Photomechanical Bending and Photosalient Effect

of Flexible Crystals of an Acylhydrazone

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Content of Supporting Information

Materials: Without any further purification, the following materials were used from their respective commercial sources: Benzhydrazide (from Alfa Aesar), 1-naphthaldehyde (from Alfa Aesar), ethanol (from CSS), glacial acetic acid (from Himedia), acetonitrile (from Spectrochem).

1.2 Synthesis and characterization of acylhydrazone derivative (Ach):
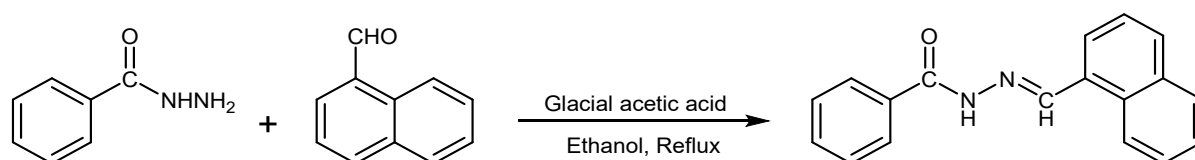
Scheme S1. Synthetic scheme of **Ach**.

Ach was synthesised by following a previously mentioned procedure.[S1] In this reaction, 1-naphthaldehyde (1.0 equivalent) was added into a round bottom flask containing the equimolar amount of Benzhydrazide (1.0 equivalent) dissolved in ethanol, and the whole reaction mixture was refluxed for 4–5 hrs after the addition of a few drops of glacial acetic acid as a catalyst. After the completion of the reaction, the obtained white precipitate was separated by filtering in a Buchner funnel, and the product was recrystallized from acetonitrile. The compound, **Ach** was then characterized by melting point determination (Figure S1), FT-IR spectroscopy (Figure S2), ^{1}H NMR (Figure S3) and single-crystal X-ray diffraction (Figure S4 and Table S1).

Ach: Yield: 81%. Melting point: ~164 °C. FT-IR: 3227 cm^{-1}, 1644 cm^{-1}, 1542 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d6) δ 11.92 (s, 1H), 9.12 (s, 1H), 8.87 (d, J = 8.4 Hz, 1H), 8.08 – 8.00 (m, 2H), 7.96 (dd, J = 16.1, 7.2 Hz, 3H), 7.68 (d, J = 7.8 Hz, 1H), 7.65 – 7.59 (m, 3H), 7.57 (t, J = 7.3 Hz, 2H).

1.3 Instrumentation: **Thermal microscopy:** The samples were put on a thermal stage (Linkam) fitted with a microscope (Leica DM 2700P) and a camera (Leica MC170HD) to measure the melting point of the synthesized compounds.

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

^{1}H NMR Spectroscopy: The NMR spectra were collected using Bruker Avance spectrometer (500 MHz and 400 MHz) and at 25 °C. Chemical shifts (in ppm) are given relative to the non-deuterated residual solvent signals of DMSO-D6 (δ = 2.5 ppm).

Single crystal X-ray diffraction: Single crystal X-ray diffraction patterns were obtained by employing Bruker D8 QUEST Eco CCD single crystal X-ray diffractometer with MoKα source (λ = 0.71073 Å) and a fine-focus sealed tube. The Apex II program[S2] was used to capture the diffraction frames and then they were integrated using Bruker SAINT.[S3] SADABS was used to carry out the absorption correction.[S4] The crystal structure was analyzed and refined using the SHELX[S5-S7] program and OLEX2[S8].

UV-Visible spectroscopy: The UV-vis spectra were acquired using the Perkin Elmer UV-vis spectrometer (in solution state Lambda 35 and in solid state Lambda 365). UV light, obtained from a mercury-xenon lamp with a wavelength of 365 nm and a power density of 361 mW cm^{-2} was irradiated on the solutions to investigate the photoswitching behavior of the synthesized compound.

Mechanical effects: Photomechanical bending motion and reversible physical deformation of the synthesised crystals were studied under Leica M80 microscope. The videos and pictures were recorded by using MC170HD camera mounted in the microscope and were analysed with the LAS software (ver. 4.9.0). Mercury-xenon UV lamp (Hamamatsu Photonics, LC8 UV spotlight source, model L9566-01A) fixed to a heat filter (Hamamatsu Photonics, model A9616-05, wavelength range 300–450 nm) was used to study the photoresponsive nature of the crystals. The UV power density was recorded by using a precalibrated light power meter (Hamamatsu, model C6080-365-03).

1.4 Computational Studies: DFT and TD-DFT studies:

Geometry optimization for the compound **Ach** was carried out using Density Functional Theory (DFT) in Gaussian 09 software package[S9] with Becke3-Lee-Yang-Parr (B3LYP) functional[S10] and 6-31G(d)[S11,S12] basis set. Further, those optimized geometries were used to perform Time-Dependent Density Functional Theory (TD-DFT) with the same functional and basis set to obtain the theoretical UV spectra.

2. Supporting Figures
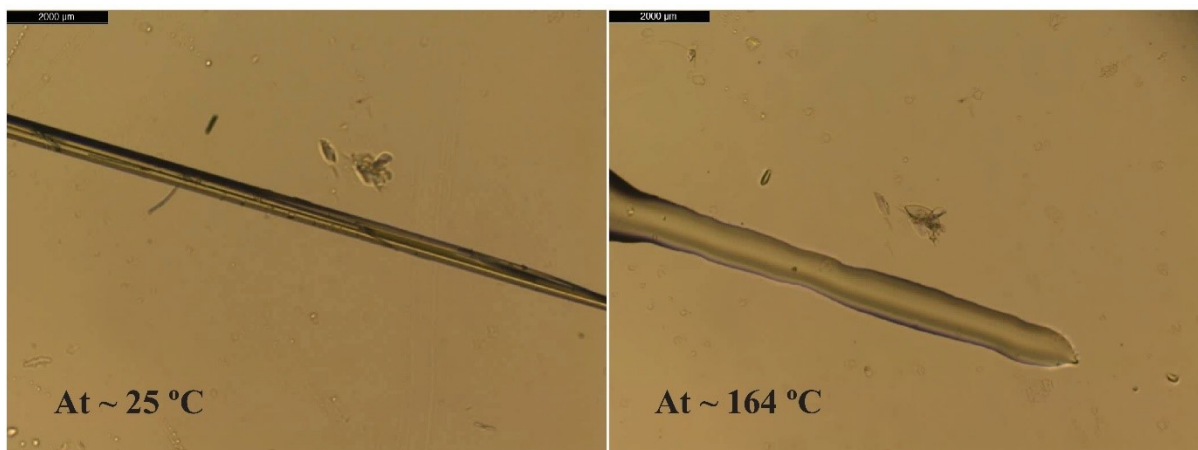
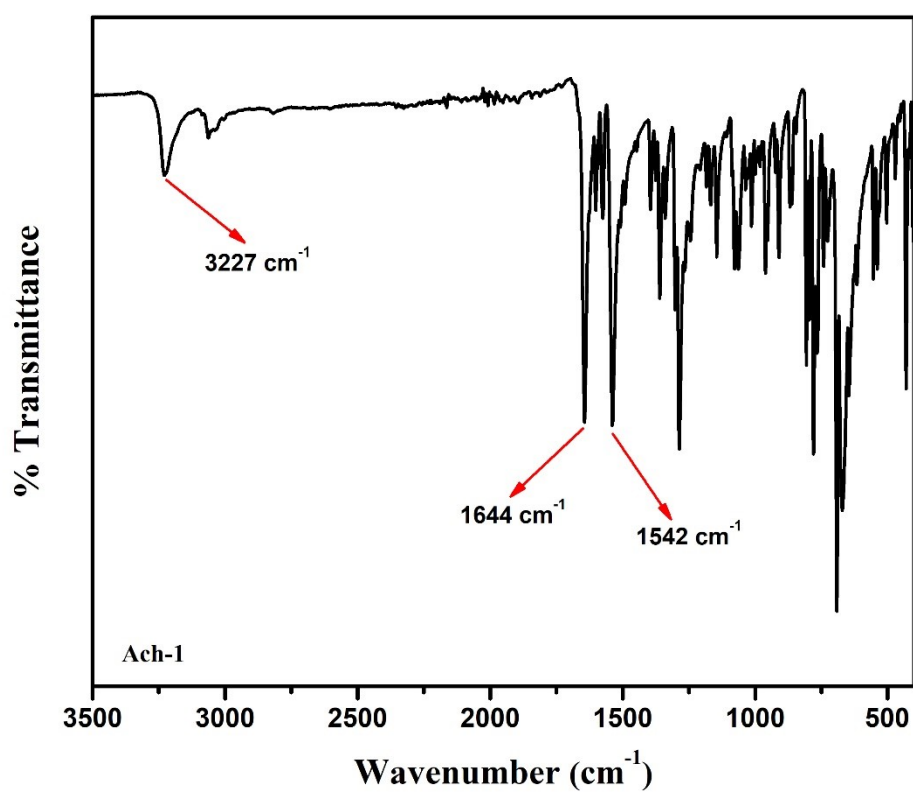**Figure S1.** Thermal microscopy images show the melting of **Ach** crystal.
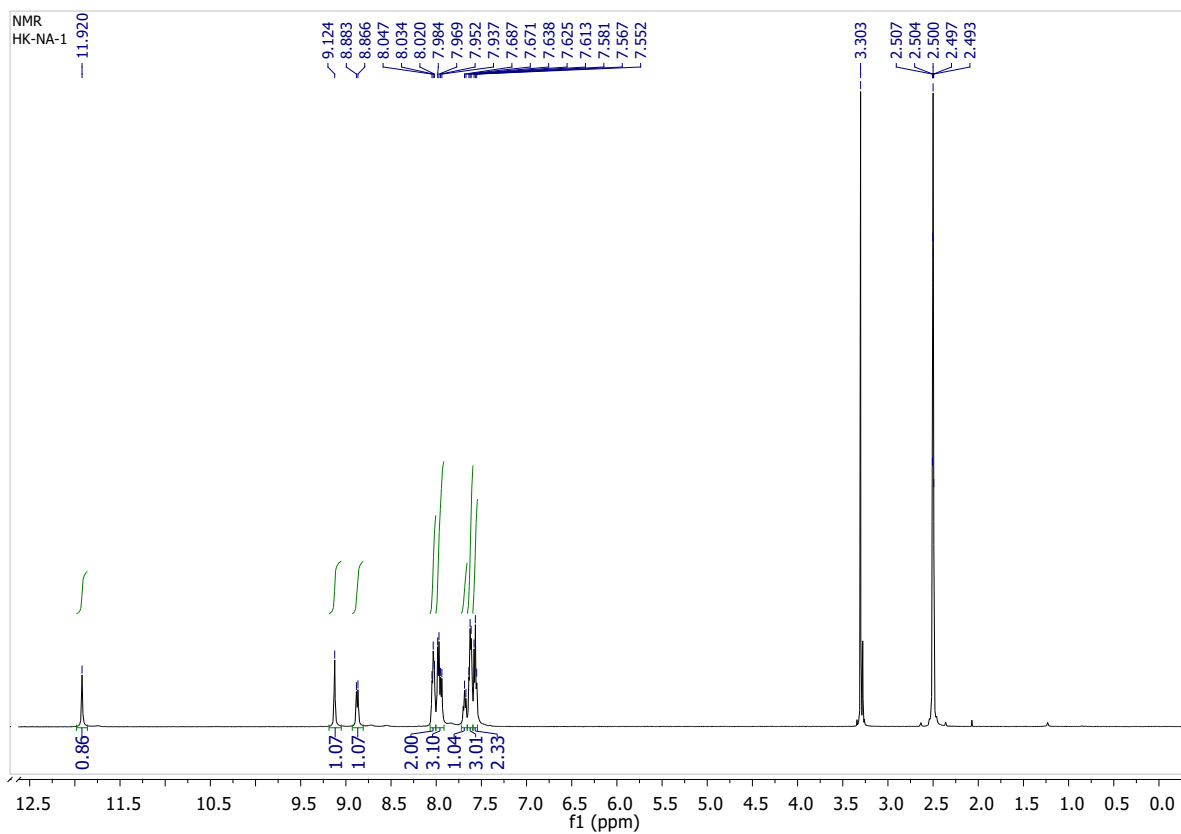

Figure S2. FT-IR spectra of **Ach.**

Figure S3. ¹H-NMR of **Ach** in DMSO-d6 solvent.
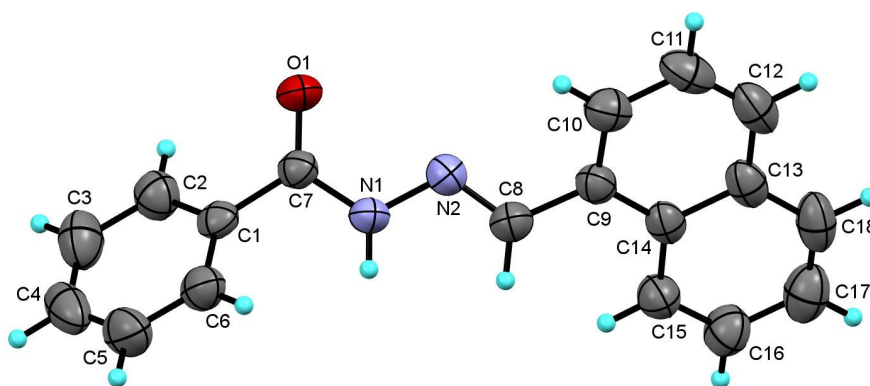

Figure S4. ORTEP diagram of **Ach** with 50% probability ellipsoid.
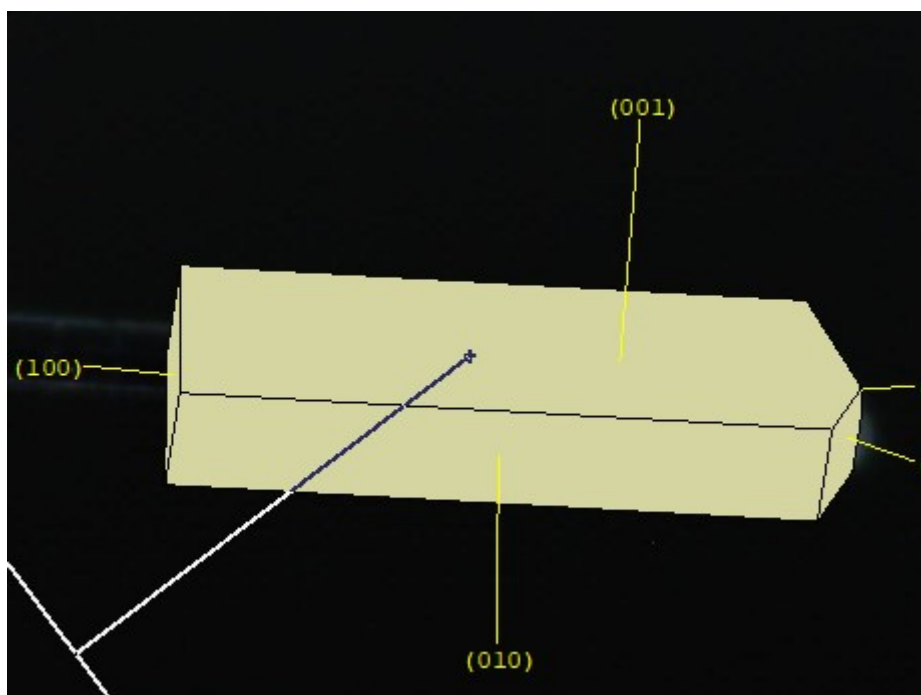
Figure S5. Face indexing of the crystal of **Ach**.
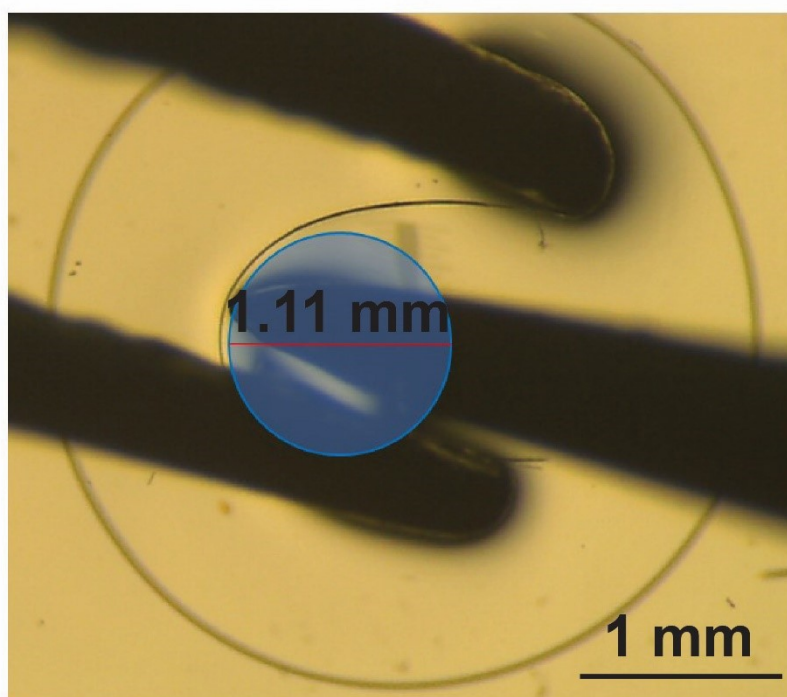
Figure S6. The radius of curvature of the bent crystals of **Ach**.
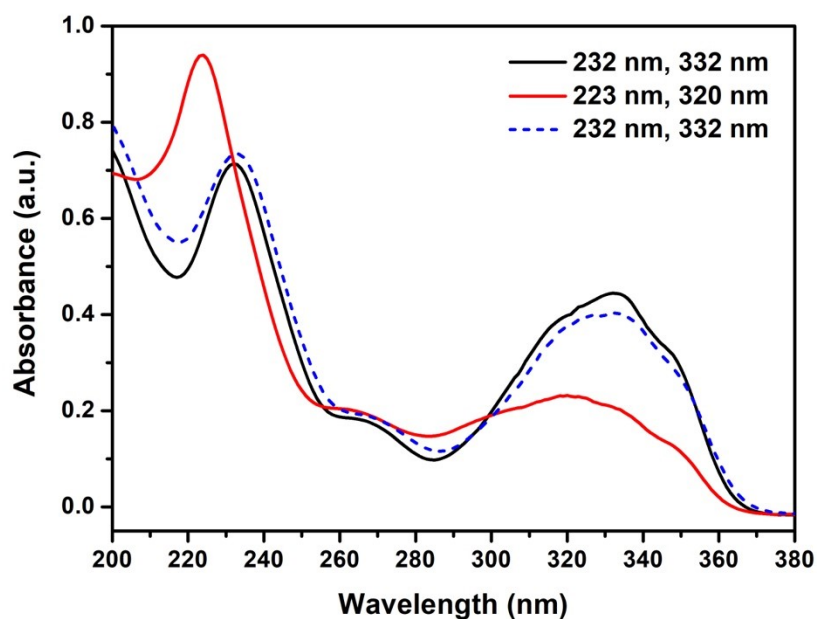
Figure S7. Solution state photoswitching of **Ach** in acetonitrile solution. The *Z* to *E* conversion is achieved by heating. The black line indicates spectra before UV irradiation, the red line indicates spectra after 5 seconds of UV irradiation, and the blue dotted line indicates spectra after heating the solution at 50 ℃ for 50 minutes.
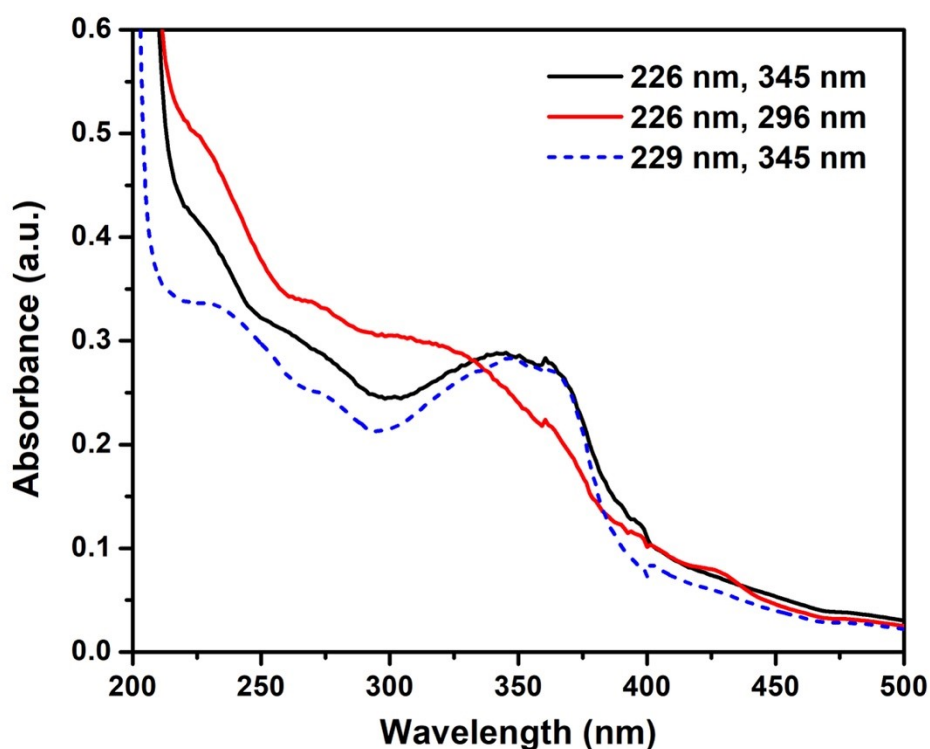
Figure S8. Solid-state UV visible spectra were recorded on a KBr pellet of **Ach**. The black line represents spectra before UV irradiation, the red line represents spectra after UV irradiation, and the blue dotted line represents spectra after heating the sample with a warm LED light.
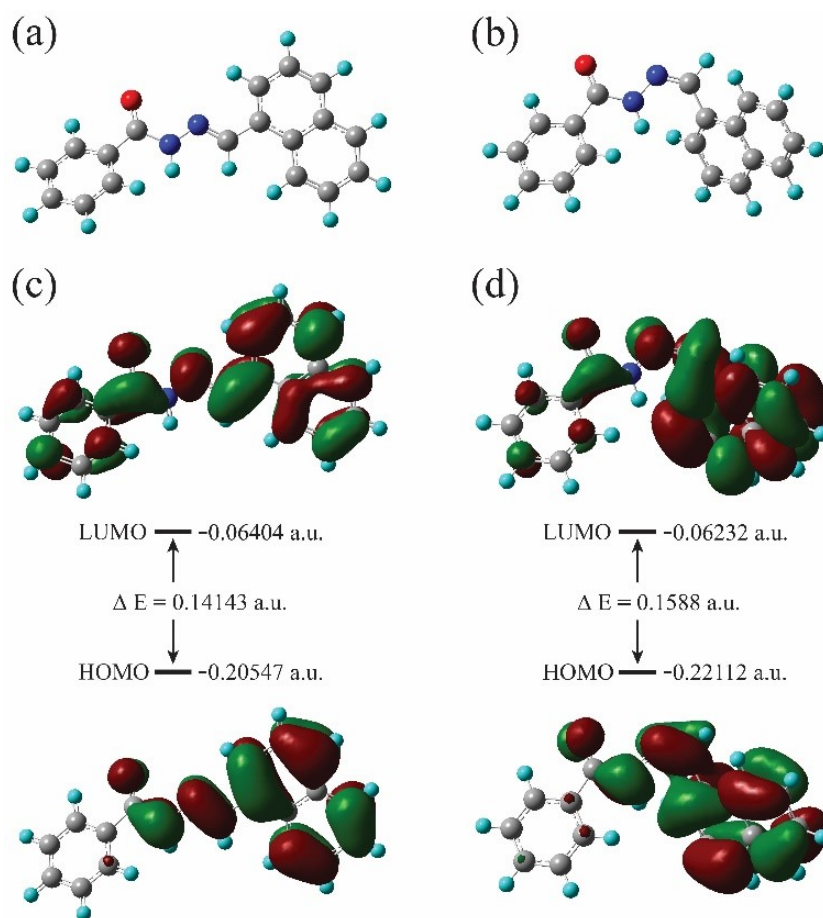
Figure S9. DFT-optimized geometry, frontier molecular orbitals and HOMO–LUMO energy gaps of **Ach** in its two different isomeric forms (a,c) *E* and (b,d) *Z*.
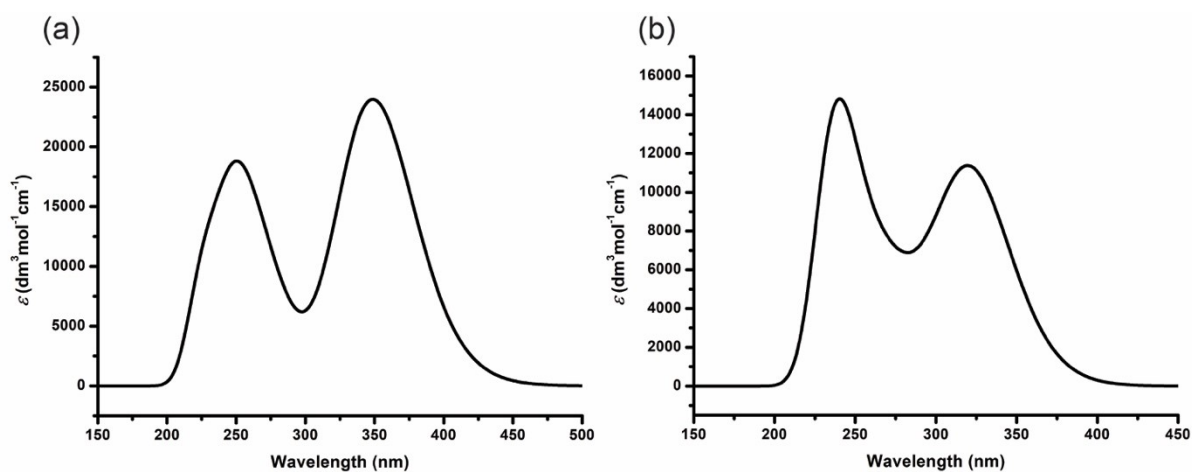
Figure S10. UV−vis absorption spectrum of (a) **Ach** (*E*), (b) **Ach** (*Z*) obtained from TD-DFT calculations at B3LYP/6-31G(d) level.
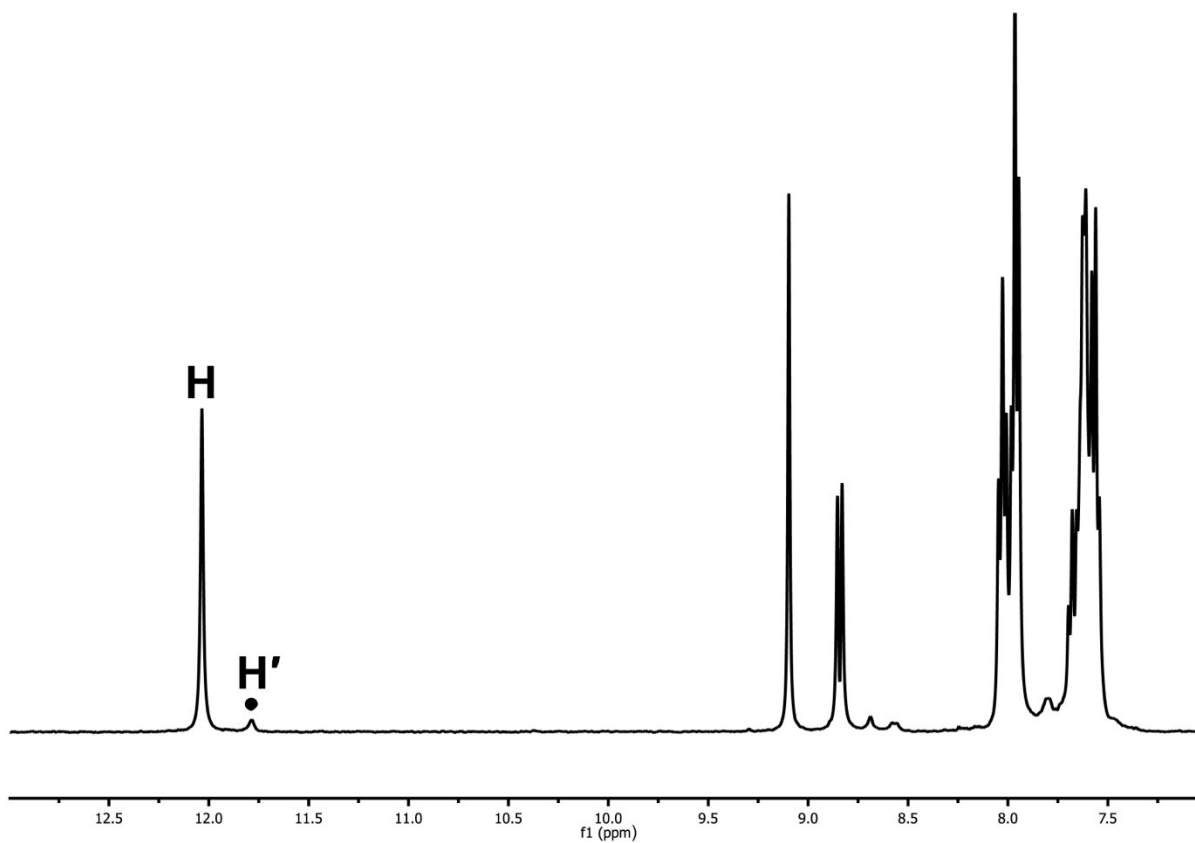
Figure S11. 1H NMR spectra recorded on a photo irradiated crystalline sample of **Ach** in DMSO-D6 solvent indicated the presence of both *E* and *Z* isomer. The H and H′ represent N—H protons of *E* and *Z* isomers, respectively.
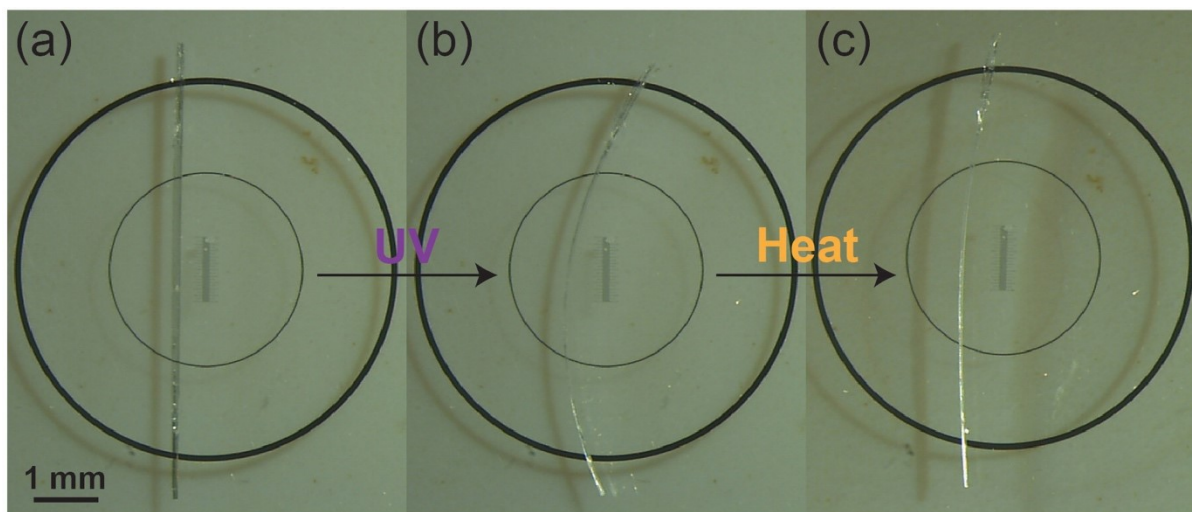
Figure S12. (a) Straight crystal of **Ach**, (b) bent by shining UV light. (c) When heated to 65 °C for one hour almost regained its original straight shape.

UV light power density (29.1 mW cm⁻²)
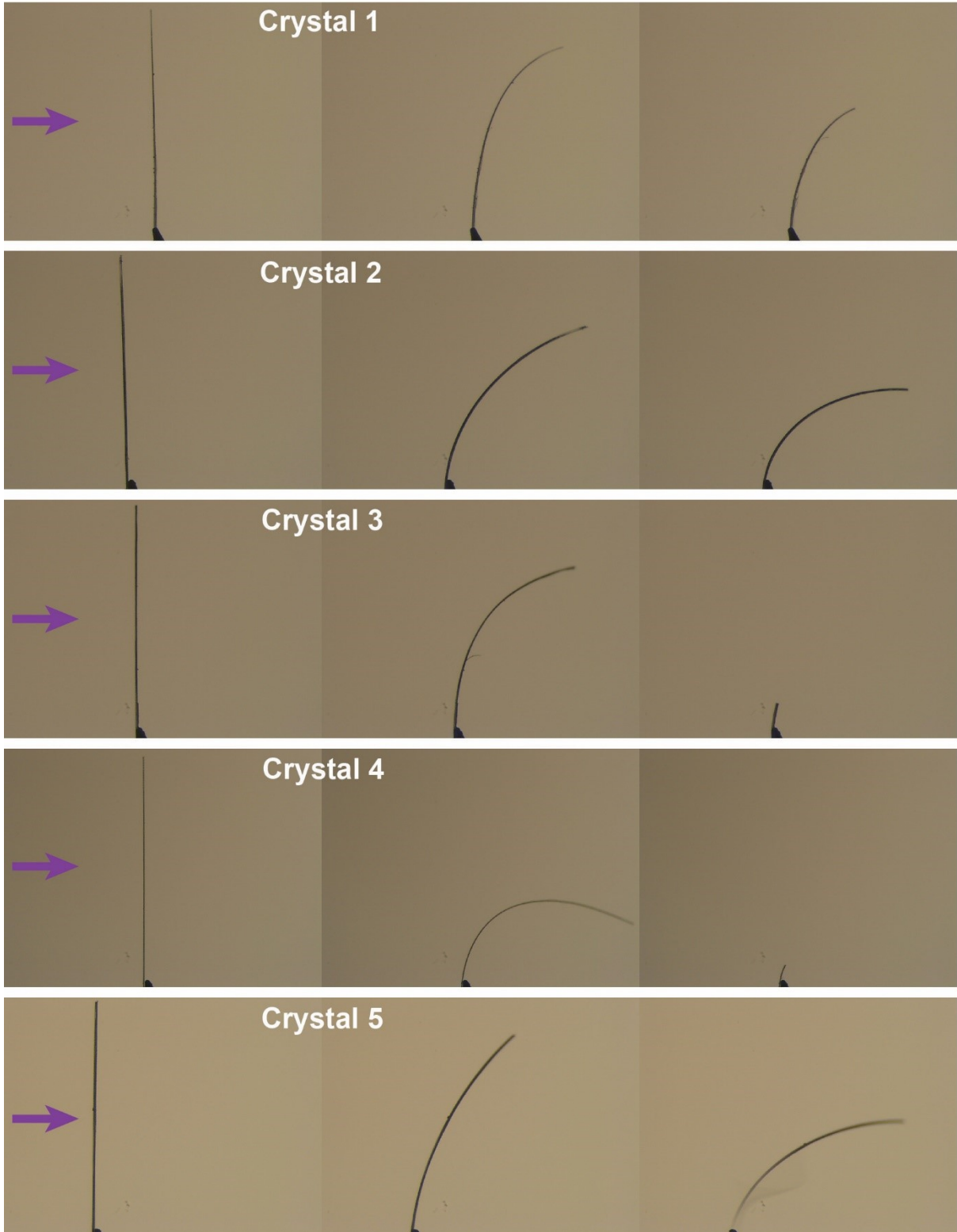
UV light power density (29.1 mW cm^{-2})

Crystal 6

Crystal 7

Crystal 8

Crystal 9

Crystal 10
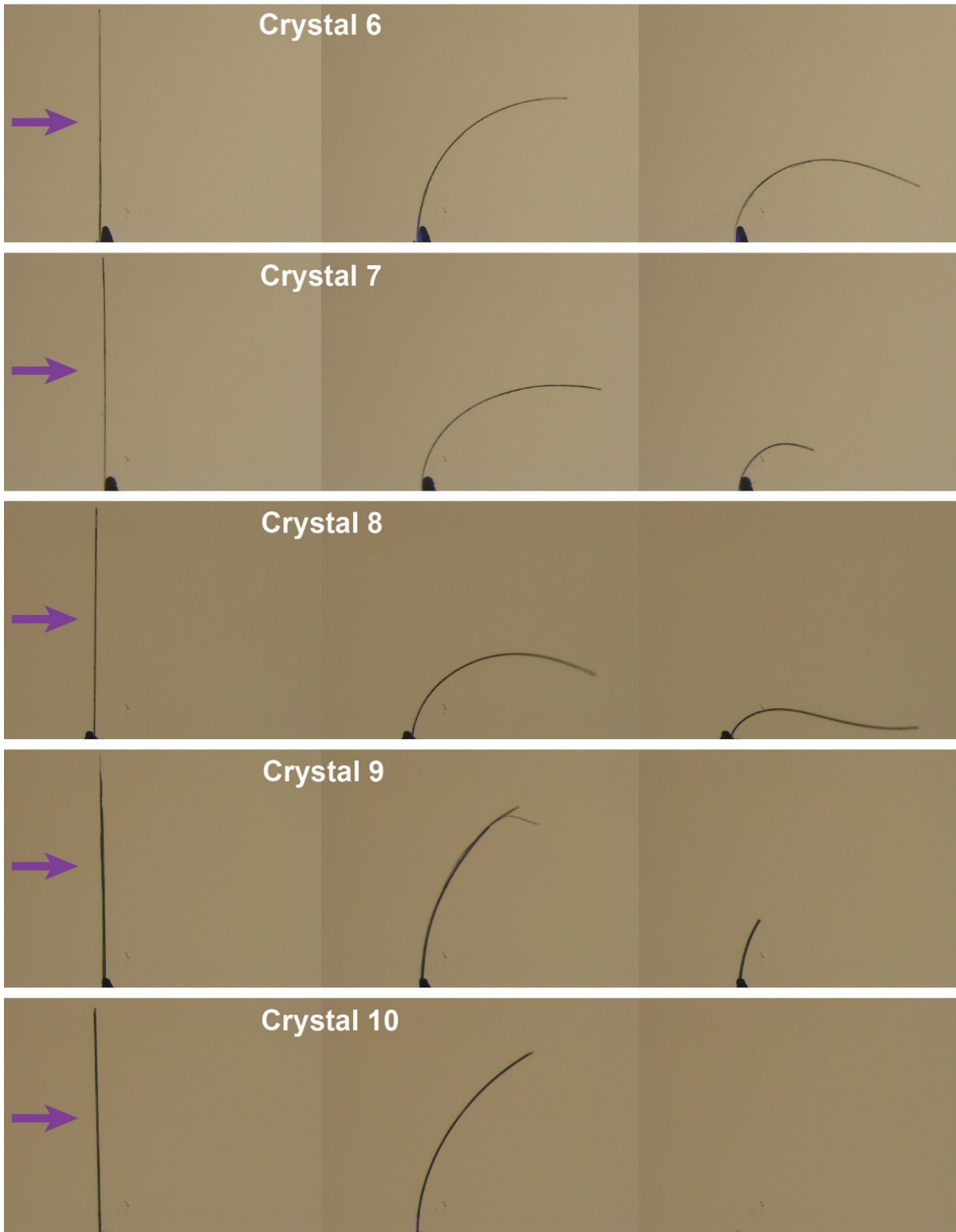
UV light power density (29.1 mW cm^{-2})
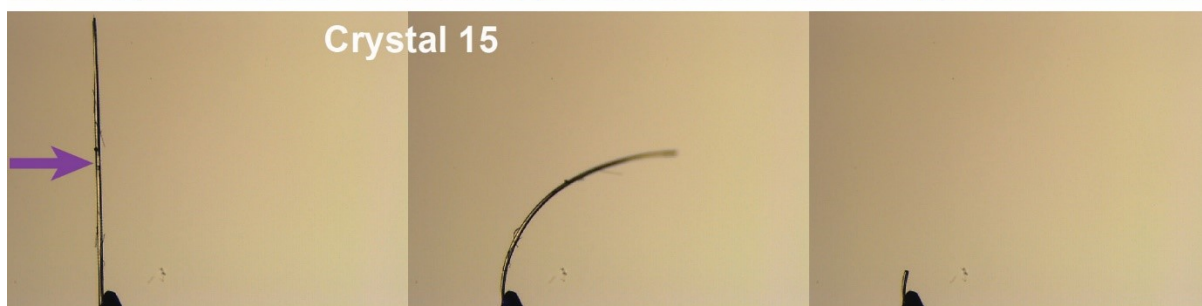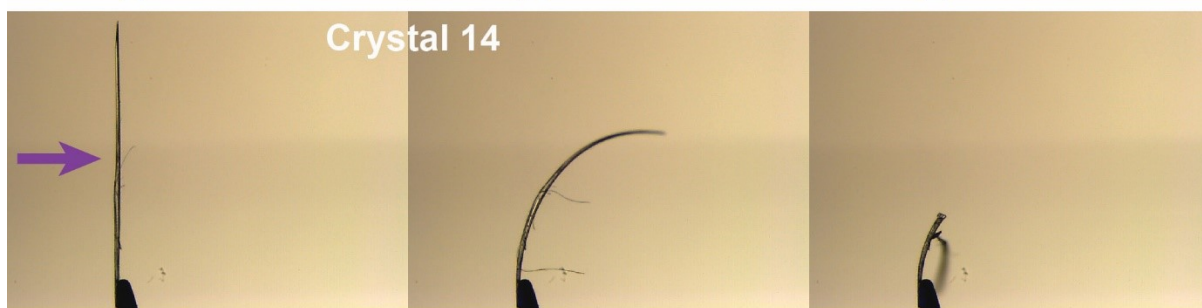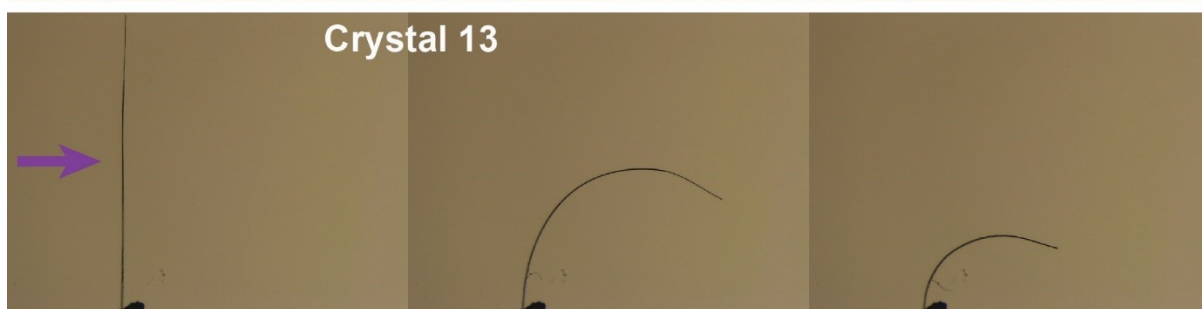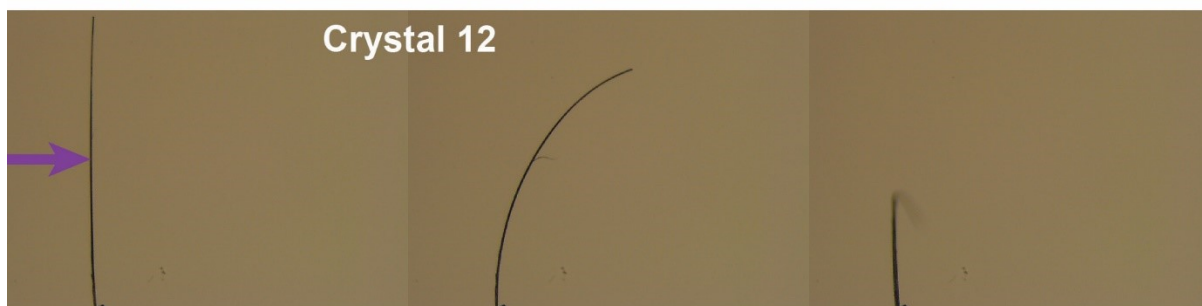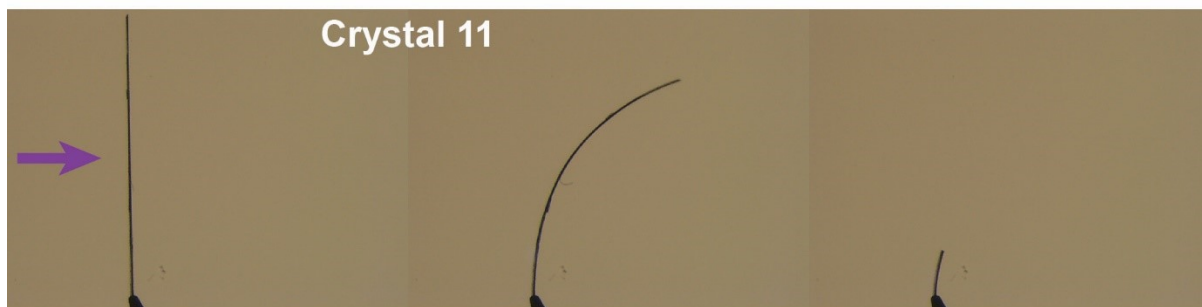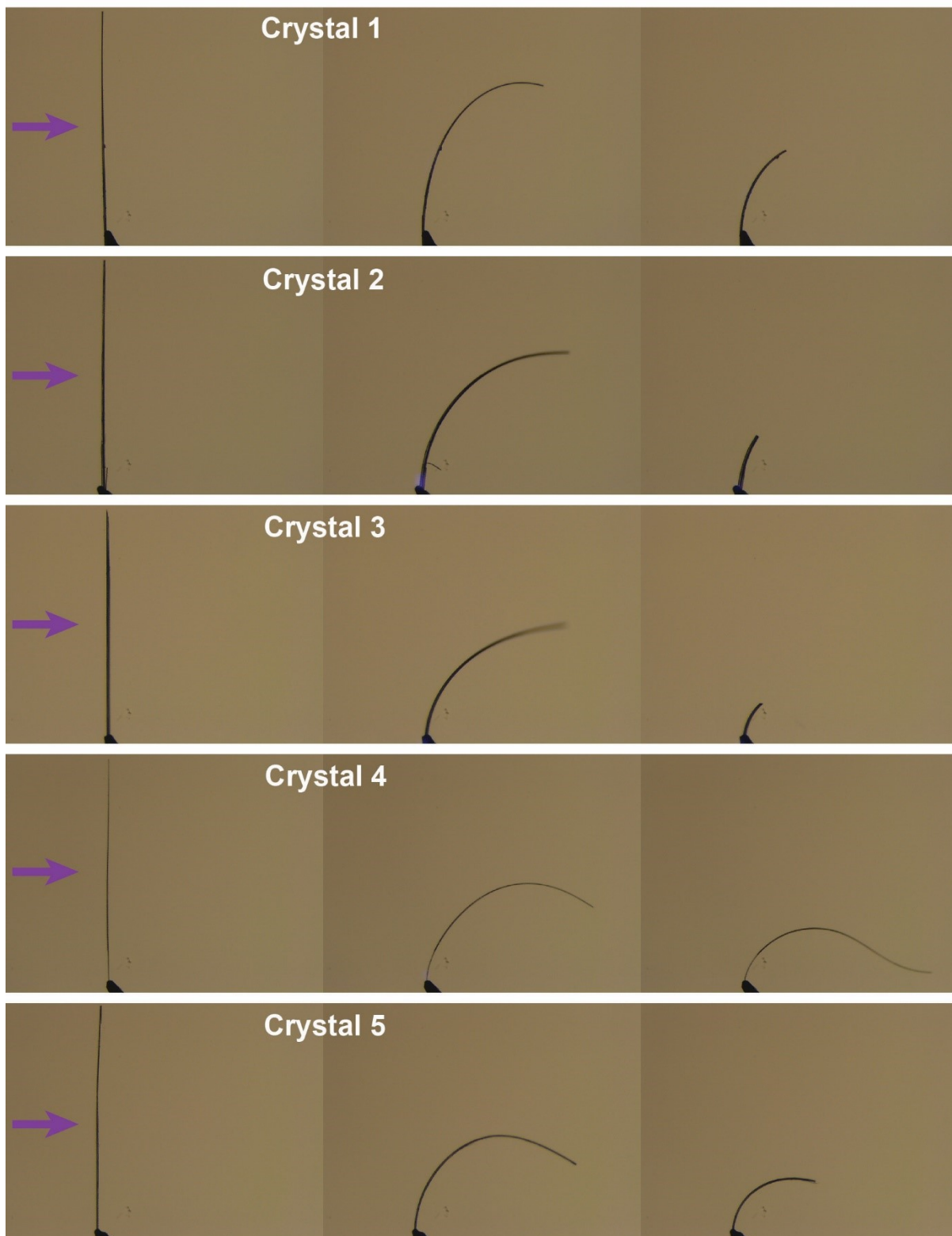
UV light power density (66.2 mW cm^{-2})

UV light power density (66.2 mW cm^{-2})

Crystal 6

Crystal 7

Crystal 8

Crystal 9

Crystal 10

UV light power density (66.2 mW cm⁻²)

Crystal 11

Crystal 12

Crystal 13

Crystal 14

Crystal 15

UV light power density (97.9 mW cm^{-2})

Crystal 1

Crystal 2

Crystal 3

Crystal 4

Crystal 5

UV light power density (97.9 mW cm^{-2})

Crystal 6

Crystal 7

Crystal 8

Crystal 9

Crystal 10
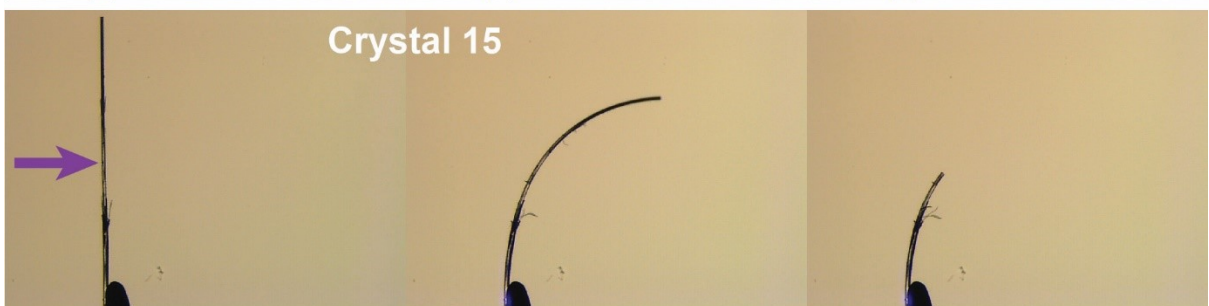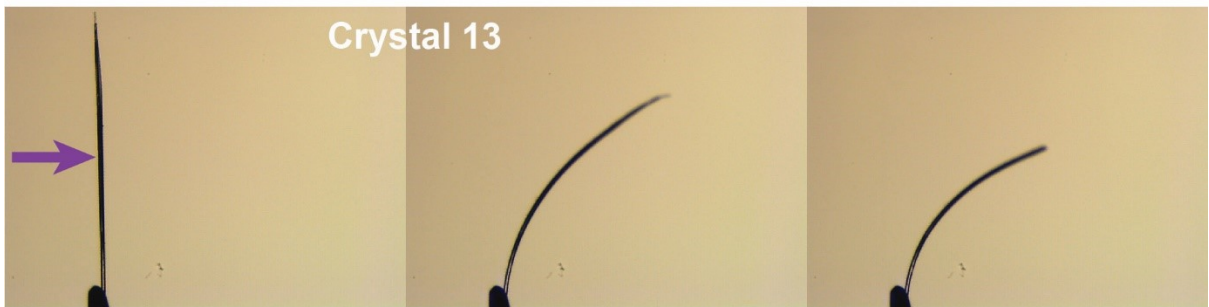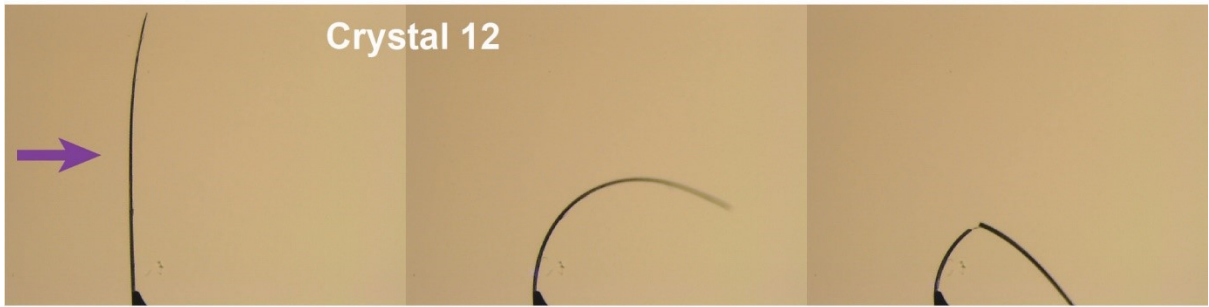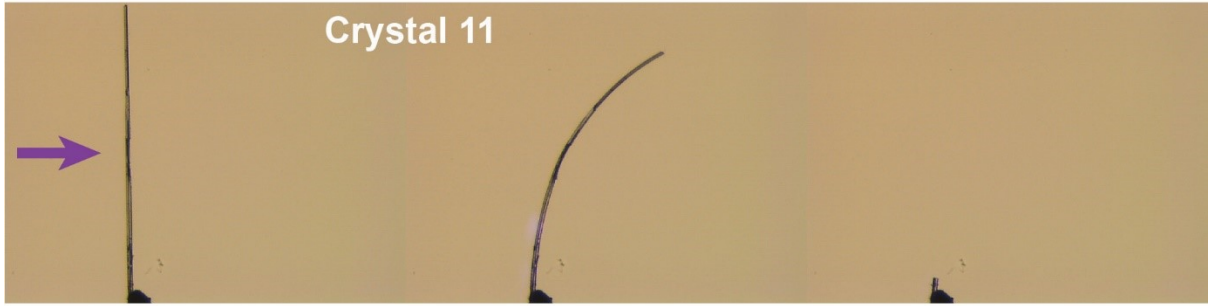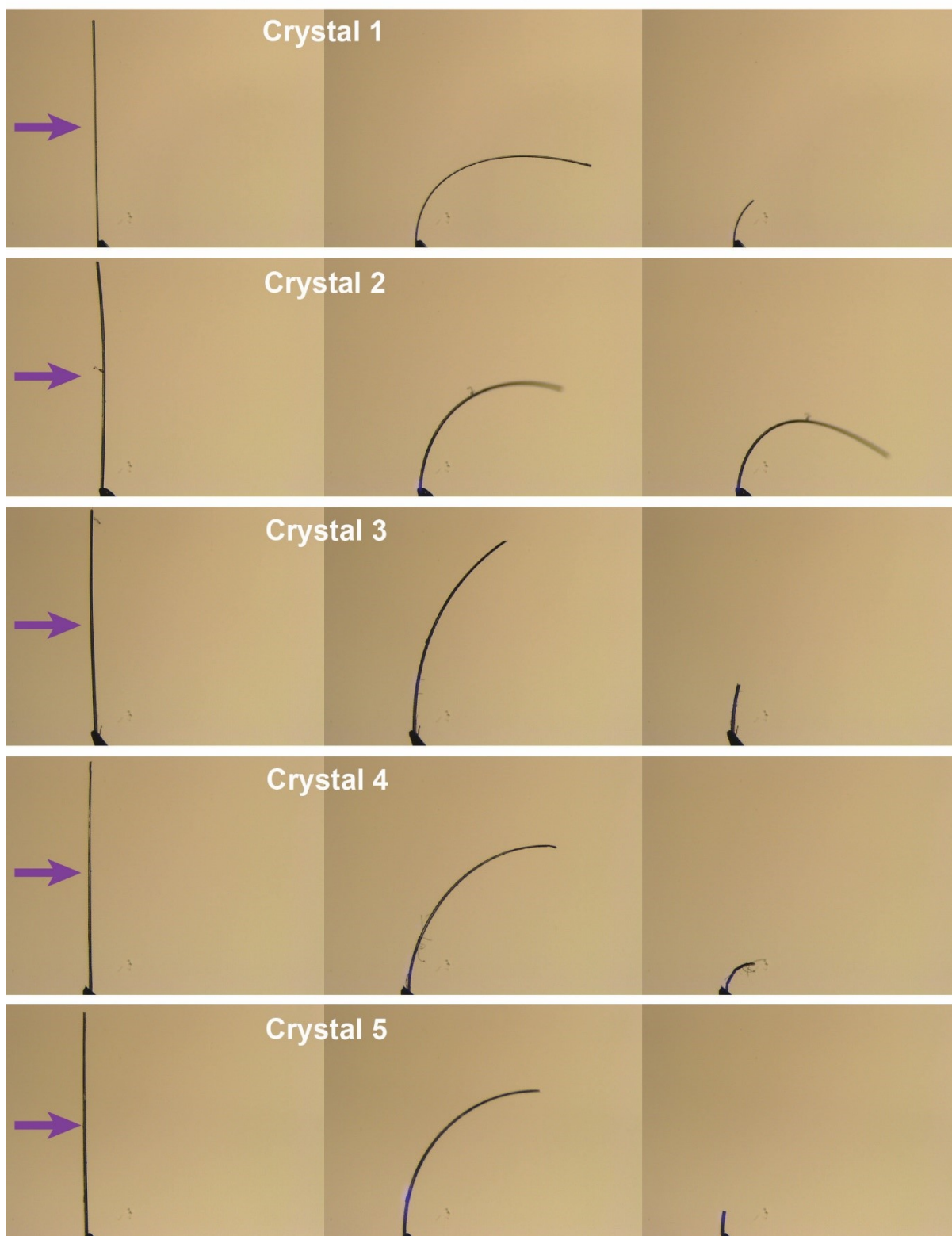
UV light power density (97.9 mW cm^{-2})

UV light power density (136.2 mW cm⁻²)

Crystal 1

Crystal 2

Crystal 3
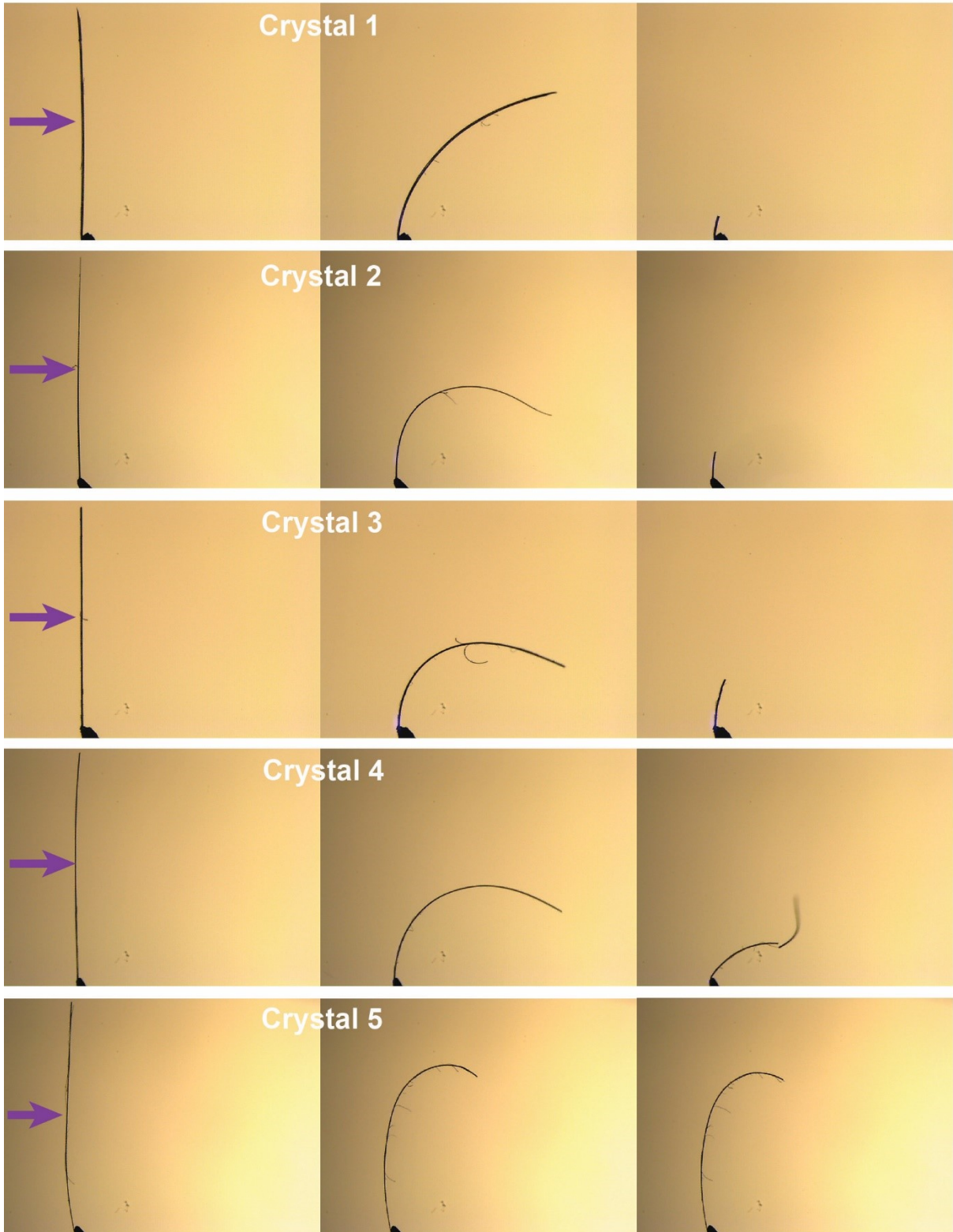
Crystal 4

Crystal 5

UV light power density (136.2 mW cm^{-2})

UV light power density (136.2 mW cm^{-2})

Crystal 11

Crystal 12

Crystal 13

Crystal 14
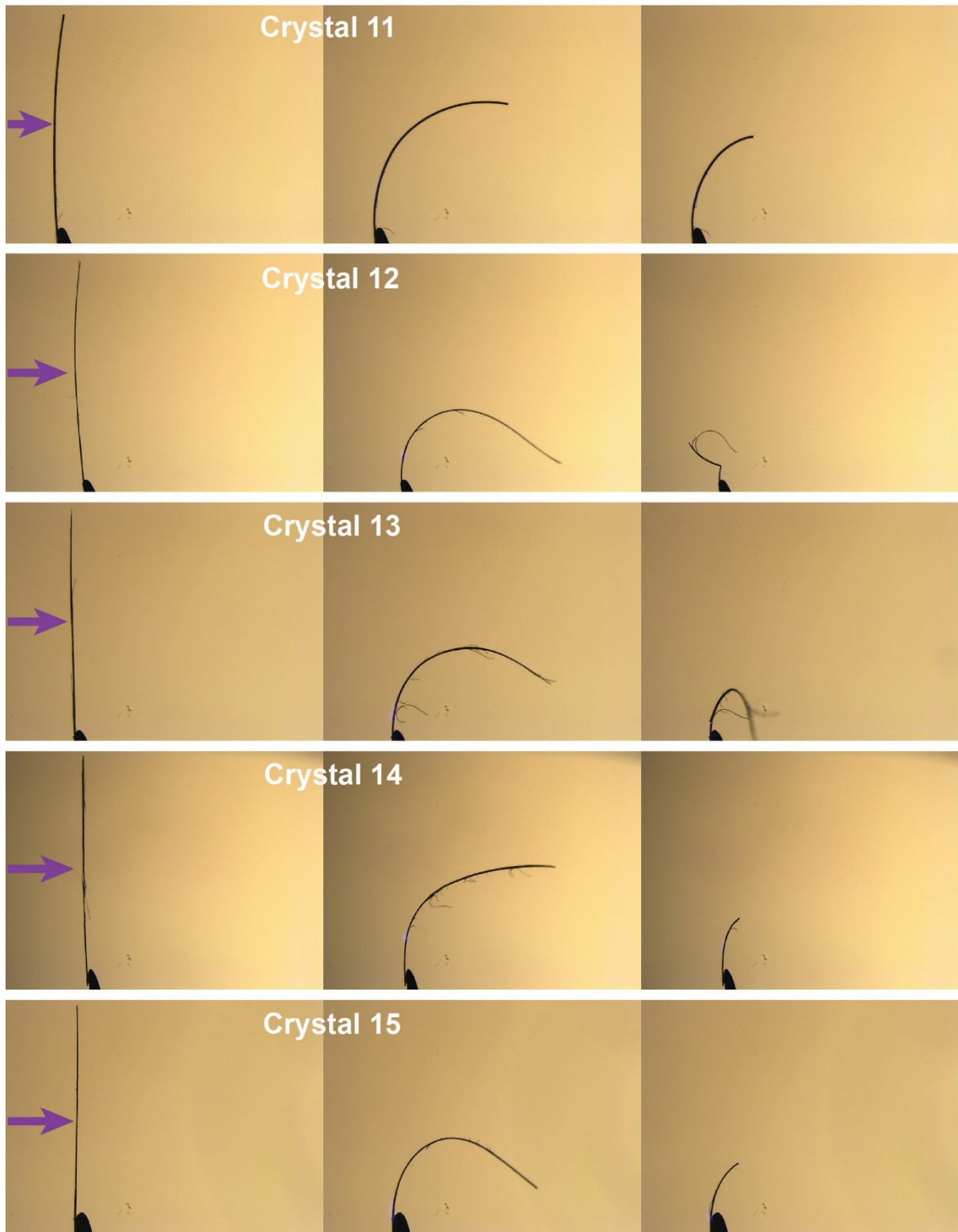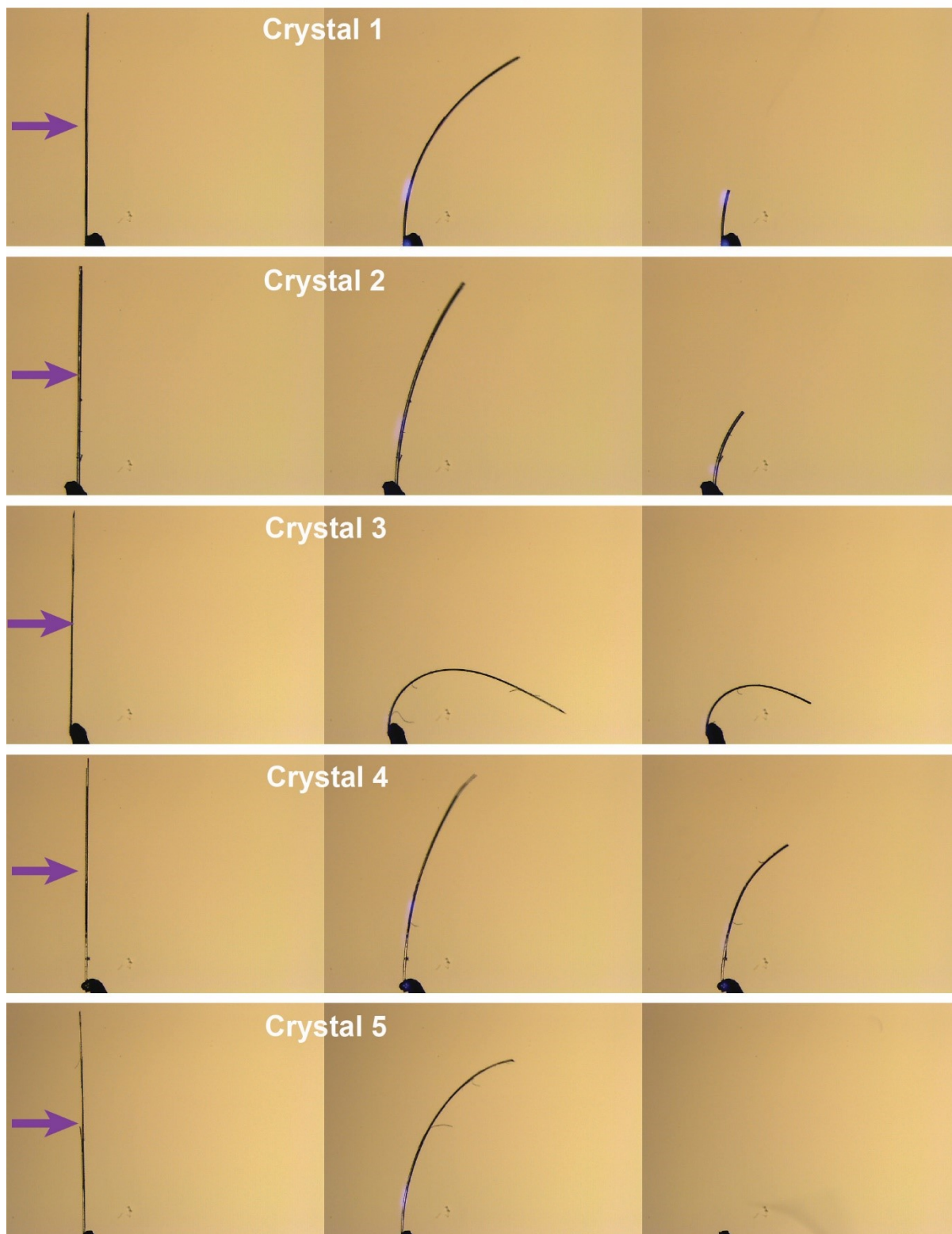
Crystal 15

UV light power density (169.9 mW cm^{-2})

UV light power density (169.9 mW cm^{-2})
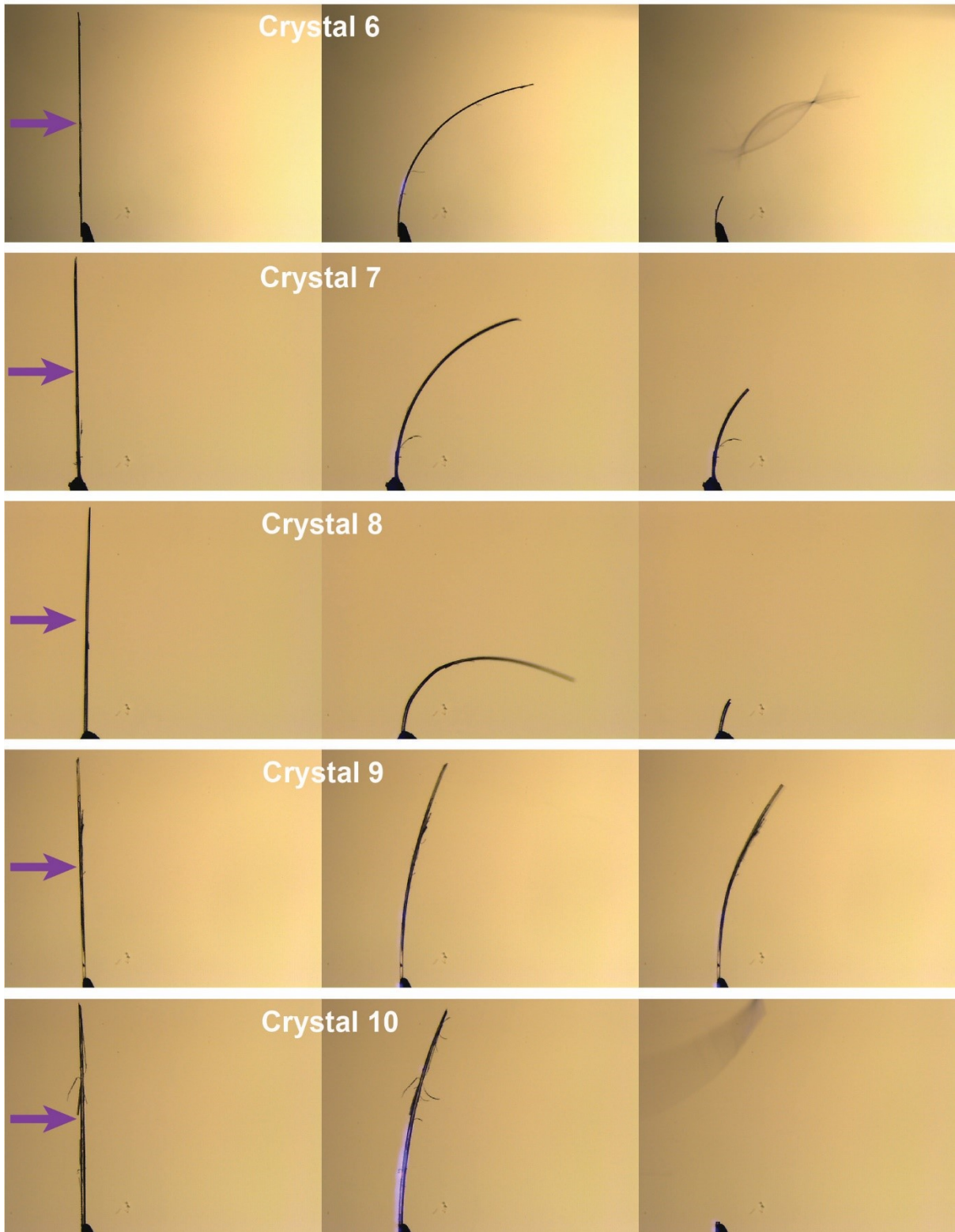
Crystal 6

Crystal 7

Crystal 8

Crystal 9
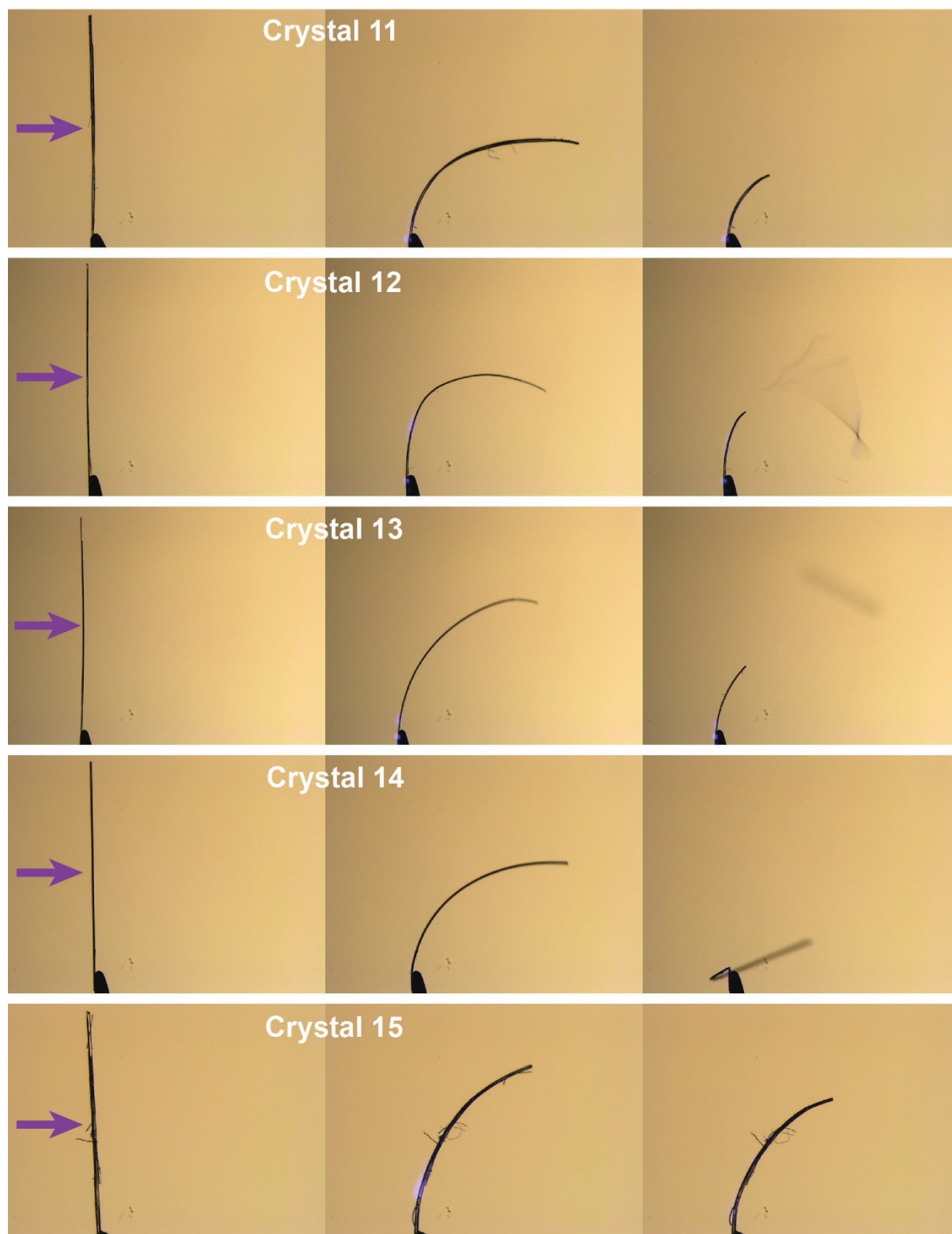
Crystal 10

Figure S13. Photomechanical behaviour of **Ach** crystals in different UV light power density. Violet colour arrows signify the direction of UV light

3. Supporting tables.

Table S1. Basic crystallographic parameters of **Ach**

|	**Ach**
Temperature / K	296.15
Radiation Source	Mo
Formula weight	273.317
Crystal system	Monoclinic
Space group	$P2_1/c$
a / Å	5.0509(5)
b / Å	12.3970(14)
c / Å	22.448(2)
α / °	90
β / °	93.489(8)
γ / °	90
Volume / Å^3	1403.0(3)
Z	4
Density / (g cm^{-3})	1.294
μ / mm^{-1}	0.082
sF_{000}	572.347
$h$min, $h$max	−6, 6
$k$min, $k$max	−14, 14
$l$min, $l$max	−26, 26
No. of measured reflections	12218
No. of unique reflections	2498
No. of reflections used	1426
Rall, Robs	0.1341, 0.0688
wR_2,all, wR_2,obs	0.1887, 0.1535
$\Delta\rho$min,max / (e Å^{-3})	−0.3758, 0.3830
$GooF$	1.0255
CCDC No.	2322612

Table S2. Summary of TD-DFT calculations for **Ach** (*E*) and **Ach** (*Z)*

Compound	Absorptions (nm)	Energy (eV)	Oscillator strength (f)	Transitions	Composition index (%)
Ach (*E*)	348.99	3.5526	0.5907	H→L	97.67
	247.11	5.0174	0.1481	H-6→L	21.33
				H-5→L	3.65
				H-2→L	3.43
				H-2→L+1	5.87
				H-1→L	12.17
				H-1→L+1	12.73
				H→L+3	6.54
				H→L+4	23.91
Ach (*Z*)	321.56	3.8557	0.2709	H→L	95.77
	235.66	5.2611	0.1302	H-5→H+3	3.83
				H-4→H	2.69
				H-4→H+1	20.65
				H-2→H+1	4.66
				H-2→H+3	2.34
				H→H+3	31.68
				H→H+4	23.48

Table S3. Mathematical equations used to calculate the various quantifiable parameters. For simplification, the radius (length of the crystal) is assumed to stay constant throughout the deflection. The equation $D = \theta R$ is a rational approximation for small angles of photomechanical bending.

Quantifiable parameter	Mathematical formulae
Calculation of elastic strain	ε (%) = t/2R × 100, where, 't' and 'R' stand for the thickness and radius of curvature of the bent crystal respectively.
Tip displacement/ Tip deflection (*D*)	D (mm) = $[(x_2 - x_1)^2 + (y_2 - y_1)^2]^{1/2}$, where x_1, x_2 are the *x* coordinates and y_1, y_2 are the *y* coordinates of any two consecutive points on the trajectories of the crystal's tip.
Angle of deflection (*θ*)	θ (rad) = (Tip displacement, *D* in mm) / (Length of the crystal, *R* in mm rad^{-1}) Also, θ (°) = (180/π) × θ (rad)

Table S4. Dimensions of 75 crystals of **Ach** and their corresponding time to display photosalient effect when exposed to varied UV light power densities.
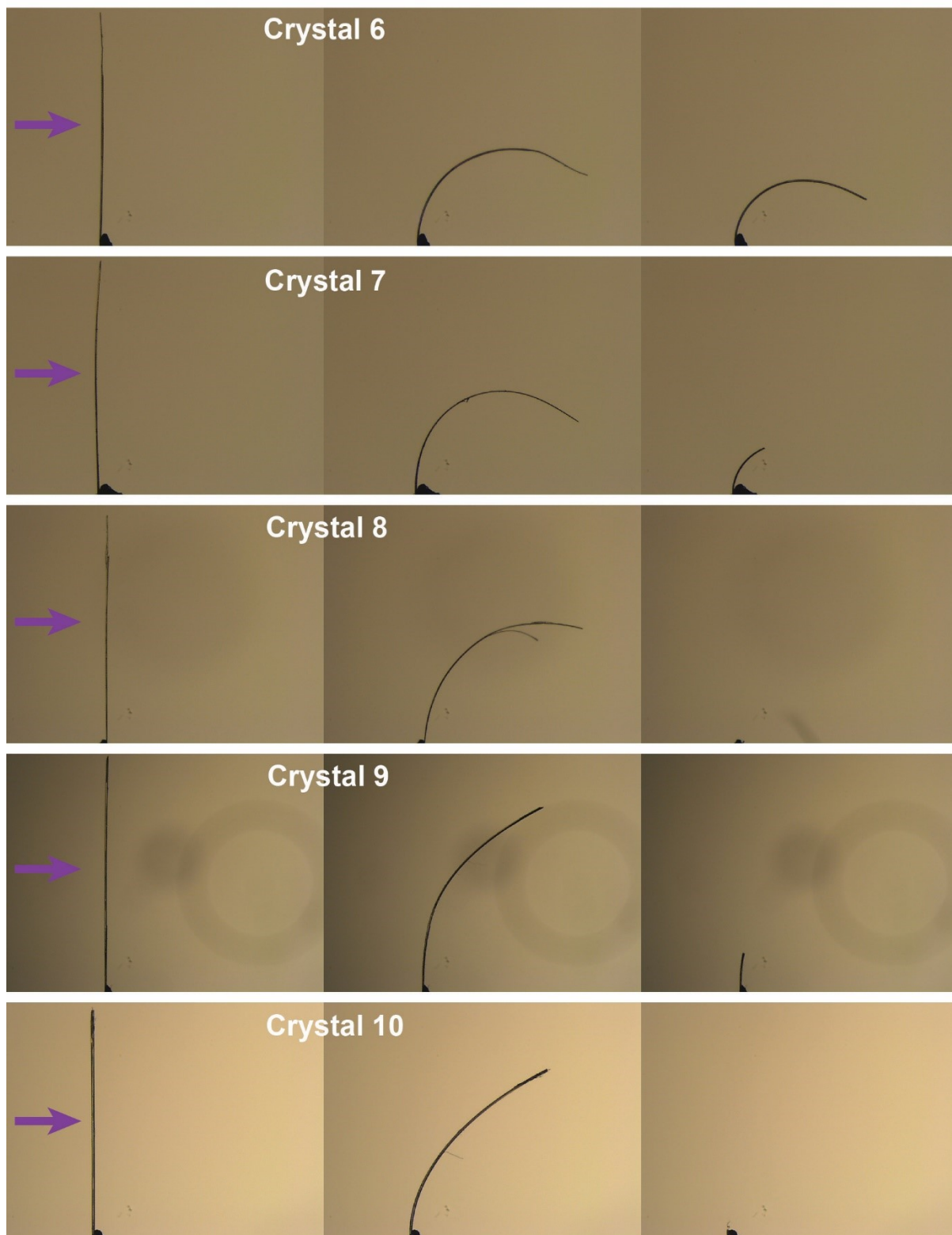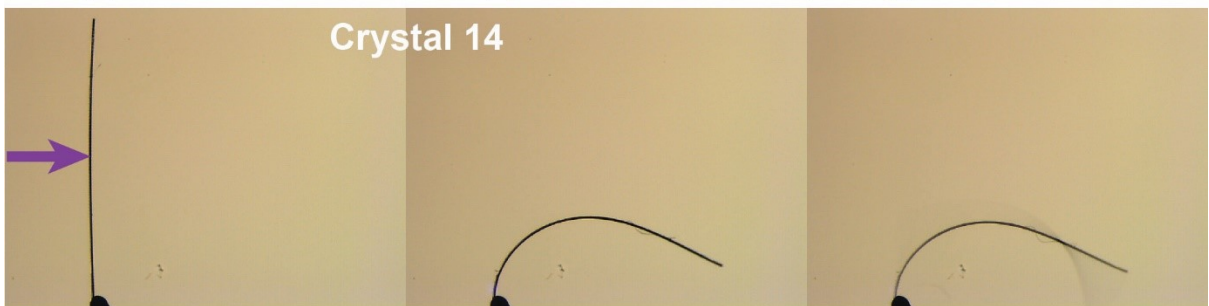
UV light power density (29.1 mW cm^{-2})

Crystal No.	Length (mm)	Width (mm)	Thickness (mm)	Surface Area (mm^2)	Time (Sec)
1	4.59	0.04	0.02	0.1836	2.89
2	4.85	0.06	0.04	0.291	13.49
3	4.14	0.05	0.035	0.207	7.33
4	5.63	0.04	0.02	0.2252	6.91
5	4.09	0.07	0.03	0.2863	4.92
6	4.8	0.04	0.03	0.192	8.26
7	4.77	0.03	0.03	0.1431	6.75
8	3.93	0.04	0.02	0.1572	28.97
9	4.04	0.06	0.04	0.2424	8.10
10	4.2	0.05	0.04	0.21	4.93
11	3.63	0.05	0.04	0.1815	4.19
12	4.32	0.05	0.035	0.216	3.71
13	5.33	0.04	0.03	0.2132	14.91
14	5.34	0.12	0.05	0.6408	12.15
15	4.93	0.08	0.05	0.3944	31.48

UV light power density (66.2 mW cm^{-2})

Crystal No.	Length (mm)	Width (mm)	Thickness (mm)	Surface Area (mm^2)	Time (Sec)
1	4	0.05	0.04	0.2	5.46
2	3.78	0.065	0.06	0.2457	18.17
3	4.02	0.08	0.03	0.3216	4.25
4	4.79	0.03	0.02	0.1437	2.13
5	4.8	0.04	0.03	0.192	10.51
6	4.69	0.04	0.03	0.1876	9.86
7	5.42	0.09	0.045	0.4878	10.28
8	6.74	0.06	0.04	0.4044	6.26
9	10.21	0.14	0.12	1.4294	18.17
10	6.49	0.11	0.06	0.7139	15.48
11	2.78	0.05	0.05	0.139	2.22
12	4.75	0.08	0.04	0.38	4.08
13	4.79	0.07	0.04	0.3353	10.57
14	4.33	0.06	0.04	0.2598	12.10
15	3.99	0.05	0.04	0.1995	9.06

UV light power density (97.9 mW cm^{-2})

Crystal No.	Length (mm)	Width (mm)	Thickness (mm)	Surface Area (mm²)	Time (Sec)
1	5.84	0.07	0.05	0.4088	4.23
2	4.82	0.07	0.04	0.3374	8.39
3	5.55	0.09	0.08	0.4995	3.09
4	5.01	0.06	0.06	0.3006	2.80
5	5.32	0.08	0.06	0.4256	4.09
6	5.48	0.07	0.04	0.3836	1.66
7	4.52	0.09	0.05	0.4068	6.92
8	5.77	0.09	0.04	0.5193	4.16
9	6.55	0.11	0.07	0.7205	2.10
10	4.44	0.07	0.05	0.3108	4.30
11	5.73	0.065	0.04	0.37245	7.89
12	7.62	0.12	0.08	0.9144	3.30
13	4.34	0.05	0.045	0.217	16.54
14	5.05	0.07	0.06	0.3535	6.20
15	4.81	0.06	0.05	0.2886	5.37

UV light power density (136.2 mW cm^{-2})

Crystal No.	Length (mm)	Width (mm)	Thickness (mm)	Surface Area (mm²)	Time (Sec)
1	5.33	0.06	0.05	0.3198	2.22
2	7.81	0.09	0.05	0.7029	1.80
3	5.9	0.05	0.04	0.295	3.01
4	7.52	0.05	0.04	0.376	1.47
5	8.89	0.06	0.04	0.5334	6.08
6	4.56	0.06	0.04	0.2736	2.36
7	5.5	0.09	0.08	0.495	1.33
8	9.63	0.11	0.07	1.0593	4.13
9	4.88	0.06	0.04	0.2928	3.91
10	3.88	0.05	0.03	0.194	4.78
11	6.13	0.06	0.06	0.3678	3.10
12	7.1	0.08	0.04	0.568	1.12
13	6	0.07	0.05	0.42	2.28
14	8.05	0.09	0.05	0.7245	2.92
15	5.62	0.06	0.04	0.3372	2.78

UV light power density (169.9 mW cm⁻²)

Crystal No.	Length (mm)	Width (mm)	Thickness (mm)	Surface Area (mm²)	Time (Sec)
1	5.18	0.07	0.06	0.3626	1.17
2	4.22	0.06	0.05	0.2532	1.11
3	5.08	0.05	0.05	0.254	22.18
4	5.16	0.06	0.05	0.3096	0.49
5	5.51	0.065	0.05	0.35815	1.01
6	8.04	0.07	0.06	0.5628	1.94
7	4.8	0.08	0.05	0.384	1.34
8	3.78	0.06	0.04	0.2268	5.29
9	6.03	0.09	0.06	0.5427	0.62
10	5.7	0.11	0.07	0.627	1.01
11	5.16	0.08	0.07	0.4128	3.33
12	7	0.07	0.05	0.49	1.35
13	7.08	0.05	0.05	0.354	0.84
14	5.51	0.05	0.04	0.2755	1.73
15	4.56	0.07	0.06	0.3192	5.81

4. Optimized coordinates.

Optimized coordinates of Ach (*E*) at B3LYP/6-31G(d) level

0 1

O	2.69368652	-2.14424757	-0.13945972
N	1.54606848	-0.16793741	0.06581140
N	0.32419204	-0.75479218	0.07658983
C	3.97491361	-0.13000901	0.00994383
C	2.70462097	-0.93143554	-0.02550051
C	-3.21179294	0.35228016	-0.03698288
C	-2.06548786	-0.51254075	0.06947925
C	-0.70013335	0.02190956	0.03450595
H	-0.56544579	1.10818844	-0.02076132
C	-4.52185085	-0.23743746	0.01911412
C	4.09247386	1.11596859	0.64369465
H	3.24683891	1.54777015	1.17288980
C	-2.25348918	-1.88226575	0.21396305

H	-1.37689654	-2.51674663	0.29153788
C	5.10281883	-0.69665872	-0.59969975
H	5.00236426	-1.67295620	-1.06244416
C	-3.13198635	1.76413673	-0.19962171
H	-2.16524284	2.25230017	-0.25691269
C	-4.65472815	-1.64119462	0.17004907
H	-5.65320971	-2.06978065	0.21027834
C	-3.54074253	-2.44629675	0.26275941
H	-3.64851125	-3.52126083	0.37712618
C	5.31306552	1.79176870	0.64774418
H	5.39676528	2.75095141	1.15128997
C	-5.66922727	0.59605207	-0.08048592
H	-6.65082619	0.13026608	-0.03471322
C	-4.26417258	2.54293815	-0.29409925
H	-4.16821313	3.61825679	-0.41827302
C	6.42533757	1.23025479	0.01871327
H	7.37505278	1.75833094	0.02055125
C	-5.54974942	1.95683589	-0.23293097
H	-6.43506502	2.58203128	-0.30826716
C	6.31811880	-0.01718772	-0.60221432
H	7.18440048	-0.46104344	-1.08505163
H	1.60874082	0.84407022	-0.02896981

Absolute Energy = -879.061435 a.u.

Number of imaginary frequencies = 0

Optimized coordinates of Ach (*Z*) at B3LYP/6-31G(d) level

0 1

O	2.97536754	2.51992845	0.15728993
N	1.12883023	1.15734405	0.21929082
N	0.24876106	2.18298048	0.36121094
C	3.31188466	0.18497695	-0.22641858
C	2.48514247	1.40970865	0.05340909
C	-2.82245897	0.25382415	0.02072056

C	-1.64263693	0.58989437	0.76754556
C	-0.99142605	1.91088830	0.57241015
H	-1.63019427	2.79213064	0.61779571
C	-3.48731869	-0.98761664	0.29254465
C	2.80992688	-0.97651375	-0.83220299
H	1.77426935	-1.02837582	-1.15802769
C	-1.16746549	-0.29661695	1.72329223
H	-0.29877725	-0.02625747	2.31810547
C	4.66996626	0.24454352	0.11609154
H	5.04817508	1.15949267	0.56017844
C	-3.35406735	1.09842269	-0.99153653
H	-2.84441450	2.02645746	-1.23088885
C	-2.95777452	-1.85972704	1.28111015
H	-3.46951078	-2.79855589	1.47843055
C	-1.82132085	-1.52368407	1.97881264
H	-1.42601967	-2.19038381	2.73992347
C	3.64909648	-2.06541309	-1.07100580
H	3.25250577	-2.95626360	-1.55031120
C	-4.65855772	-1.31987388	-0.43959673
H	-5.15613127	-2.26267770	-0.22508628
C	-4.49280620	0.74663255	-1.68262004
H	-4.88311588	1.40651532	-2.45247165
C	4.99497478	-2.00497623	-0.70663617
H	5.64686344	-2.85467707	-0.89106795
C	-5.15502739	-0.47196505	-1.40309438
H	-6.05185560	-0.73782999	-1.95574945
C	5.50443327	-0.84566939	-0.11534480
H	6.55371497	-0.79171898	0.16177901
H	0.79102340	0.19943424	0.24067542

Absolute Energy = -879.057079 a.u.

Number of imaginary frequencies = 0

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6. Legends to the Supporting Movies:

Video S1: Elastic bending of **Ach** single crystal.

Video S2: Photoresponsive behaviour of a bunch of **Ach** single crystals.

Video S3: Photoresponsive behaviour of individual **Ach** single crystals.