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Supplementary Information

Multiple Stimuli-Responsive Flexible Crystal with 2D Elastic Bending, Plastic Twisting and Photoinduced Bending Capabilities

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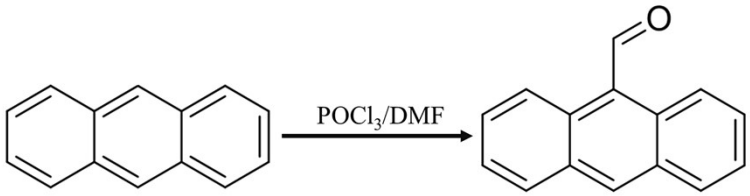
Contents

Experiments

1. one-step synthesis of 9-Anthraldehyde:



Scheme S1. Synthesis of 9- Anthraldehyde.

Anthracene (5.0 g, 28.1 mmol) was added into the phosphorus oxychloride (4 mL, 45 mmol), and the mixture was heated at 90 °C for 1 h under stirring. DMF (4 mL, 50 mmol) was dropwise added into the mixture over 0.5 h. The mixture was heated at 95 °C for 15 h with stirring, and then was cooled to 60 °C. Subsequently, 40 mL of deionized water (60 °C) was added by a peristaltic pump, and the mixed solution was heated to 65 °C for 0.5 h. The PH of the mixed solution was adjusted to 5 by dropwise adding saturated sodium acetate saturated aqueous solution under the fast stirring. After 0.5h, the mixed solution was cooled to room temperature without stirring, and it was extracted with DCM. Finally, the organic phase was evaporated with reduced pressure, then yellow solid (4.5g, 78% yield) was obtained.

2. Crystal growth:

1 mL CH_2Cl_2 solution (0.2 M) was added into a test tube, and 4 mL hexane was added carefully along the tube wall to the top of the CH_2Cl_2 solution, forming distinct solvent layer. Then, the test tube was blocked with a stopper at 5°C for 5-7 days to obtain acicular single crystals.

Crystal information

Table. S1 Crystallographic information table of 9-Anthraldehyde crystal.

Formula	$C_{15}H_{10}O$
Formula weight	206.23
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a / Å	4.0806
b / Å	14.045
c / Å	17.078
α / °	90
β / °	90
γ / °	90
Z, Z'	4,1
Volume / Å^3	978.77
R-factor (%)	5.11
CCDC Number	1510568

Face index

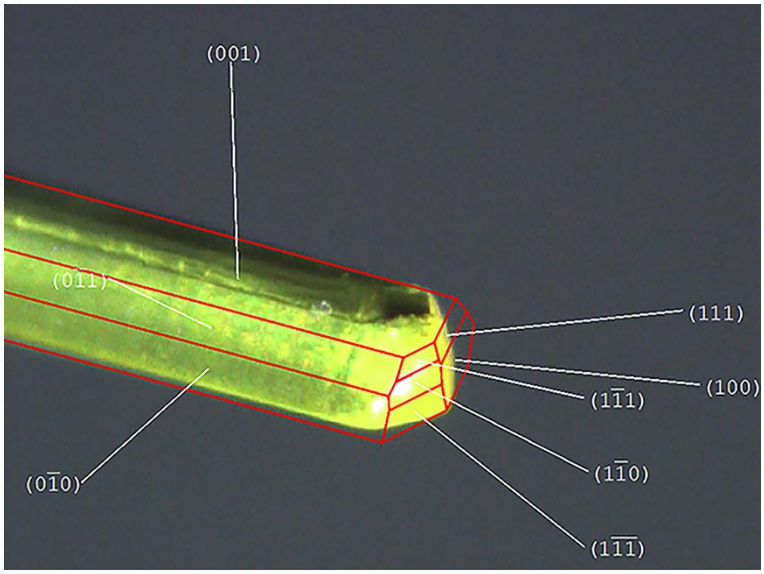


Fig.S1 Face index of 9- Anthraldehyde crystal.

Elastic strain calculation

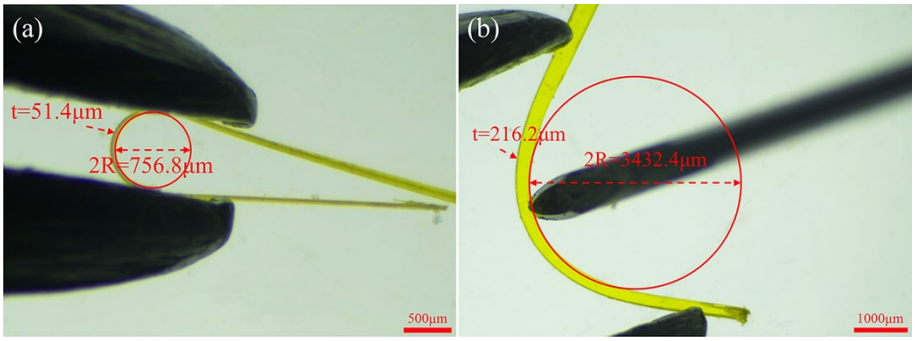


Fig.S2 Elastic strain calculation of 9AA crystal (a) bending along [001] direction; (b) bending along [010] direction.

$$\varepsilon_1 = \frac{t}{2R} = \frac{51.4}{756.8} \times 100\% = 6.8\%$$

$$\varepsilon_2 = \frac{t}{2R} = \frac{216.2}{3432.4} \times 100\% = 6.3\%$$

SEM images of twisted 9-AA crystals

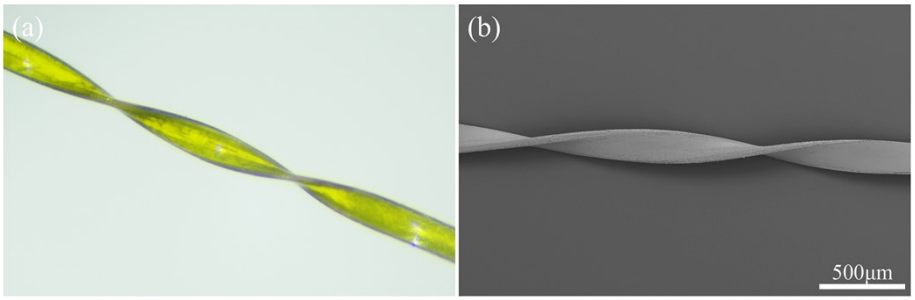


Fig.S3 Optical images (a) and Scanning Electron Microscopy (SEM) images (b) of twisted 9-AA crystals.

PXRD and DSC of original and twisted 9-AA crystals

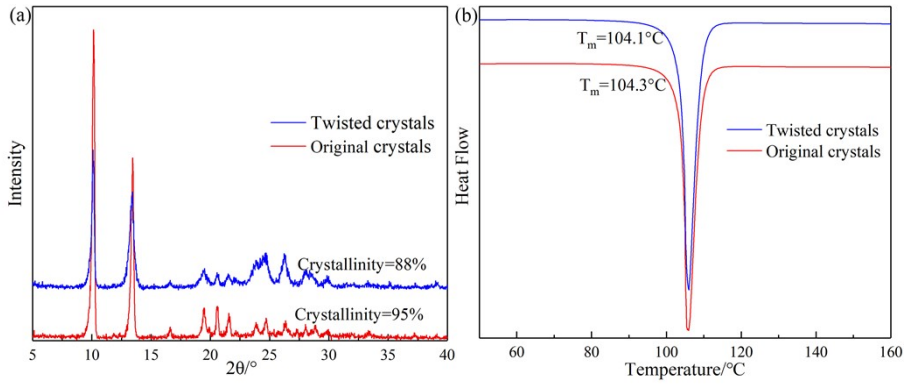
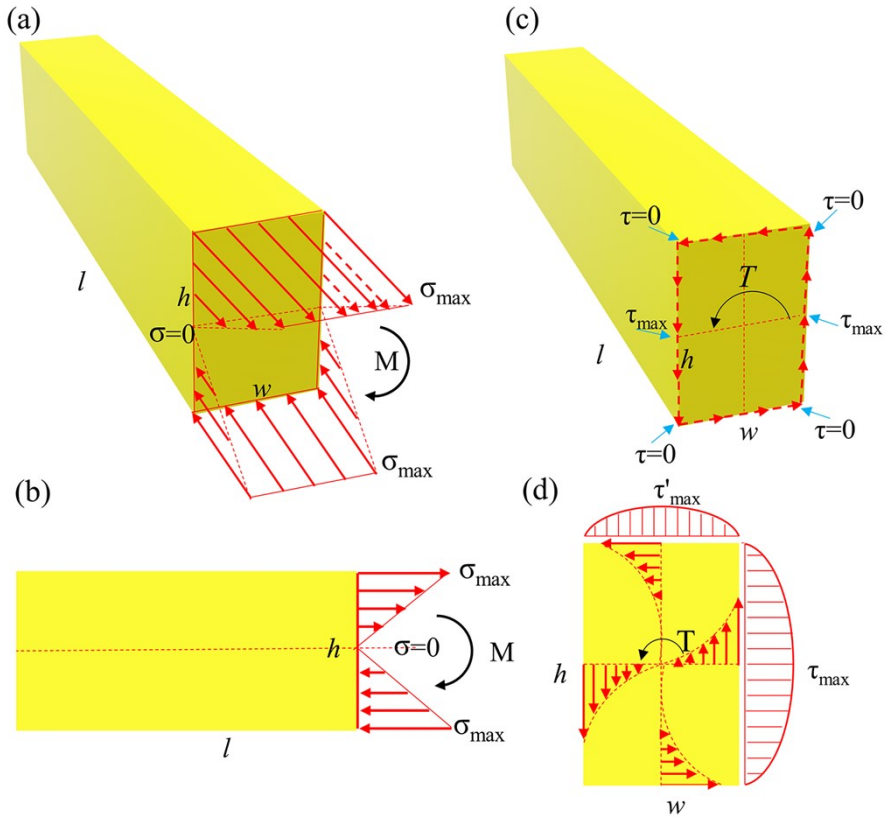


Fig.S4 PXRD and DSC curves of original and twisted 9-AA crystals

Stress distributions of bending process and twisting process



Scheme S2. Stress distributions of bending process (a), (b) and twisting process (c), (d).

Indenter impressions and 3D scans of 9-AA crystals

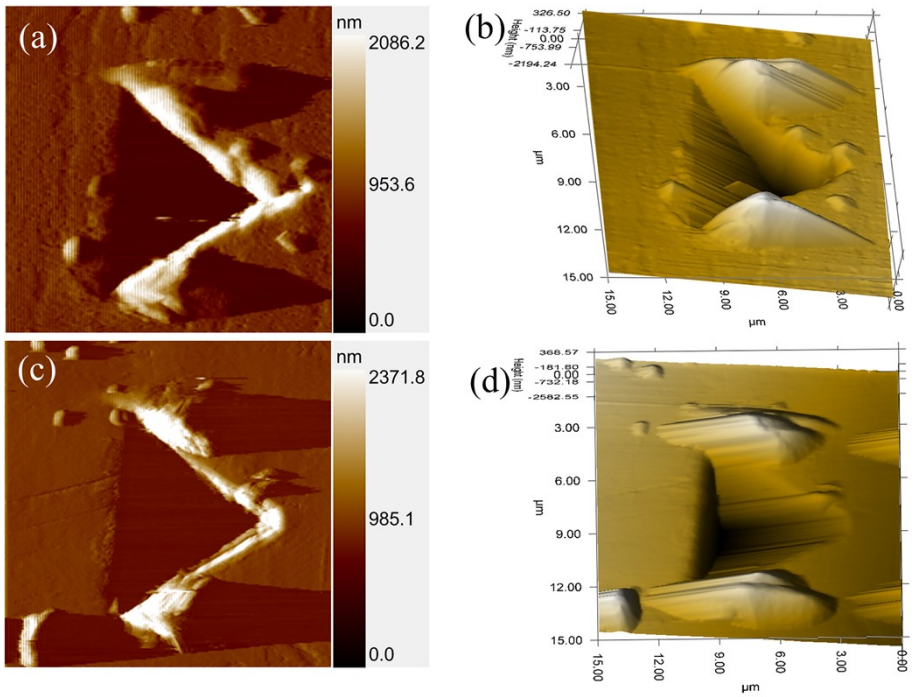


Fig. S5 Indenter impressions of 9-AA crystals on (001) plane (a) and (010) plane (c); 3D scans of indented areas of 9-AA crystals on (001) plane (b) and (010) plane (d).

Schematic illustration of molecular layers and indenter directions.

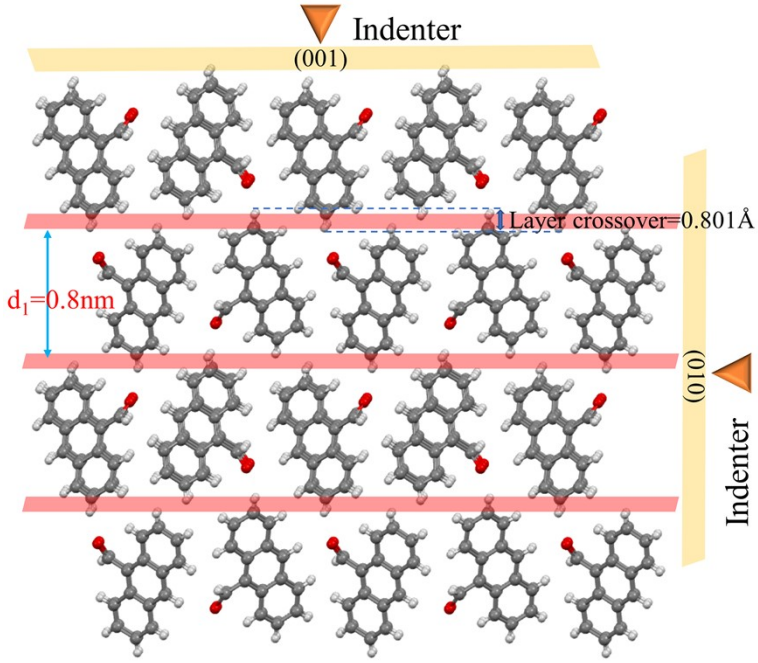


Fig.S6 Schematic illustration of molecular layers and indenter directions.

Three-dimensional topologies of energy framework

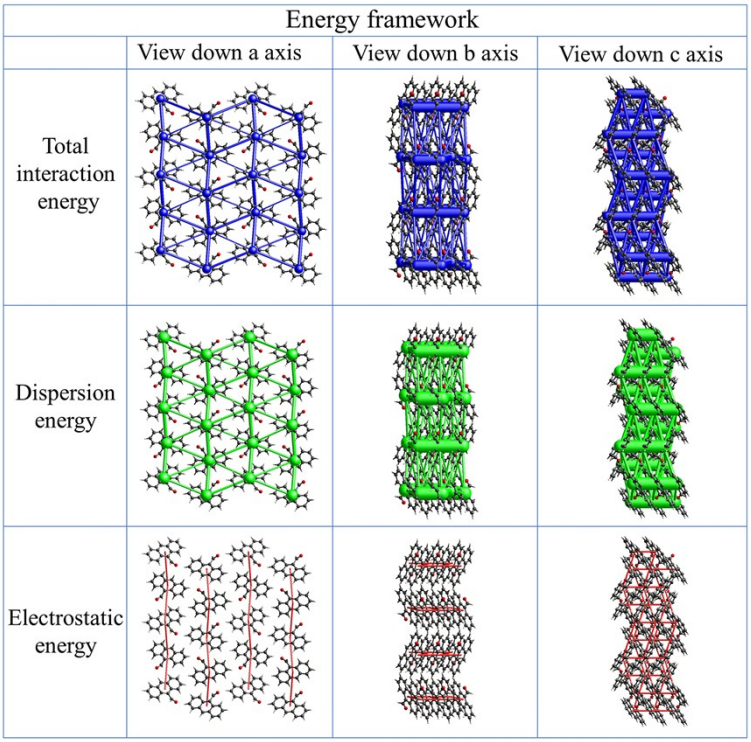
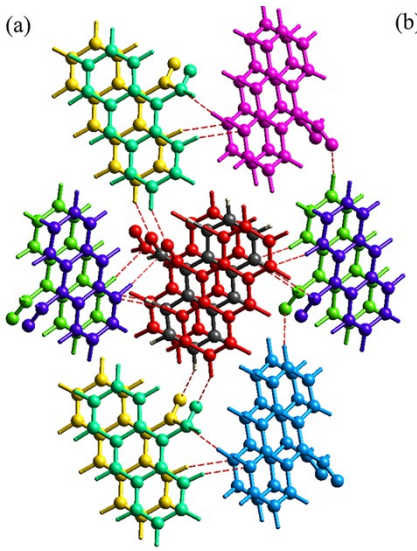


Fig.S7 Three-dimensional topologies of energy framework for 9AA

Molecular structure pairs and the interaction energies

(a)



(b)

	N	Symop	R	E_{ele}	E_{pol}	E_{dis}	E_{rep}	E_{tot}
	2	x, y, z	4.08	-7.4	-1.8	-71	45.6	-42.8
	2	-x+1/2, -y, z+1/2	9.84	-3.3	-1.1	-7.6	5.2	-7.7
	2	-x, y+1/2, -z+1/2	7.22	-4.5	-1.8	-19.5	14.1	-14.3
	2	-x+1/2, -y, z+1/2	9.12	-3.4	-1.4	-12.1	7.3	-10.6
	2	x+1/2, -y+1/2, -z	9.33	-0.5	-0.5	-9.1	5.5	-5.4
	2	-x, y+1/2, -z+1/2	7.43	-6.5	-1.5	-17.4	13.1	-15
	2	x+1/2, -y+1/2, -z	9.83	-1.9	-0.3	-9.7	6.6	-6.6

Fig.S8 Molecular structure pairs and the interaction energies obtained from energy frameworks. Scale factors are in the bottom right table.

Illustration of segregated interaction energies

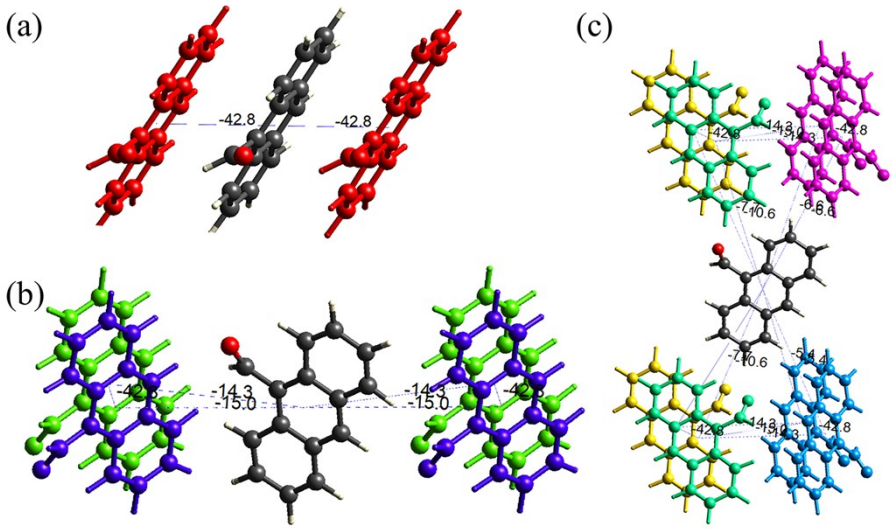


Fig.S9 Illustration of calculated total interaction energies of π-stacking columns (a), inter-columns (b), and slip planes (c).

Fluorescence lifetime and quantum yield

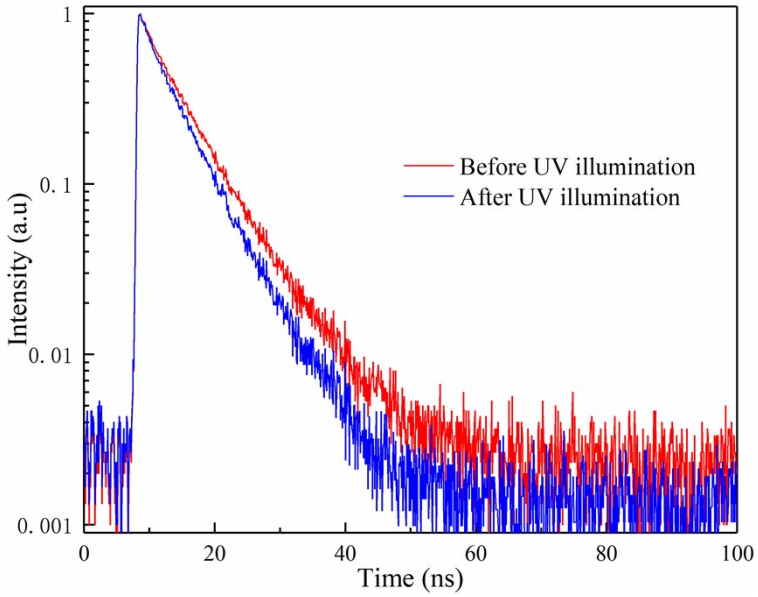


Fig. S10 Fluorescence lifetime of 9-AA crystals before and after illumination

Table. S2 Fluorescence lifetime and quantum yield measurement data

Sample	τ_1(ns)	τ_2(ns)	τ(ns)	Φ_F (%)
Before UV illumination	1.5893	6.3606	6.1702	1.76

After UV illumination	0.8287	5.5587	5.4845	1.53