Electronic Supplementary Information

Quantifiable Stretching-Induced Fluorescence Shifts of an Elastically Bendable and Plastically Twistable Organic Crystal

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Contents

General information

All chemicals for syntheses were purchased from commercial sources. The solvents for syntheses were analytical-reagent grade without further purification. 1H and $^{13}C\{^{1}H\}$ NMR spectra were measured on a Bruker Avance 500 MHz spectrometer with tetramethylsilane as the internal standard. UV−vis absorption spectra were recorded by a Shimadzu UV-2550 spectrophotometer. Stretching tests were carried out on the No. 5944 universal materials tester produced by American ITW group Engstrang Corporation. The emission spectra were recorded by a Shimadzu RF-5301 PC spectrometer or a Maya2000 Pro CCD spectrometer. Differential scanning calorimetric (DSC) measurements were performed on a TA DSC Q20 instrument.

1. Synthesis and characterizations

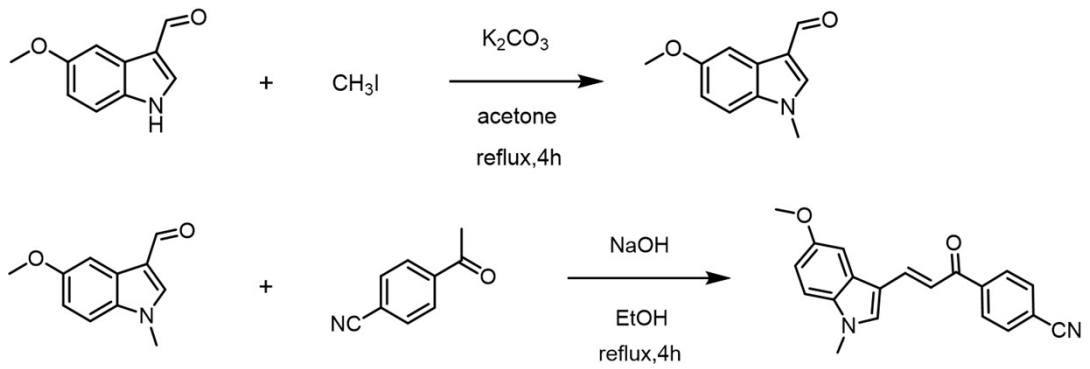


Fig. S1 The synthetic procedure of target compound

5-Methoxy-1H-indole-3-carbaldehyde (1.75 g, 10 mmol) were dissolved in 50 mL acetone, and K_2CO_3 (4.15 g, 30 mmol) was added. Then 1 mL CH_3I was injected into the solvent, the mixture was refluxed for 4 h. After cooling to room temperature, K_2CO_3 was filtered and the solvent was removed by reduced pressure distillation. Then 80 mL ethanol was poured into the flask. 4-Acetylbenzonitrile (1.45 g, 10 mmol) and NaOH (0.08 g, 2 mmol) were added into the solvent, the mixture was refluxed for 4 h. The generated precipitate was filtered and washed with ethanol to give the crude product, which was purified by vacuum sublimation deposition to produce compound as a yellow solid (1.99 g, 63% yield). ^{1}H NMR (500 MHz, DMSO-d6) δ 8.26–8.19 (m, 2H), 8.13 (s, 1H), 8.07 (s, 1H), 8.03 (dd, J = 9.1, 2.8 Hz, 1H), 7.58–7.43 (m, 3H), 6.96 (dd, J = 8.8, 2.4 Hz, 2H), 3.88 (s, 3H), 3.84 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d6) δ 188.18, 155.89, 142.61, 140.21, 137.47, 133.52, 133.16 (2C), 129.15 (2C), 127.02, 118.88, 114.82, 114.67, 112.64, 112.21, 112.04, 103.41, 56.11, 33.77.

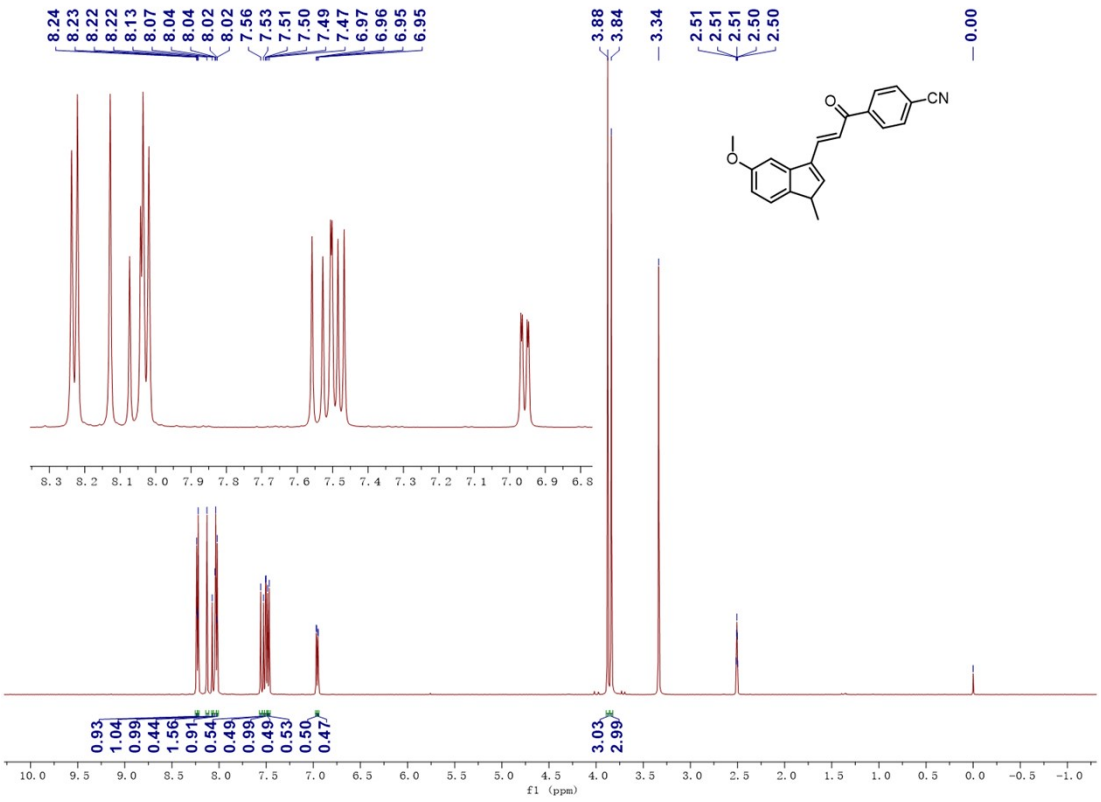


Fig. S2 ^{1}H NMR spectrum of compound (500 MHz, DMSO-d6).

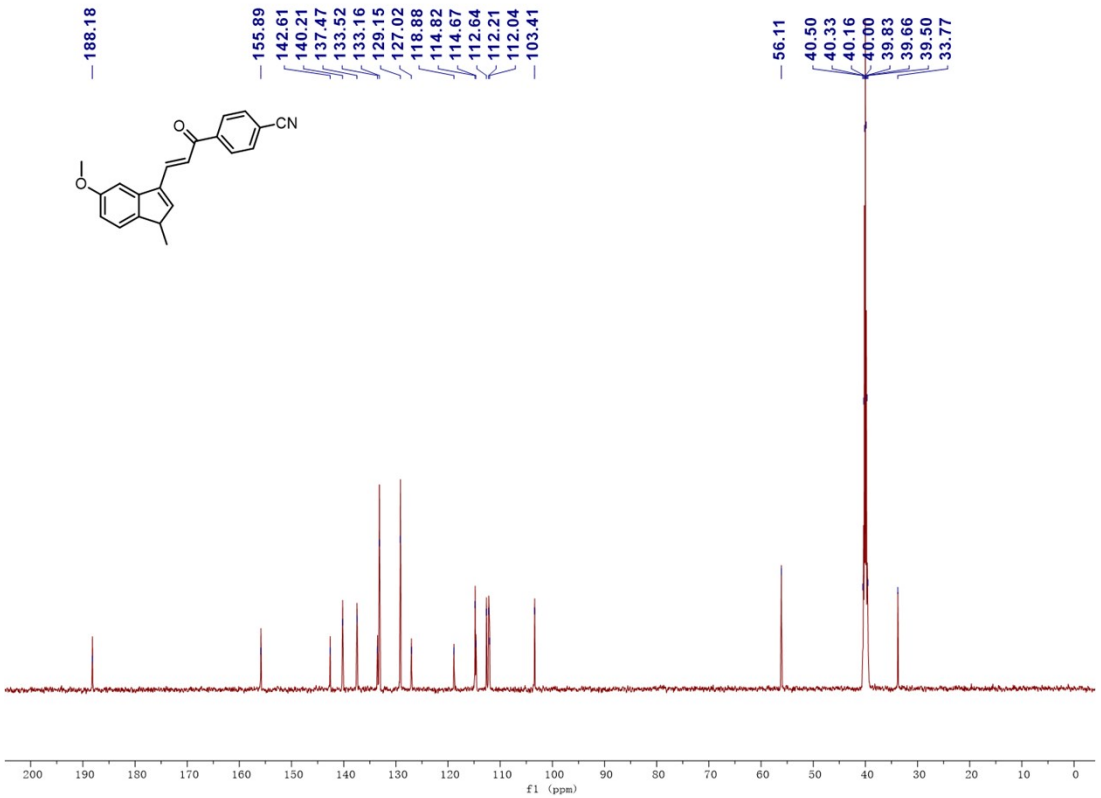


Fig. S3 ^{13}C{^{1}H} NMR spectrum of compound (126 MHz, DMSO-d6).

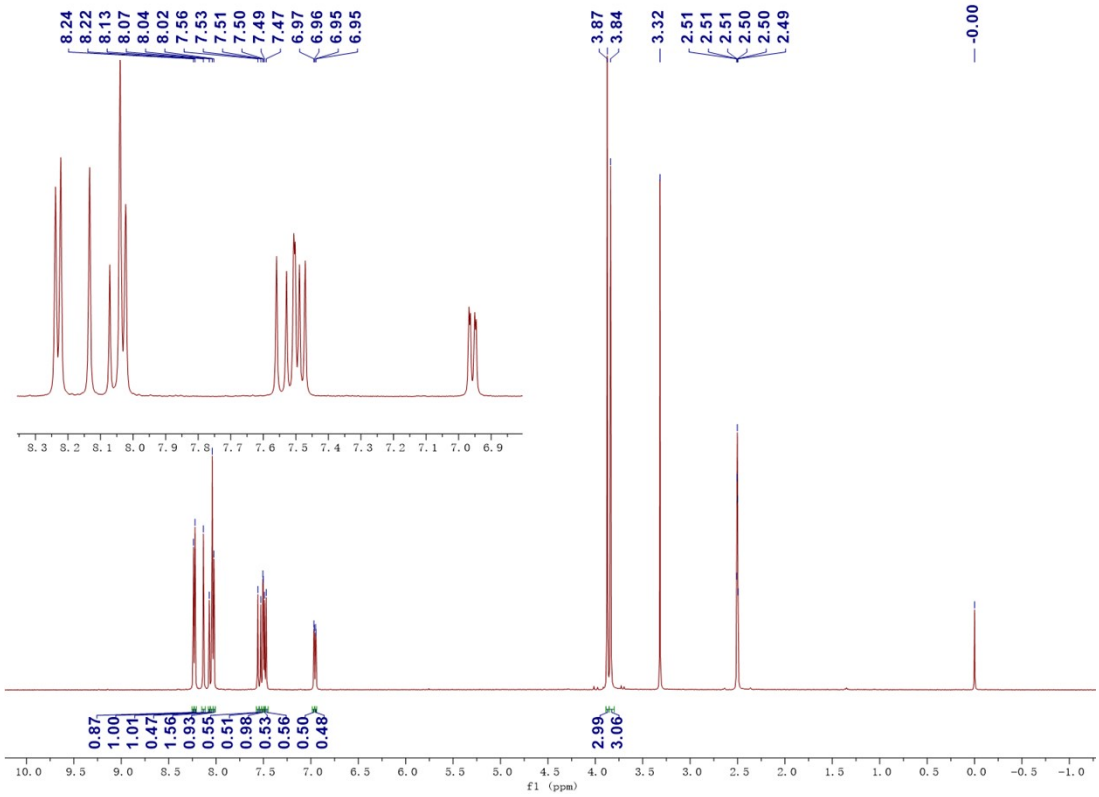


Fig. S4 ^{1}H NMR spectrum of compound after 365 nm irradiation (power: 16.7 mW/cm^2) for 5 minutes (500 MHz, DMSO-d6).

2. Photophysical properties

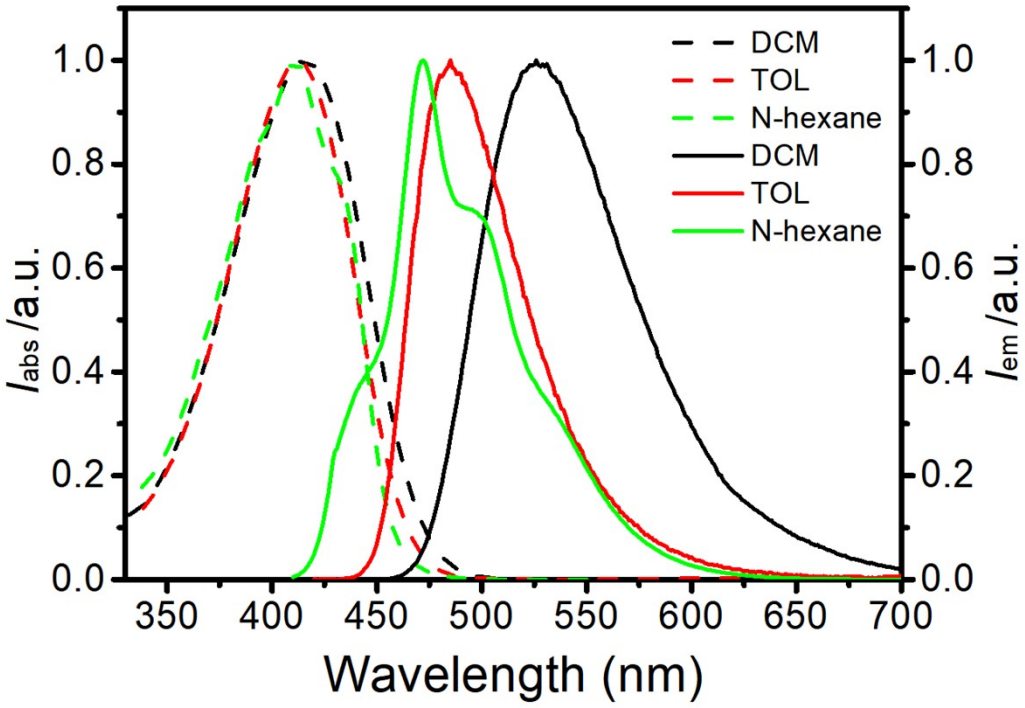


Fig. S5 Absorption and emission spectra of compound at different solvents.

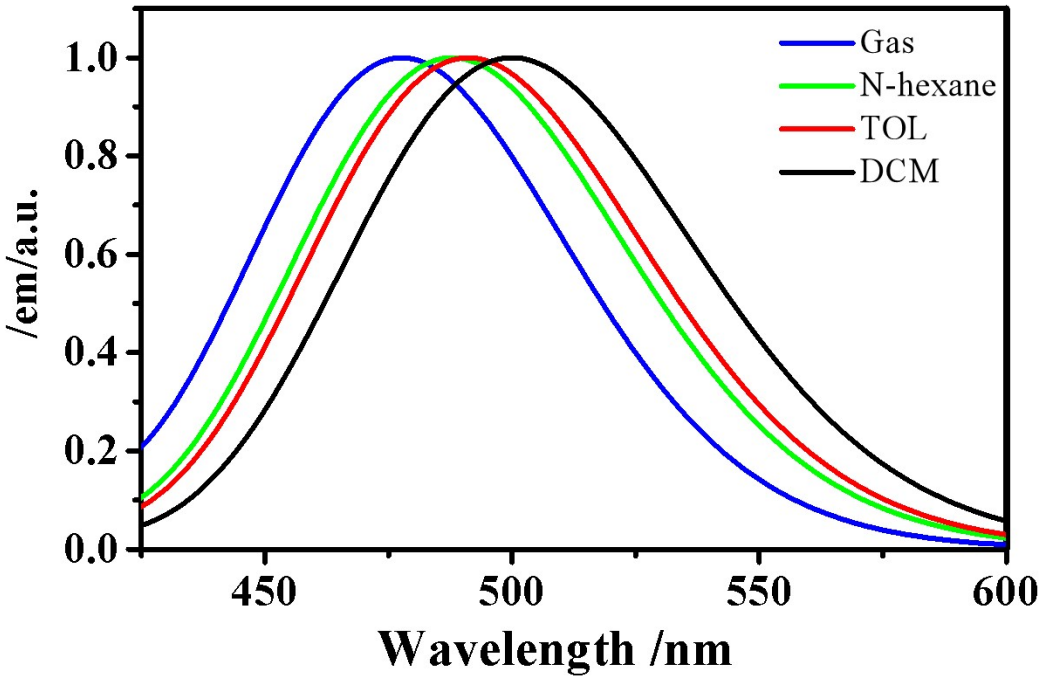


Fig. S6 Simulated emission spectra at different solvent.

	ε^a	State	ΔE (eV)	λ_{em} (nm)	Excitation
gas	0	S_1	2.57	482	HOMO → LUMO (81%); HOMO → LUMO+1 (6 %)
Hexane	1.88	S_1	2.52	492	HOMO → LUMO (84%); HOMO → LUMO+1 (7 %)
TOL	2.37	S_1	2.50	495	HOMO → LUMO (84%); HOMO → LUMO+1 (7 %)
DCM	8.93	S_1	2.46	504	HOMO → LUMO (86%); HOMO → LUMO+1 (7 %)

[a]: ε is the dielectric coefficient of the solvent.

Table S1. Emissions and dominant orbital excitations obtained from TD-DFT calculations in different solvent and gas phase.

Experimental section: the TD-DFT calculations were performed to investigate the emission behavior of MMIAB at different solvent with a polarizable continuum model (PCM). The BMK functional with inclusion of 42% non-local Hartree Fock exchange and 6-31G (d, p) basis set were adopted to optimize the excited states. Geometry optimizations and emission spectra simulations were carried out using the Gaussian 09 package.

3. Thermal property

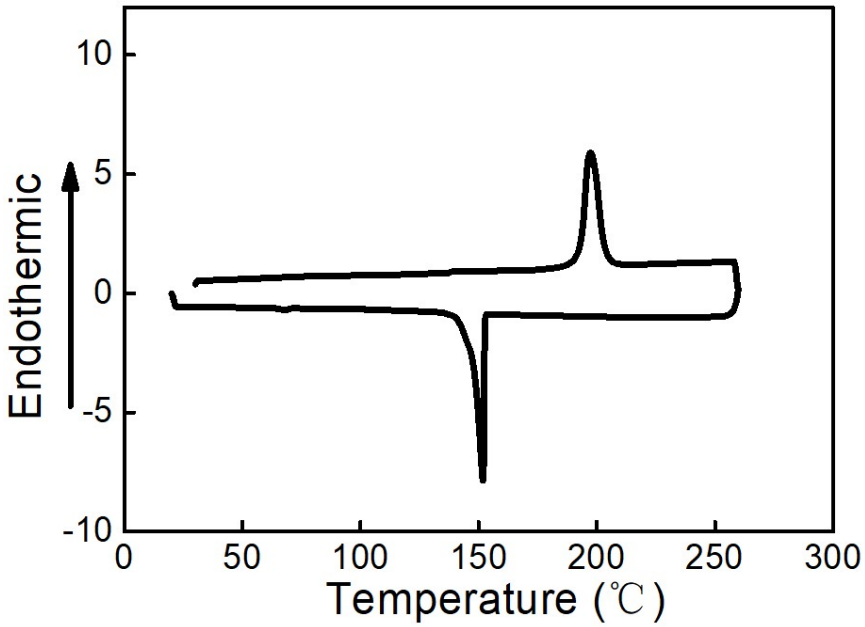


Fig. S7. DSC curve of the crystals.

4. Strain of elastic and twisted-elastic crystals

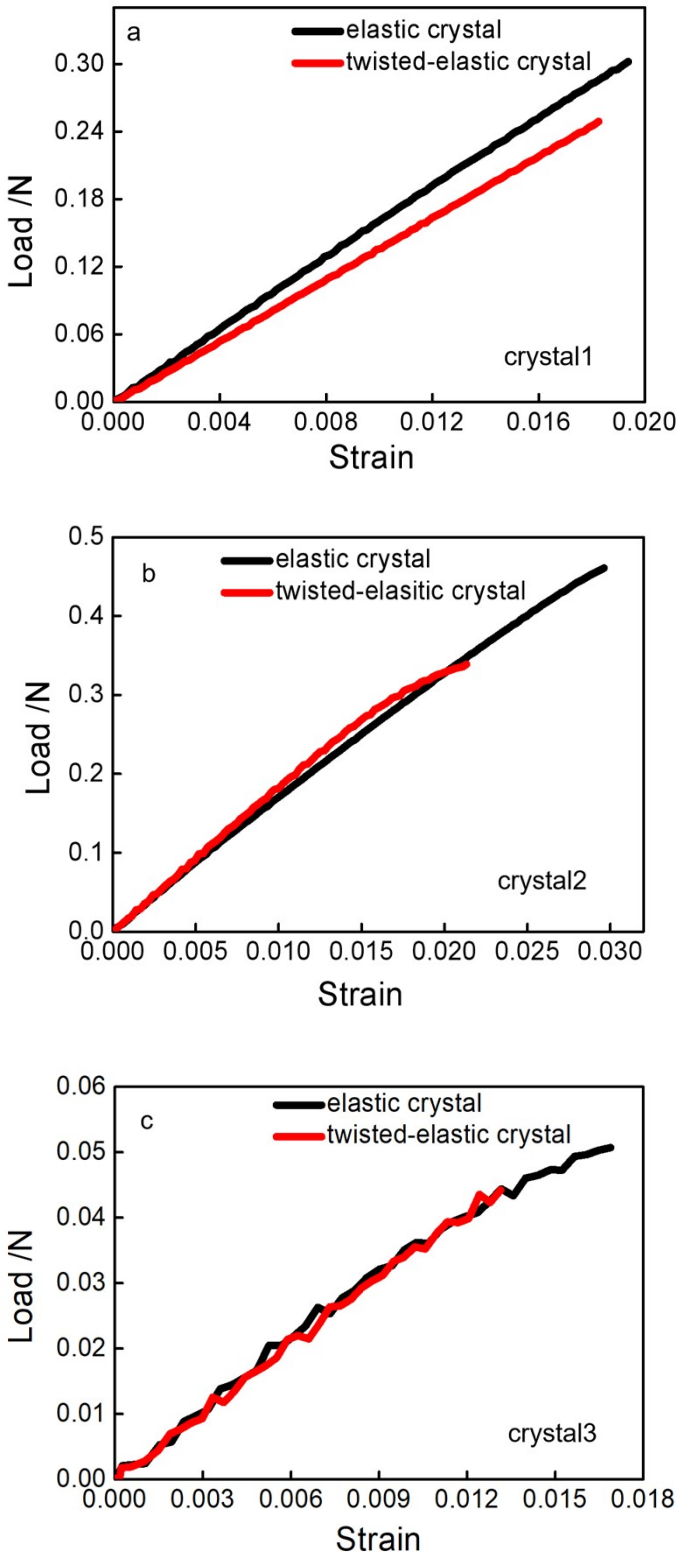


Fig. S8. Tenslie tests of elastic and twisted-elastic parts of crystals.

5. Spectra test of a crystal in different parts

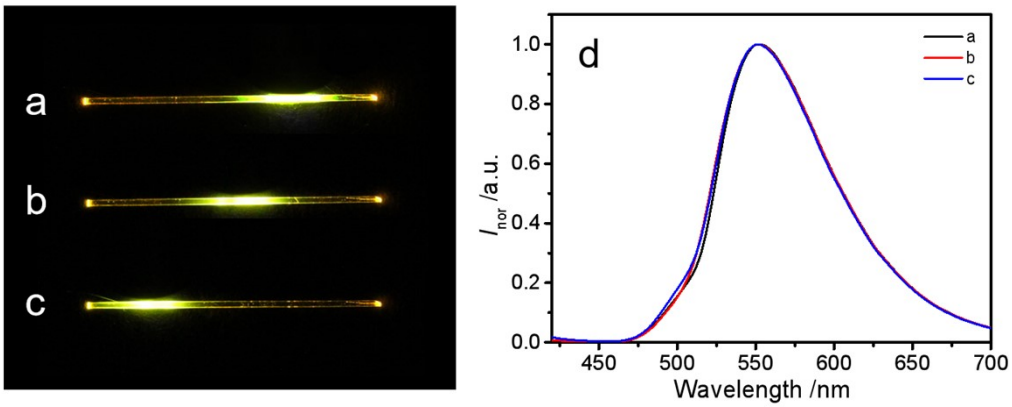


Fig. S9 Photos of different detecting points of a crystal and their emission spectra.

6. Tensile tests

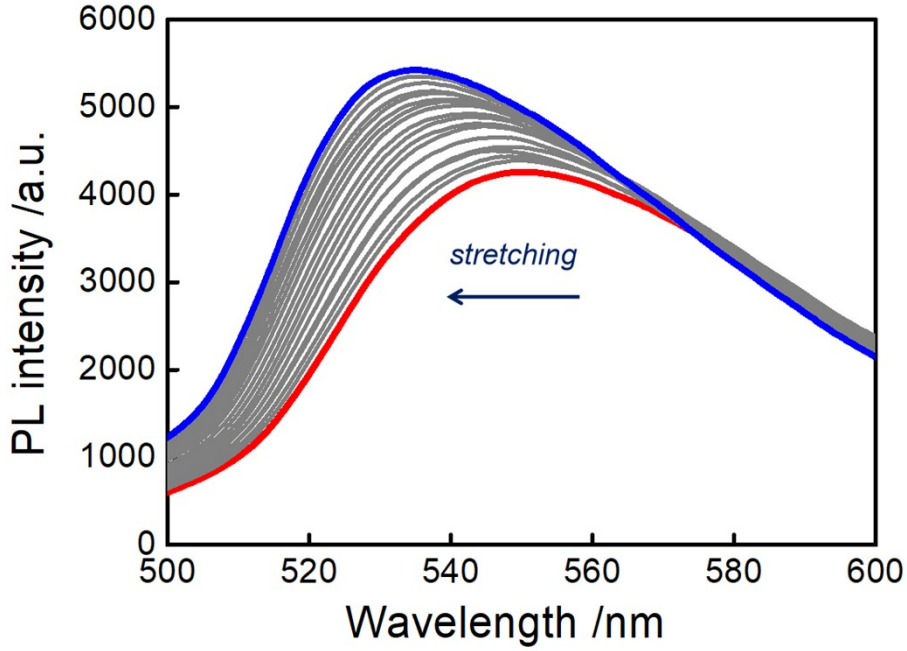


Fig. S10 The fluorescence intensity of one crystal under different strain.

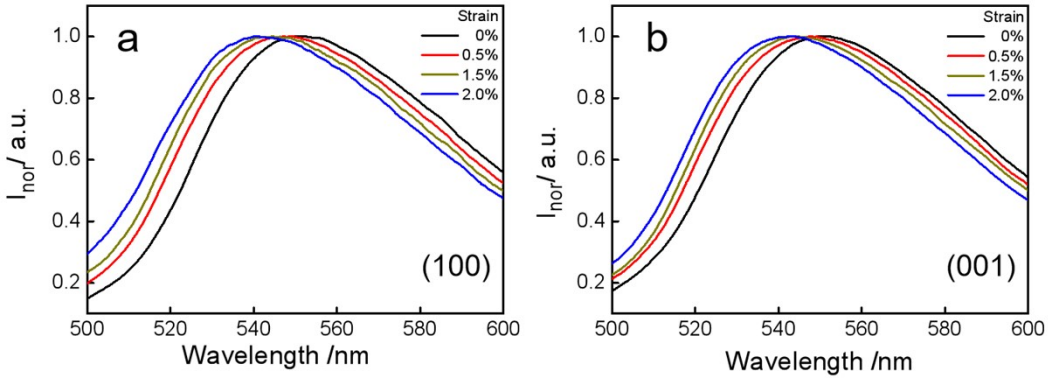


Fig. S11 The emission spectra of different faces of one stretching crystal.

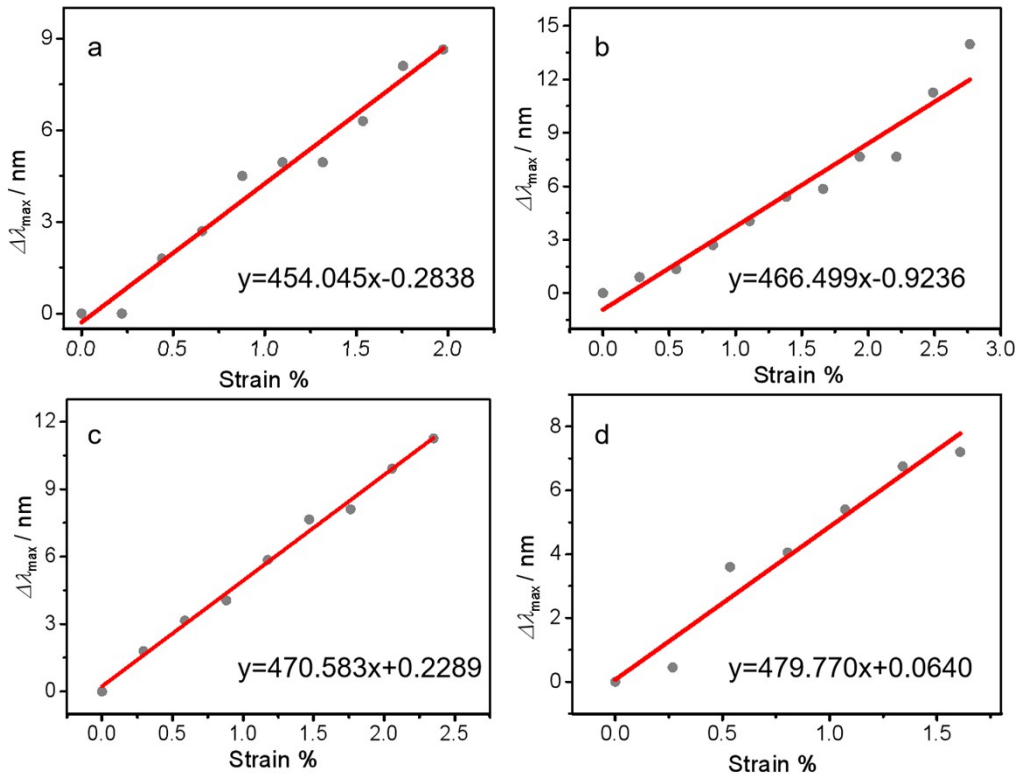


Fig. S12 Wavelength changes-strain linear fit curves of four different crystals.

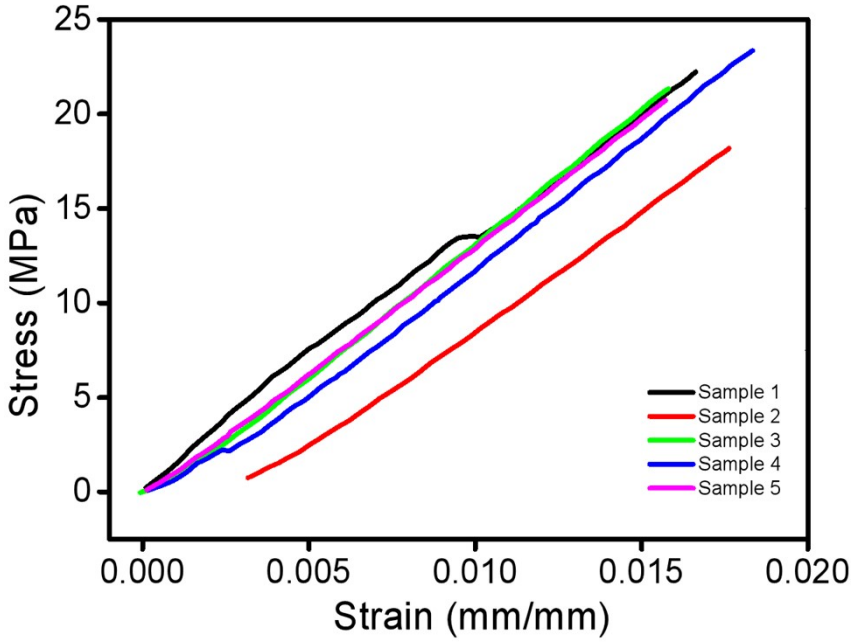
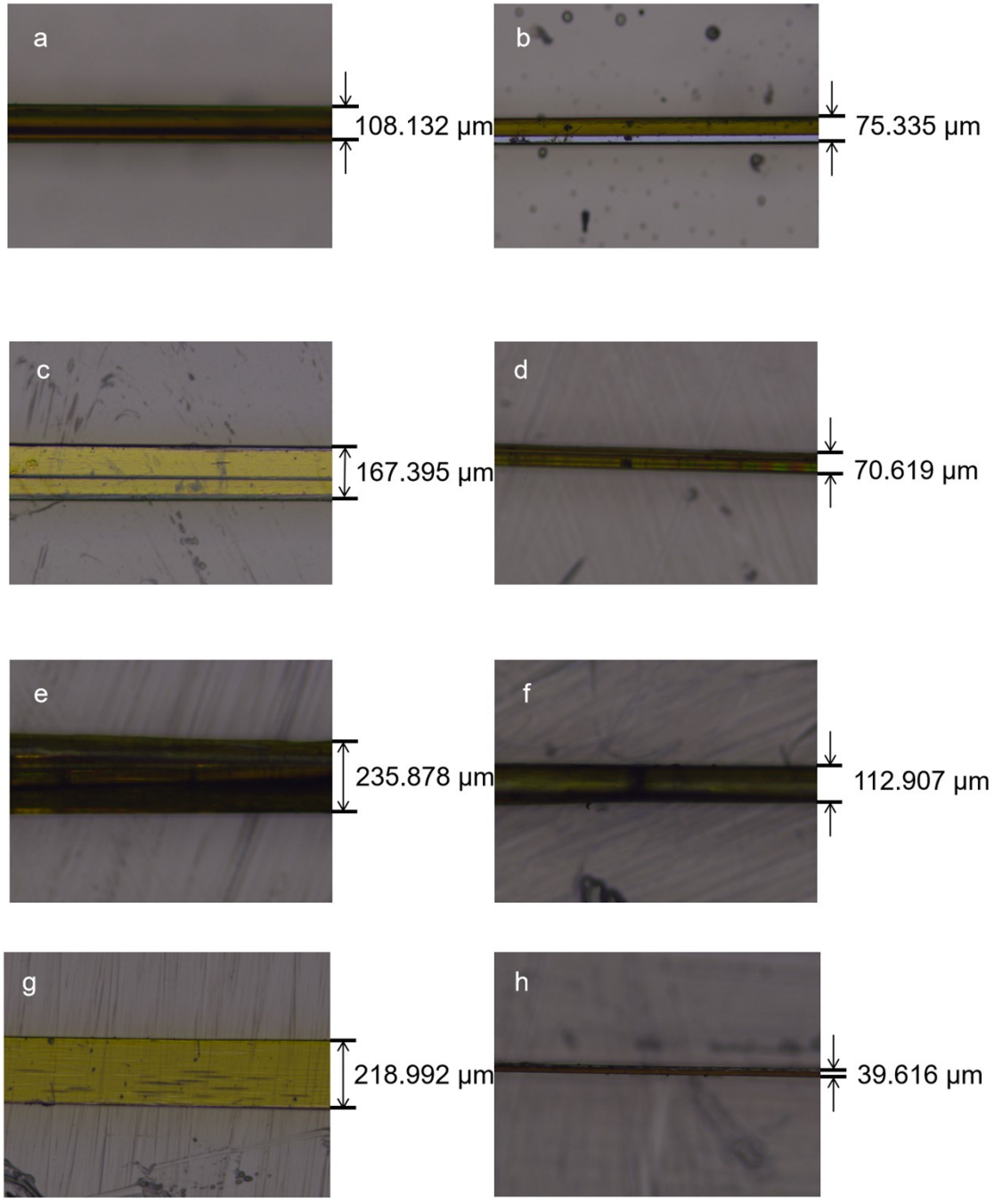


Fig. S13 Stress-strain curves of five crystals in tensile test.

Serial number	Modulus /GPa
1	1.3
2	1.2
3	1.4
4	1.3
5	1.3

Table S2. The modulus of five crystals.



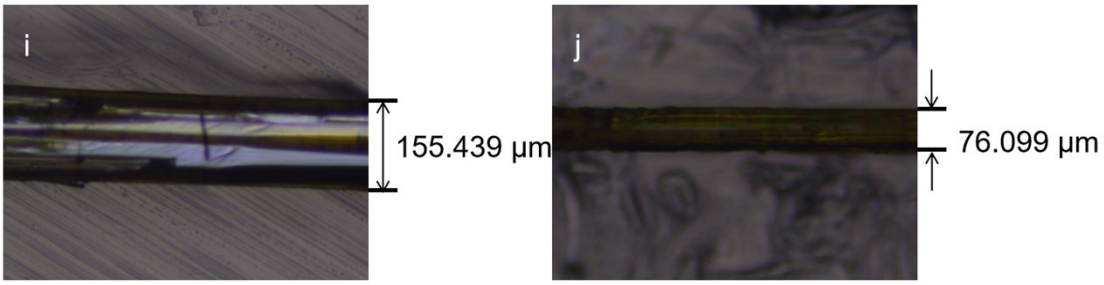


Fig. S14 Microphotographs and sizes of five samples.

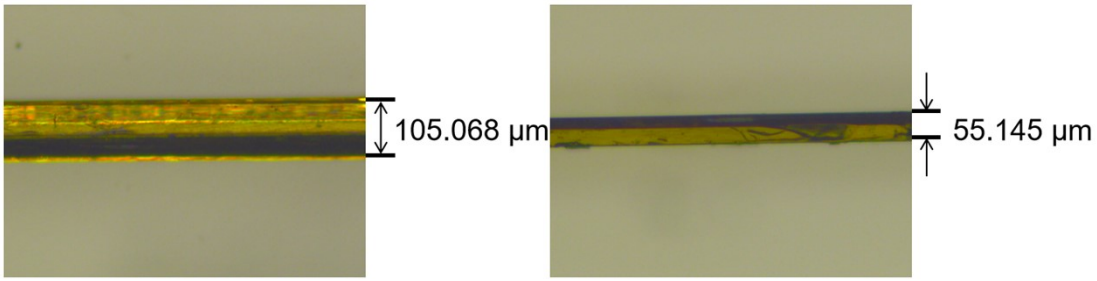


Fig. S15 Microphotographs and size of blue-shifted 17 nm crystal.

7. X-ray diffraction analysis

Powder X-ray diffraction data of crystal were collected on a Rigaku SmartLab 3 diffractometer with Cu•Kα radiation.

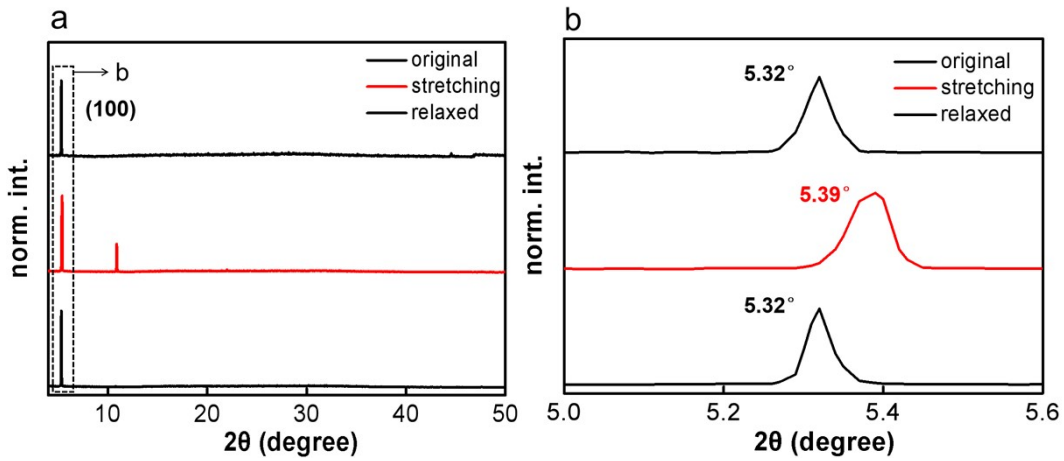


Fig. S16 XRD patterns of the crystals in original, stretching and relaxed state.

8. Tension sensing characteristic curve

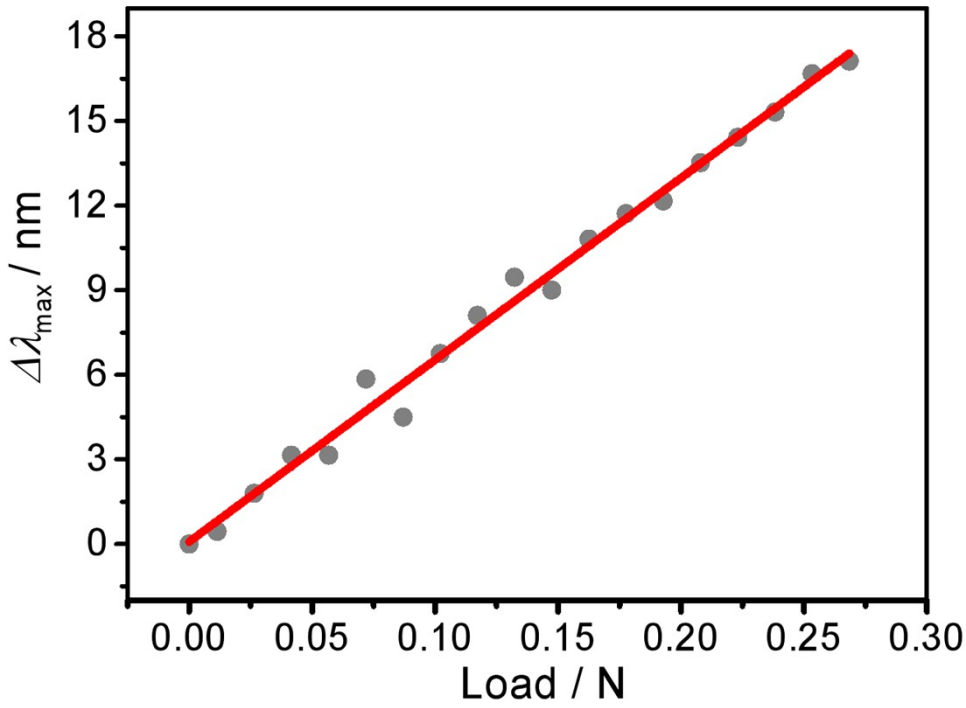


Fig. S17 Tension sensing characteristic curve. The data was fitted by a function of y=a+bx, where a and b are 0.082 and 64.50, respectively.

9. X-ray crystallographic analysis

Single crystal X-ray measurements. Diffraction data of crystals were collected on a Rigaku RAXIS-PRID diffractometer. The structures were solved with direct methods using the Olex2 programs and refined with full-matrix least-squares on F2. Non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were calculated and refined isotropically. The crystallographic information has been deposited at the Cambridge Crystallographic Data Centre (CCDC). CCDC number: 2106756

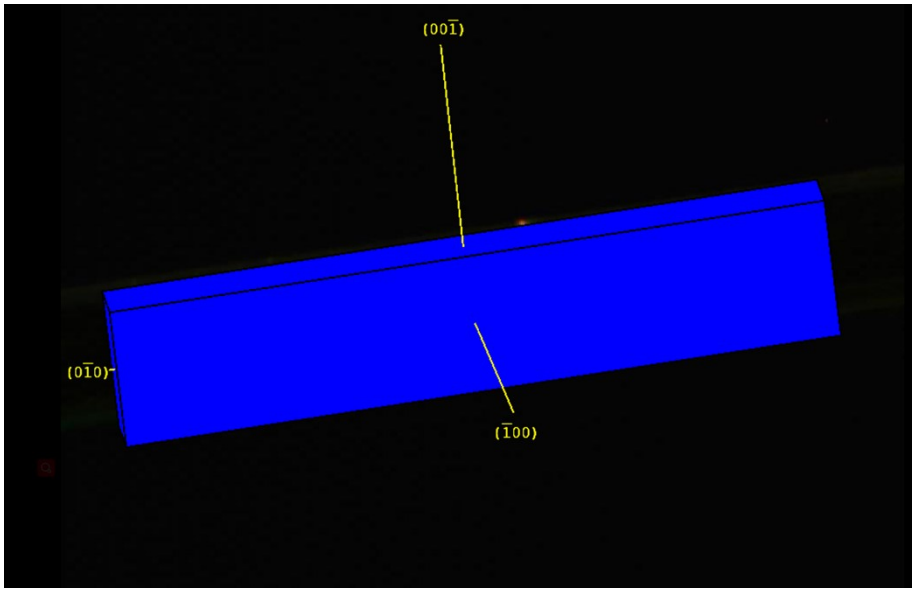


Fig. S18 Growth morphology of crystal.

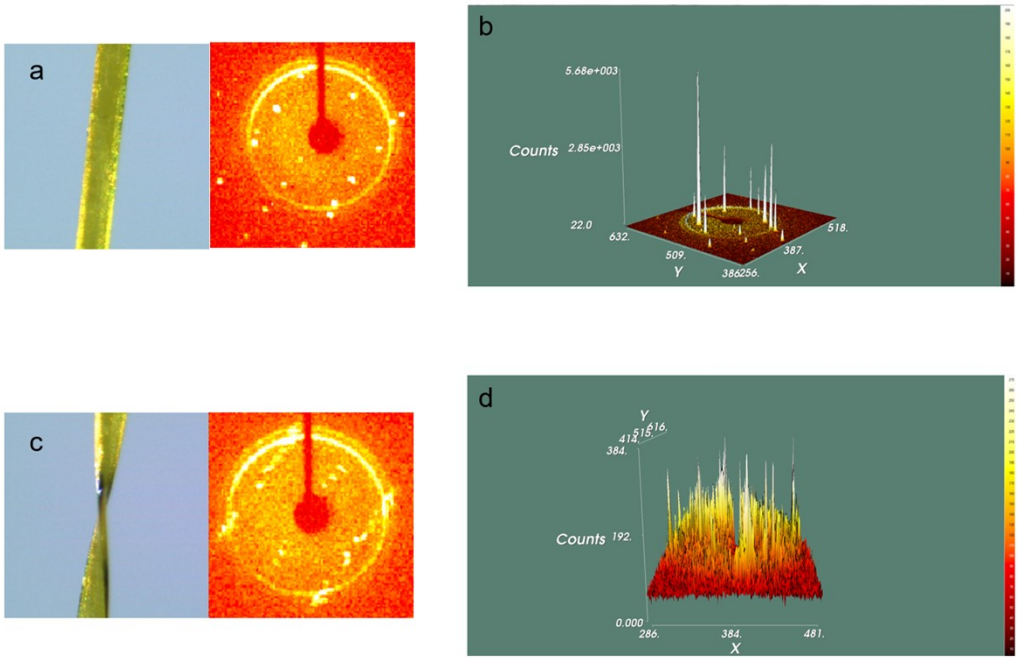


Fig. S19 a) Photo and X-Ray diffraction patterns of crystal straight part. b) Diffraction peaks of straight part. c) Photo and X-Ray diffraction patterns of twist part. d) Diffraction peaks of twist part.

10. Theoretical calculation

Experimental section. theoretical calculations were performed by ORCA using CAM-B3LYP/def2-SV(P). With Grimme D3 dispersion correction without any optimization. The dimer was utilized as the model created by the initial crystal structure and dimerscan.

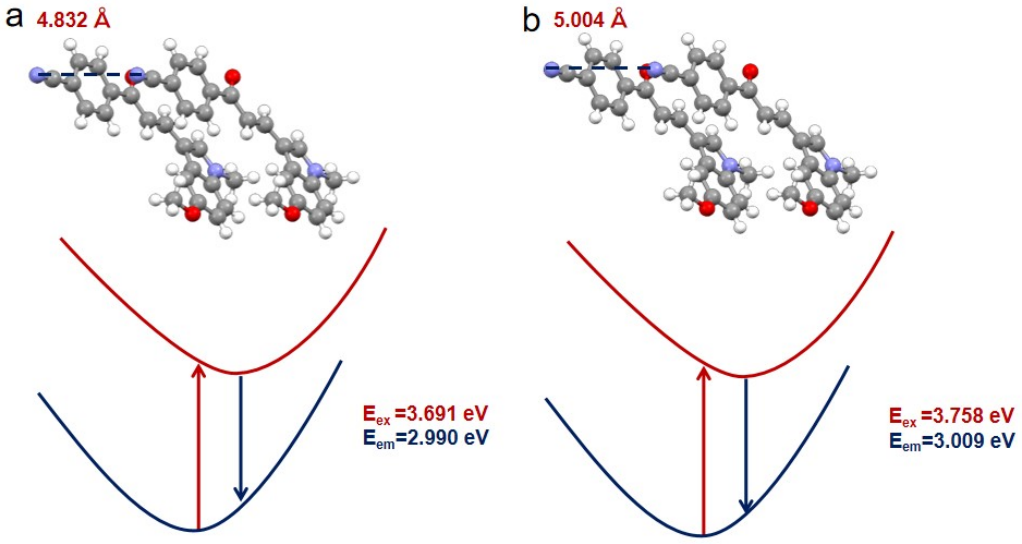


Fig. S20 The calculated distance, excitation energy and emission energy in dimer of initial (a) and stretching (b) state.