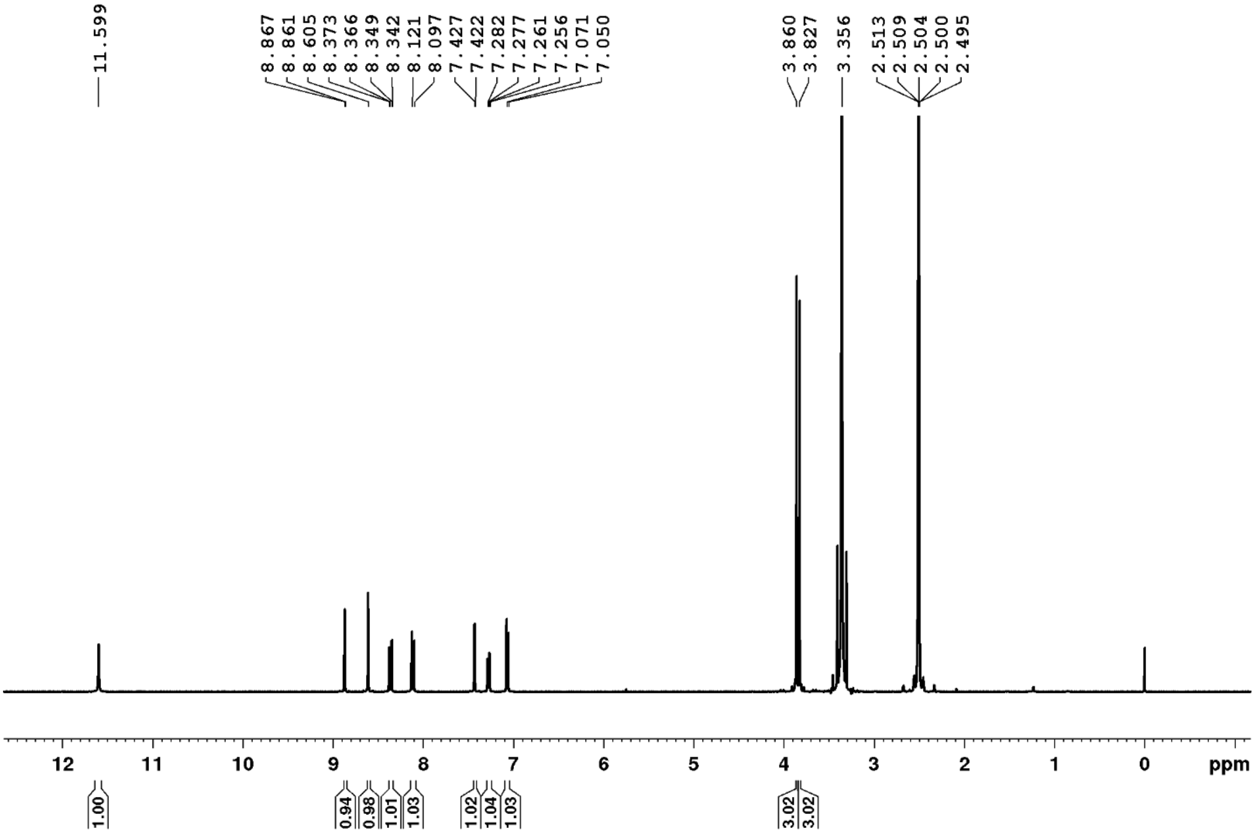


Figure S2. 1H NMR spectra of compound **1**. (DMSO-d_6,δ, ppm): 11.60 (s, 1H); 8.86 (d, J=2.4Hz 1H); 8.60 (s, 1H); 8.36 (dd, J=9.6, 2.8Hz, 1H); 8.11 (d, J=9.6Hz, 1H); 7.42 (d, J=2.0Hz, 1H); 7.27 (dd, J=8.4, 2.0Hz, 1H); 7.06 (d, J=8.4Hz 1H); 3.86 (s, 3H); 3.83 (s, 3H)

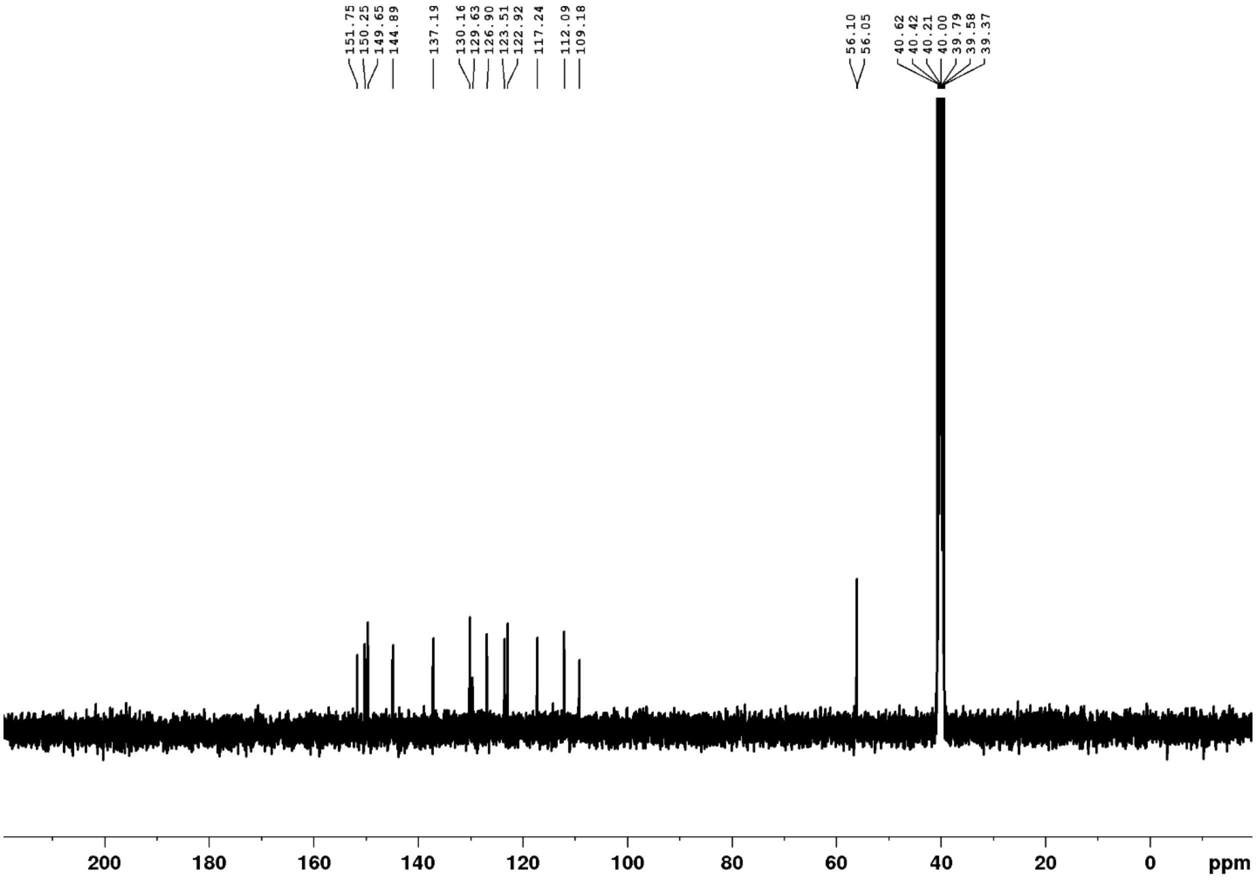


Figure S3. ^{13}C NMR NMR of compound **1**. (DMSO-d6): δ 151.7, 150.2, 149.6, 144.8, 137.1, 130.1, 129.6, 126.9, 123.5, 122.9, 117.2, 112.0, 109.1, 56.10, 56.05

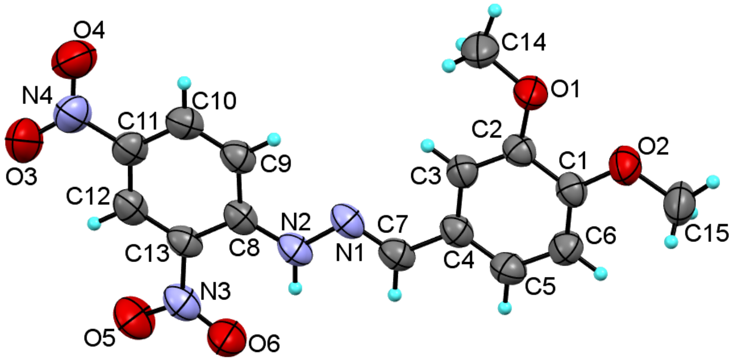


Figure S4. Ortep of the single crystal of the synthesised hydrazone with 50% probability ellipsoid.

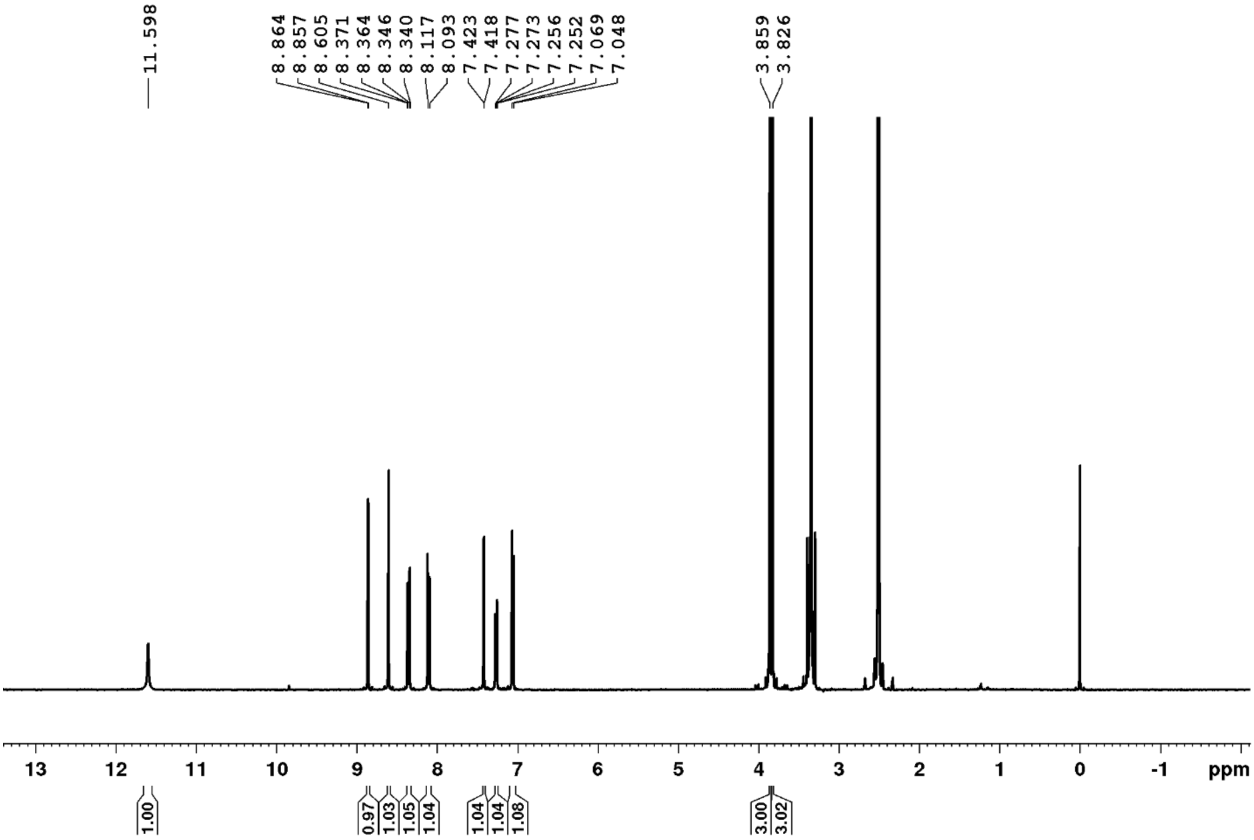


Figure S5. 1H NMR spectra of compound **1** in the polycrystalline state. (DMSO-d$_6$, δ, ppm): 11.60 (s, 1H); 8.86 (d, J=2.4Hz 1H); 8.60 (s, 1H); 8.36 (dd, J=9.6, 2.8Hz, 1H); 8.11 (d, J=9.6Hz, 1H); 7.42 (d, J=2.0Hz, 1H); 7.27 (dd, J=8.4, 2.0Hz, 1H); 7.06 (d, J=8.4Hz 1H); 3.86 (s, 3H); 3.83 (s, 3H)

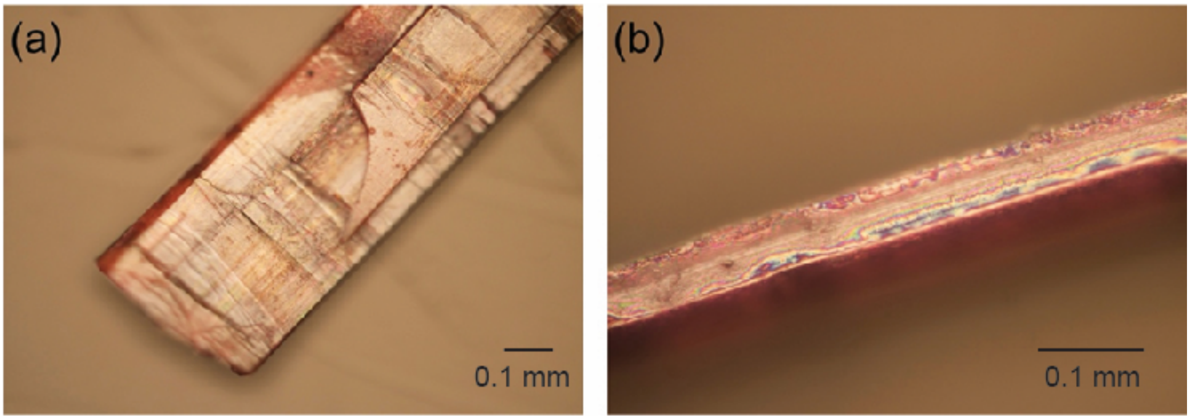


Figure S6. Optical microscopy images of the surfaces of the polycrystalline aggregate (a) wider face and (b) side view.

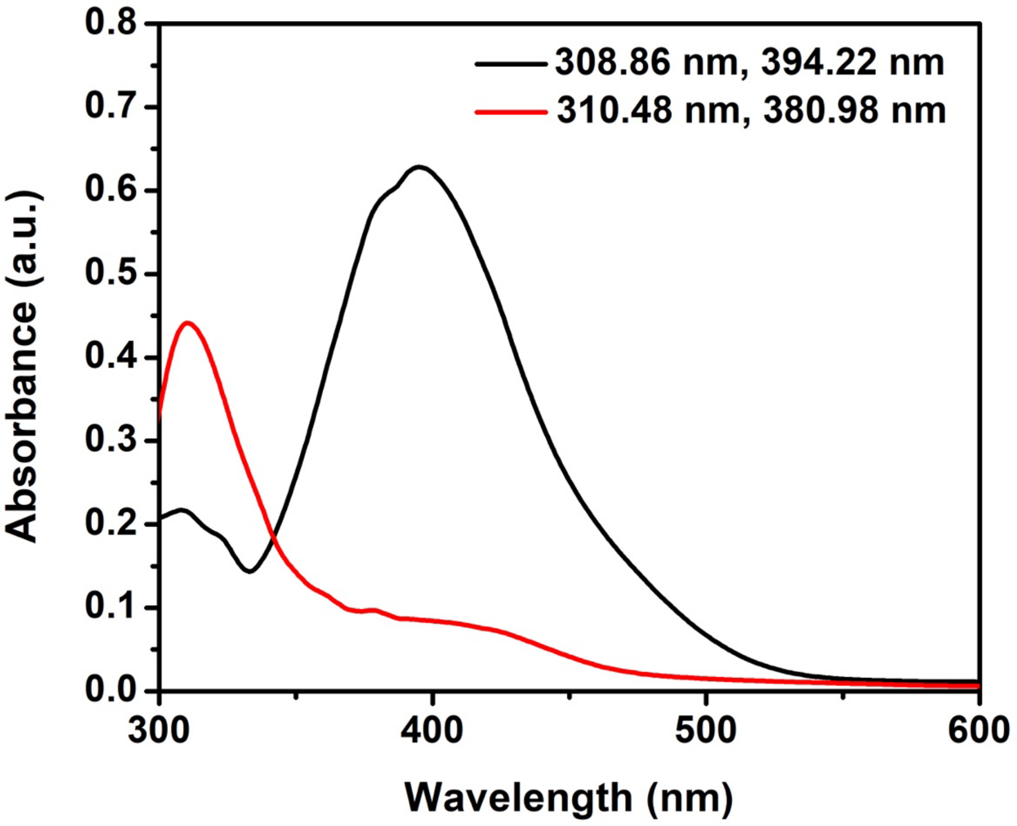


Figure S7. UV-Vis absorption spectra of the synthesised hydrazone in THF solution. Colour codes: black-before UV irradiation; red-after UV irradiation at 25°C. The numbers in the spectra correspond to the λ_{max} values.

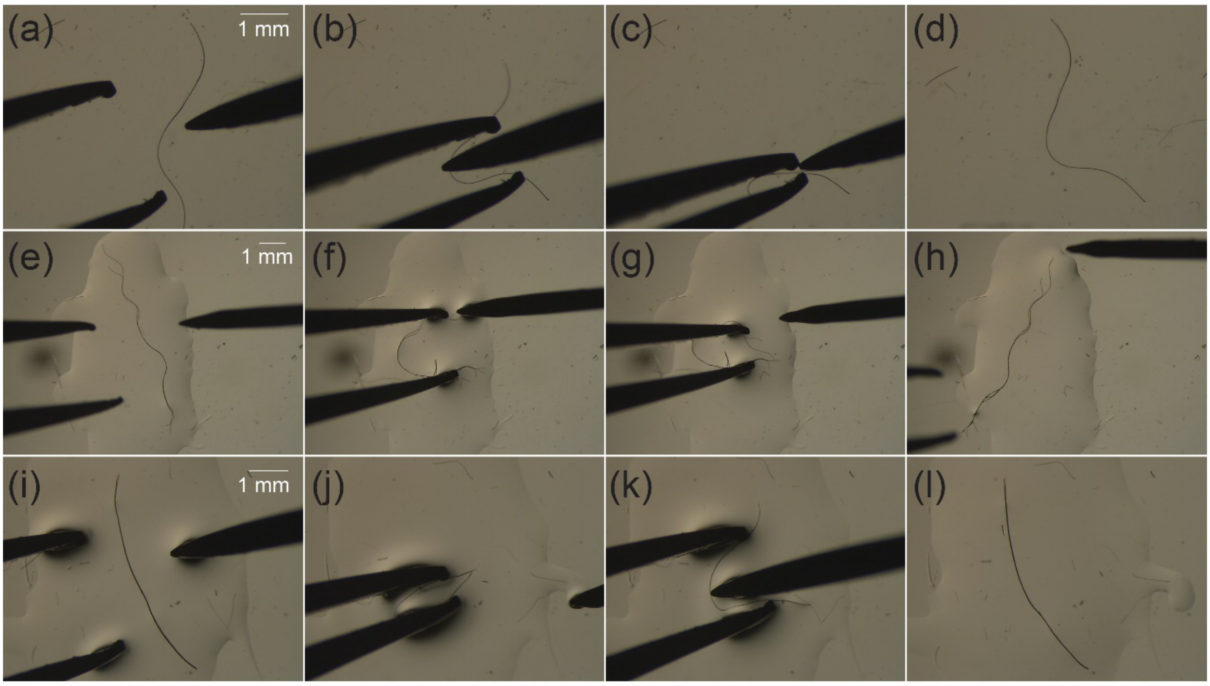


Figure S8. Elastic deformation of the polycrystalline aggregate.

3. Supporting Table

Table S1. Crystallographic parameters.

	Compound **1**
Temperature / K	296
Radiation Source	Mo
Formula weight	346.30
Crystal system	Orthorhombic
Space group	*P*bca
a / Å	17.3887(9)
b / Å	7.8689(4)
c / Å	23.0857(9)
α / °	90
β / °	90
γ / °	90
Volume / Å^3	3158.8(3)
Z	8
Density / (g cm^{-3})	1.4562
μ / mm^{-1}	0.115
sF_{000}	1440.8782
h_{min}, h_{max}	-21, 20
k_{min}, k_{max}	-9, 8
l_{min}, l_{max}	-29, 28
No. of measured reflections	15945
No. of unique reflections	3298
No. of reflections used	1396
R_{all}, R_{obs}	0.1571, 0.0570
$wR_{2,\mathrm{all}}$, $wR_{2,\mathrm{obs}}$	0.1698, 0.1252
$\Delta\rho_{\mathrm{min,max}}$ / (e Å^{-3})	-0.4067, 0.4208
GooF	0.9820
CCDC No.	2174174

4. Supporting References

S1. Bruker, APEX II, Bruker AXS Inc., Madison, Wisconsin, USA, 2012.
S2. Bruker, SAINT, Bruker AXS Inc., Madison, Wisconsin, USA, 2012.
S3. Bruker, SADABS, Bruker AXS Inc., Madison, Wisconsin, USA, 2001.
S4. G. M. Sheldrick, Acta Crystallogr., Sect. A: Found. Adv., 2015, **71**, 3–8.
S5. G. M. Sheldrick, Acta Crystallogr., Sect. A: Found. Adv., 2008, **64**, 112–122.
S6. C. B. Hübschle, G. M. Sheldrick and B. Dittrich, J. Appl. Crystallogr., 2011, **44**, 1281–1284.
S7. O. L. Brady and G. V. Elsmie, *Analyst* 1926, **51**, 77-78.