Supporting Information

Intense Red Emissive Organic Crystals with Elastic Bending Ability and Optical Waveguiding Behaviour

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Materials. All chemicals were obtained from Energy Chemical or TCI Chemical Co. at the highest purity available. Absolute solvents (over molecular sieves) and starting materials obtained from commercial source were used without further purification.

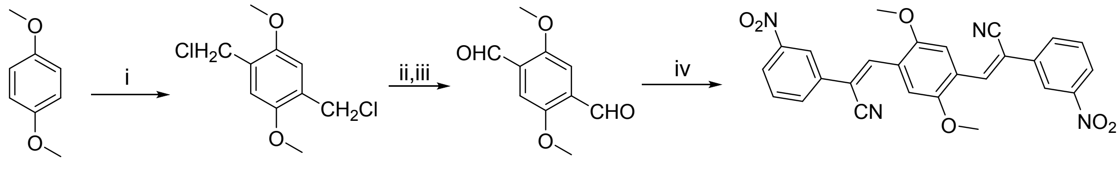
Instrumentation: Starting materials for organic syntheses were obtained from commercial sources and used as received. ^{1}H spectra were measured on a Bruker Avance 400 MHz spectrometer and ^{13}C spectra were measured on a Bruker Avance 500 MHz spectrometer with tetramethylsilane as the internal standard. Mass spectra were recorded on a GC/MS mass spectrometer. Element analyses were performed on a Flash EA1112 spectrometer. UV−vis absorption spectra were recorded by a Shimadzu UV-2550 spectrophotometer. The emission spectra were recorded by a Shimadzu RF-5301 PC spectrometer or a Maya2000 Pro CCD spectrometer. The absolute fluorescence quantum yields were measured on an Edinburgh FLS920 spectrometer combined with a calibrated integrating sphere. The fluorescence lifetimes were measured on Edinburgh FLS920 using a time-correlated single-photon (TCSPC) module. Thermogravimetric analyses (TGA) were performed on a TAQ500 thermogravimeter at a heating rate of

10 °C min^{-1} under nitrogen. The scanning electron microscopy (SEM) images were acquired from a field emission scanning electron microscope (Hitachi SU8020).

Single-crystal X-ray diffraction. Single crystal X-ray diffraction data were collected on a Rigaku RAXIS-PRID diffractometer using the ω-scan mode with graphitemonochromator Mo Kα radiation. The structures were solved with direct methods using the SHELXTL programs and refined with full-matrix least squares on F^2. Non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were calculated and refined isotropically. The crystallographic data have been deposited with Cambridge Crystallographic Data Centre (CCDC). CCDC number: 2055692 (Cry-**1O**) and 2055693 (Cry-**1R**).

Optical waveguide measurements. The crystal slice was irradiated by the third harmonic (355 nm) of a Nd:YAG (yttrium-aluminum-garnet) laser at a repetition rate of 10 Hz and a pulse duration of about 10 ns. The energy of laser was adjusted by using the calibrated neutral density filters. The beam was focused into a stripe whose shape was adjusted to 3.3 × 0.6 mm by using a cylindrical lens and a slit. The emission was detected at one end of the crystal using a Maya2000 Pro CCD spectrometer.

Synthesis



a **c** **1**

Scheme S1. The synthetic route of the compound **1**.

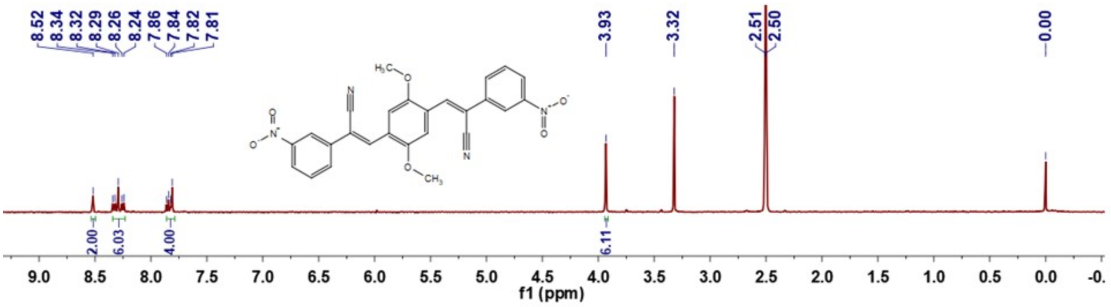
i: A mixture of hydroquinone dimethyl (6.90 g, 50 mmol), paraformaldehyde (3.0 g) and 50% formaldehyde aqueous solution (5.0 mL) in 30 mL of 1,4-dioxane was heated to reflux. 5.0 mL concentrated hydrochloric acid was added every 30 min or twice. Then 30 mL concentrated hydrochloric acid was added after 3 hours. After cooling down to room temperature dry white precipitate **a** was obtained by vacuum filtration for later use.

ii: A mixture of precipitate **a** and hexamethylenetetramine (18.0 g) in 50 mL of chloroform was heated to reflux for 24 hours. After cooling down to room temperature dry white precipitate **b** was obtained by vacuum filtration for later use.

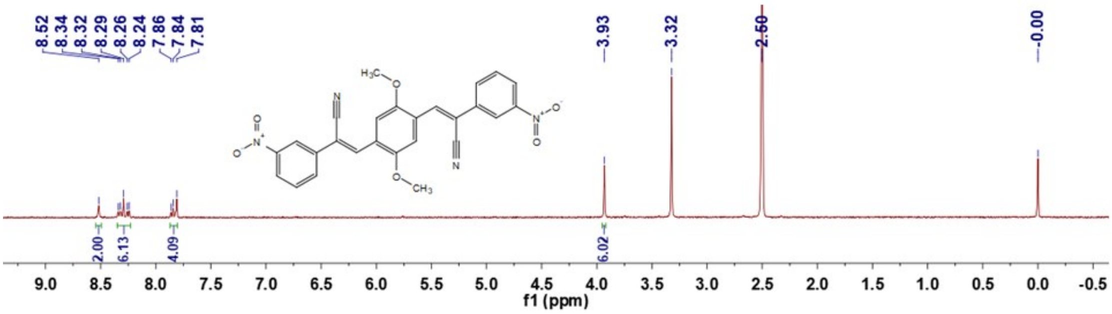
iii: A mixture of precipitate **b** and acetic acid in 30 mL of water was heated to reflux for 24 hours. After cooled to room temperature, the reaction mixture was poured into 200 mL of cold water and extracted by 20 mL of dichloromethane for three times. After dichloromethane solution was dried by anhydrous sodium sulfate and evaporated, golden precipitate **c** was obtained for later use.

iv: A mixture of precipitate **c**, sodium methoxide (0.05 g) and 3-nitrophenylacetonitrile in 30 mL of methanol was stirred in room temperature for 2 hours. The resulting precipitate was obtained by vacuum filtration and the pure yellow product **1** was obtained by silica gel column chromatograph (DCM) in 25% yielding. ^{1}H NMR (400 MHz, DMSO) δ 8.52 (s, 2 H), 8.35–8.23 (m, 6 H), 7.87–7.80 (m, 4 H), 3.93 (s, 6 H). ^{13}C NMR (126 MHz, CDCl3) δ 152.19, 148.83, 138.17, 136.28, 132.04, 130.24, 125.49, 123.89, 120.84, 117.52, 110.45, 110.27, 77.01, 56.45. MS m/z: 482.21 [M]+ (calcd: 482.12). Anal. calcd (%) for $C_{26}H_{18}N_4O_6$: C, 64.73; H, 3.76; N, 11.61. Found: C, 64.75; H, 3.71; N, 11.57.

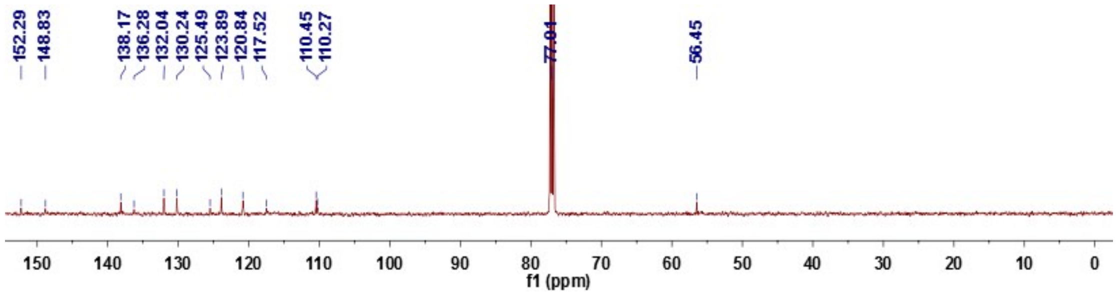
Crystal growth: Dissolve massive compound in dichloromethane to produce a saturated solution. Add 2.0 mL saturated solution into each of the two glass tubes separately, 6.0 mL ethanol into tube 1 and 6 mL n-hexane into tube 2 respectively along the tube wall without destroying the previous solution surface then seal the tube with parafilm. Two different organic phases gradually diffuse with each other with time goes by. After standing at room temperature for one week, orange crystal was obtained in tube 2. After standing at room temperature for two weeks, red crystal was obtained in tube 1.



^{1}H NMR spectrum of compound **1** (*Cry*-**1R** ,400 MHz, DMSO).



^{1}H NMR spectrum of compound **1** (*Cry*-**1O** ,400 MHz, DMSO).



^{13}C NMR spectrum of compound **1** (126 MHz, $CDCl_3$).

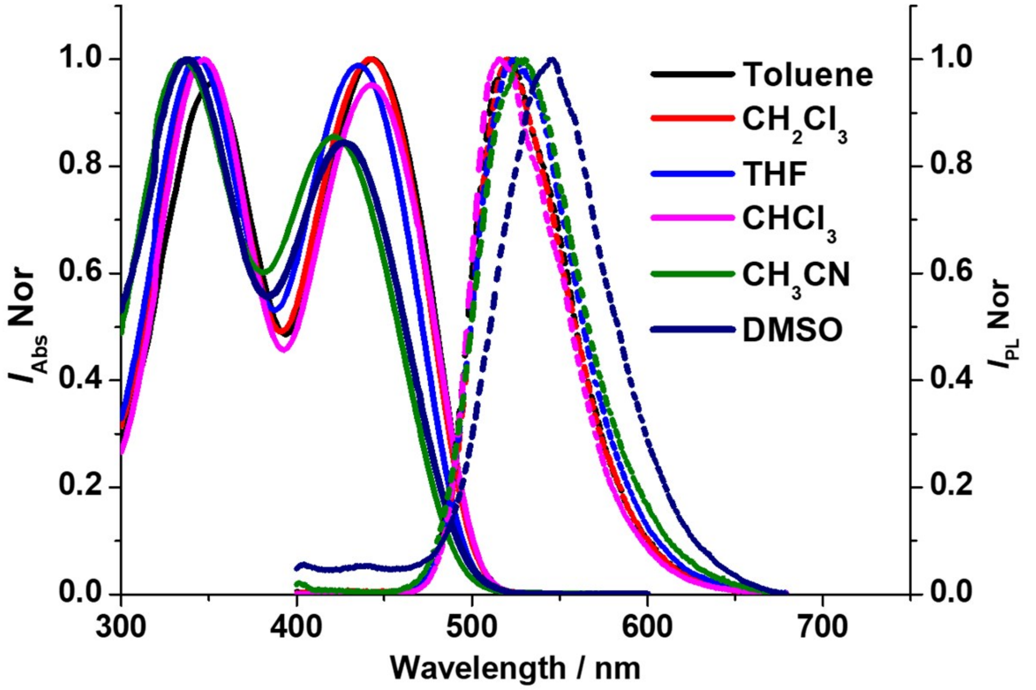


Figure S1. Absorption (solid line) and fluorescence spectra (dashed line) in various solvents.

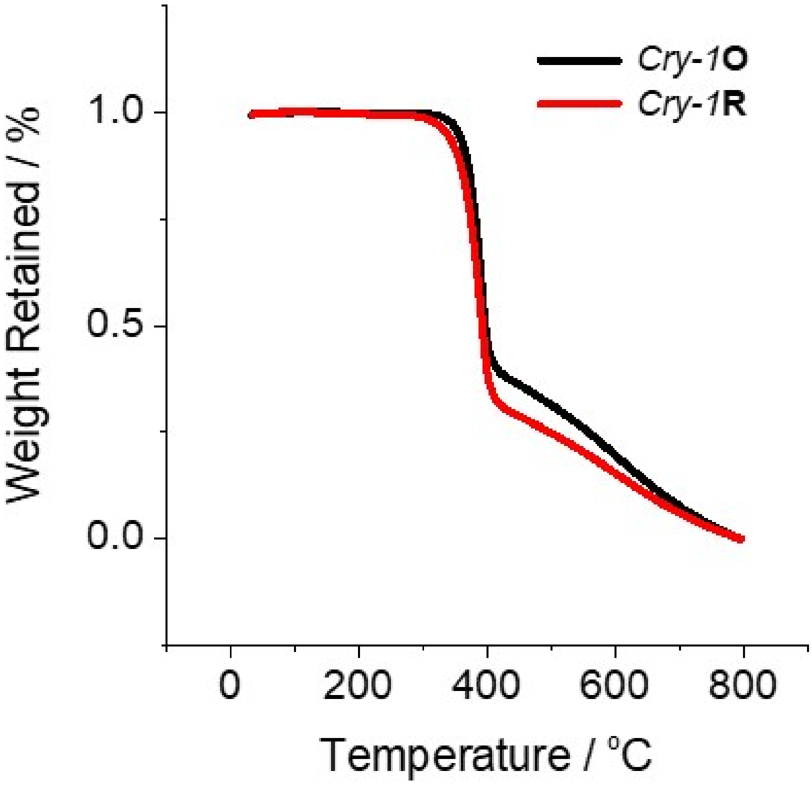


Figure S2. TGA analysis of *Cry*-**1O** and *Cry*-**1R**

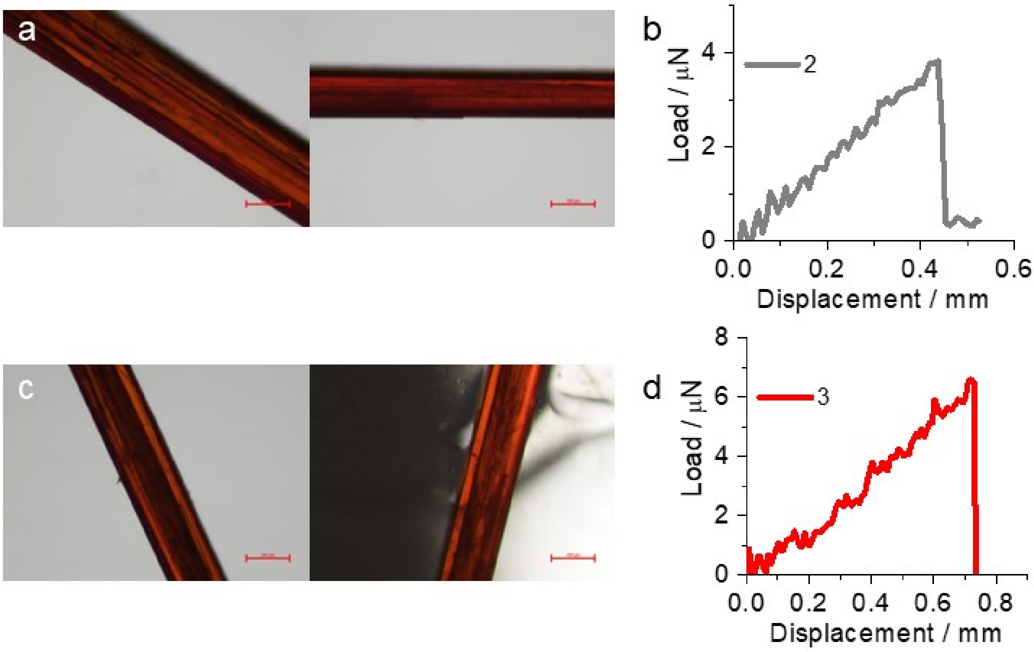


Figure S3. Microscope images (a,c) of the other 2 three-point bending experiments and the corresponding displacement-load curve (b,d)

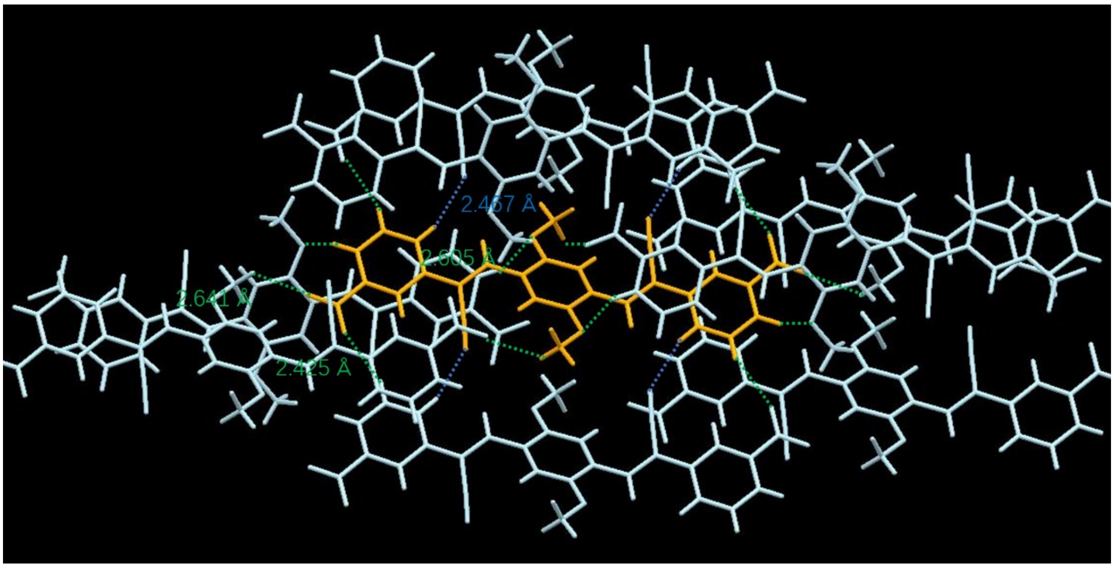


Figure S4. Intermolecular hydrogen bonds (marked by broken lines) between a molecule and neighboring ones in *Cry*-**1O**.

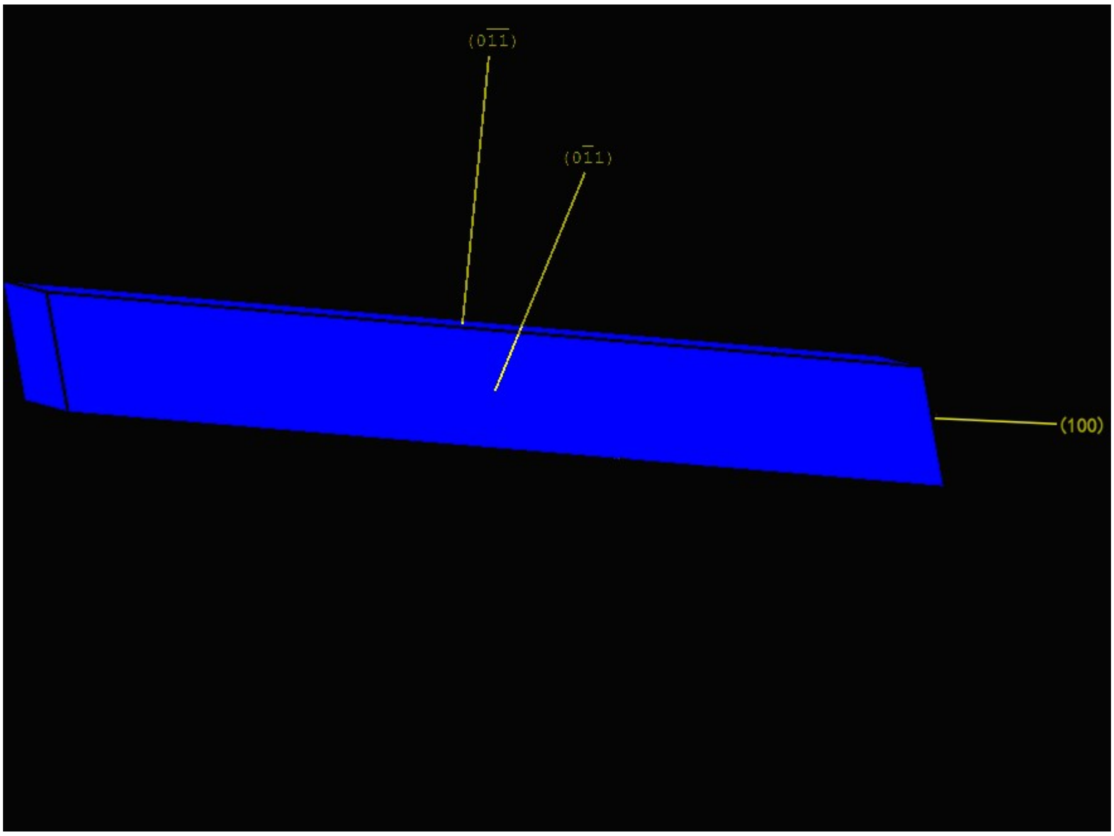


Figure S5. Determination of crystal faces of *Cry*-**1R** by X-ray diffraction.

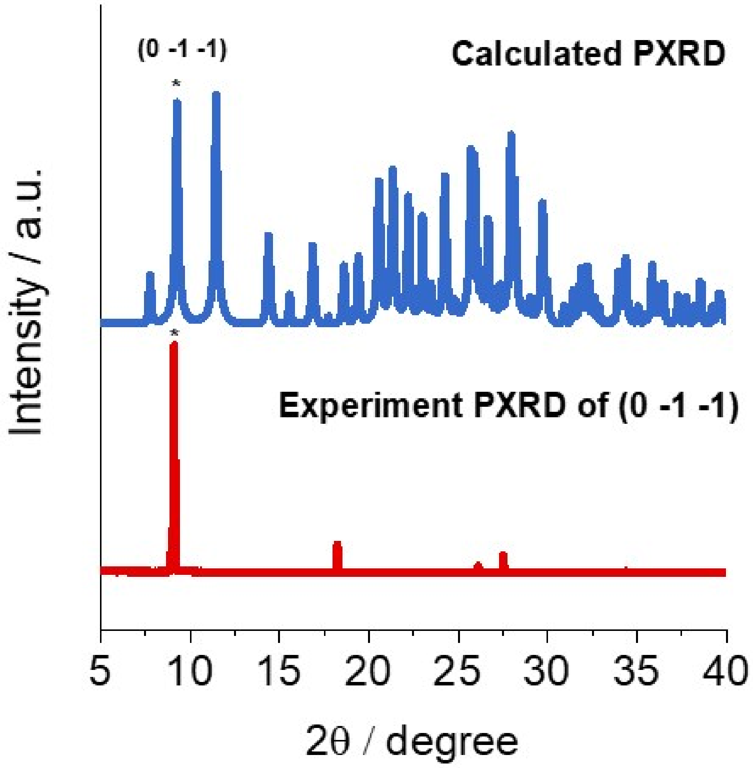


Figure S6. Calculated and experimental PXRD patterns of the Cry-1R (0-1-1) face.

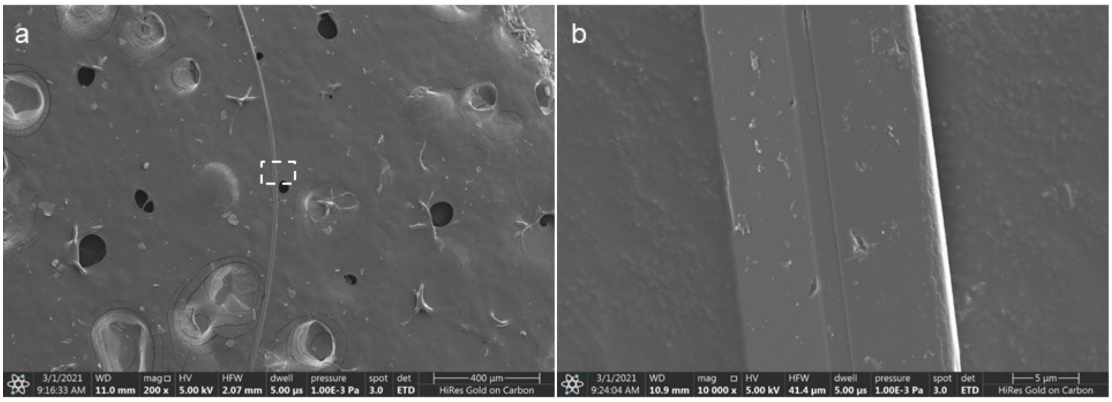


Figure S7. SEM images of the Cry-1R in bent state (a: 200X magnification b:10000X magnification)