Supporting Information

Substituent-modulated organic single crystals with rapid natural light photomechanical response

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1.1 Experimental section

1.2 Synthesis

(Z)-3-(anthracen-9-yl)-2-phenylacrylonitrile (**Z-3AN2PA**), (Z)-3-(anthracen-9-yl)-2-(4-(trifluoromethyl)phenyl)acrylonitrile (**Z-3AN2PA-CF_3**), (Z)-3-(anthracen-9-yl)-2-(3,5-difluorophenyl)acrylonitrile (**Z-3AN2PA-2F)** was synthesized by Knoevenagel condensation reaction. 9-anthracenecarboxaldehyde, phenyl acetonitrile, 4-(Trifluoromethyl)phenylacetonitrile and 3,5-Difluorophenylacetonitrile were purchased from commercial sources and used without further purification.

Synthesis of Z-3-(anthracen-9-yl)-2-phenylacrylonitrile (**Z-3AN2PA**): Phenyl acetonitrile (0.01 mol, 1.17 g) was taken in 25 mL absolute ethanol. To the alcoholic solution, NaOMe (0.01 mol, 0.54 g) was added and stirred vigorously for 15 min. To this stirred mixture, a solution of 9-anthracenecarboxaldehyde (0.01 mol, 2.06 g) in 25 mL of absolute ethanol was added slowly and stirred for 24h at room temperature. The shining yellow powder obtained were washed with excess absolute ethanol. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.97 (s, 1H), 8.76 (s, 1H), 8.26 – 8.16 (m, 2H), 8.09 (d, J = 8.0 Hz, 2H), 8.04 – 7.92 (m, 2H), 7.66 – 7.54 (m, 7H).

Synthesis of Z-3-(anthracen-9-yl)-2-(4-(trifluoromethyl)phenyl)acrylonitrile (**Z-3AN2PA-CF_3**): 4-(Trifluoromethyl)phenylacetonitrile (0.01 mol, 1.85 g) was taken in 25 mL absolute ethanol. To the alcoholic solution, NaOMe (0.01 mol, 0.54 g) was added and stirred vigorously for 15 min. To this stirred mixture, a solution of 9-anthracenecarboxaldehyde (0.01 mol, 2.06 g) in 25 mL of absolute ethanol was added slowly and stirred for 4h at room temperature. The shining orange-yellow powder obtained were washed with excess absolute ethanol. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.18 (s, 1H), 8.79 (s, 1H), 8.22 (q, J = 4.0 Hz, 4H), 8.15 – 8.08 (m, 2H), 7.99 (d, J = 8.0 Hz, 2H), 7.71 – 7.55 (m, 4H).

Synthesis of Z-3-(anthracen-9-yl)-2-(3,5-difluorophenyl)acrylonitrile (**Z-3AN2PA-2F**): 3,5-Difluorophenylacetonitrile (0.01 mol, 1.53 g) was taken in 25 mL absolute ethanol. To the alcoholic solution, NaOMe (0.01 mol, 0.54 g) was added and stirred vigorously for 15 min. To this stirred mixture, a solution of 9-anthracenecarboxaldehyde (0.01 mol, 2.06 g) in 25 mL of absolute ethanol was added slowly and stirred for 24h at room temperature. The shining yellow powder obtained were washed with excess absolute ethanol. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.15 (s, 1H), 8.78 (s, 1H), 8.23 – 8.15 (m, 2H), 8.14 – 8.05 (m, 2H), 7.74 (dt, J = 8.0, 4.0 Hz, 2H), 7.67 – 7.56 (m, 4H), 7.55 – 7.40 (m, 1H).

1.3 Crystal Growth

0.01 g of **Z-3AN2PA**、**Z-3AN2PA-CF3** and **Z-3AN2PA-2F** was dissolved in 5 mL of DCM, 5 mL of EtOH, and 1 mL of water. And then the solutions were left to evaporate in the dark at room temperature for 2-3 days to afford the corresponding crystals.

1.4 Single-crystal X-ray diffraction.

The single-crystal X-ray diffraction data of **Z-3AN2PA**, **Z-3AN2PA-CF$_3$**, **Z-3AN2PA-2F** were collected on an Xtalab Synergy at 150K,303.15K and 100K with CuKα radiation (λ = 1.54184 Å) and refined using the OLEX2- 1.5 suite of programs. The detailed crystallographic data for **Z-3AN2PA**, **Z-3AN2PA-CF$_3$**, **Z-3AN2PA-2F** are summarized in Table S5. The crystallographic datas for **Z-3AN2PA**, **Z-3AN2PA-CF$_3$**, **Z-3AN2PA-2F** were deposited with the Cambridge Structure Database Centre (CCDC) with number of 2469131, 2429964 and 2429965 for **Z-3AN2PA**, **Z-3AN2PA-CF$_3$** and **Z-3AN2PA-2F**, respectively.

1.5 Characterization.

Powder X-ray diffraction (PXRD) data were collected at ambient temperature on a Rigaku standard Ultima IV diffractometer using a CuKα radiation, with a scan speed of 5° min^{-1}, and 2θ ranging from 5° to 50°. For all samples, the experimental backgrounds were not corrected. The scanning electron microscopy (SEM) images were acquired on a JSM-7800F microscope with a primary electron energy of 10 kV. The UV-visible spectra were collected using a UV-2700 spectrometer with background correction. The FT-IR spectra were recorded using a Nicolet is50 IR spectrometer. A high-power UV LED spot lamp source (HEIGHT-LED, HTLD-4II) (maximum at 365nm and 450 nm) was utilized to investigate the photomechanical motions of the single crystals. The optical power density was measured on a HEIGHT-LED Meter LED (illumination distance 1.5 cm: 4500 mW, 3400 mW). The ^{1}H NMR spectra were recorded on a Bruker Avance II 400 MHz NMR spectrometer. The fluorescence spectra were recorded on a HITACHI F-4700 fluorescence spectrometer.

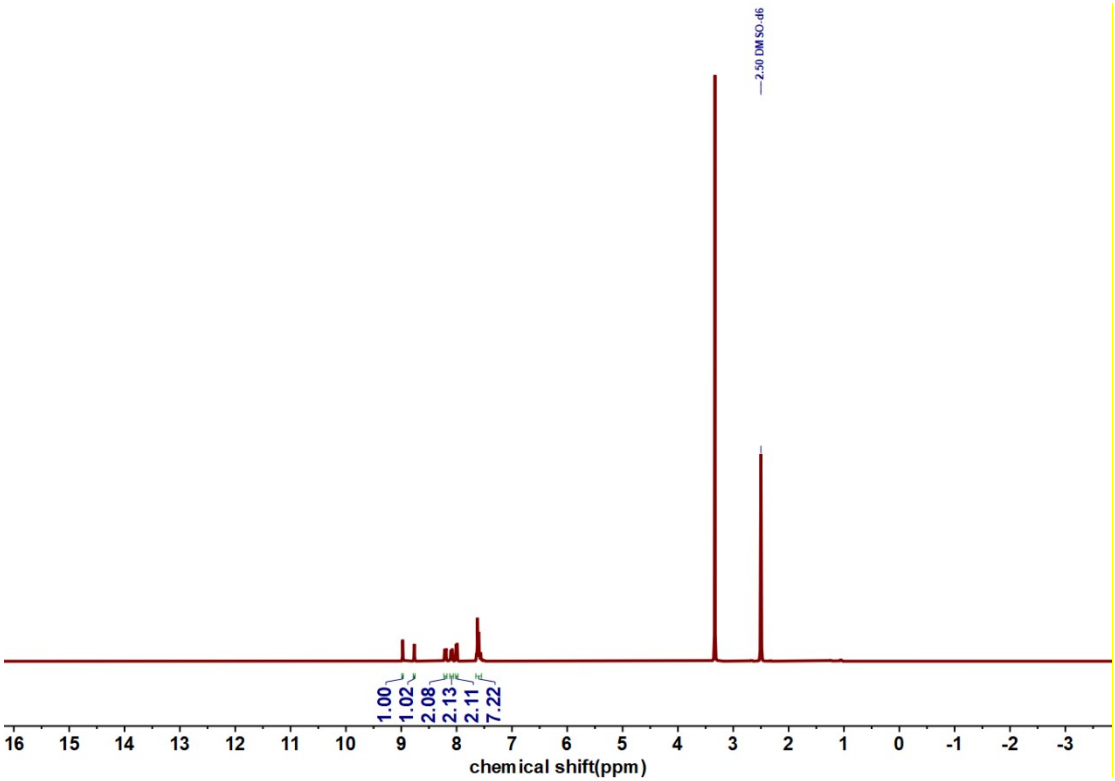

Fig. S1. 1H NMR spectrum (400 MHz, DMSO-d_6) of **Z-3AN2PA.**

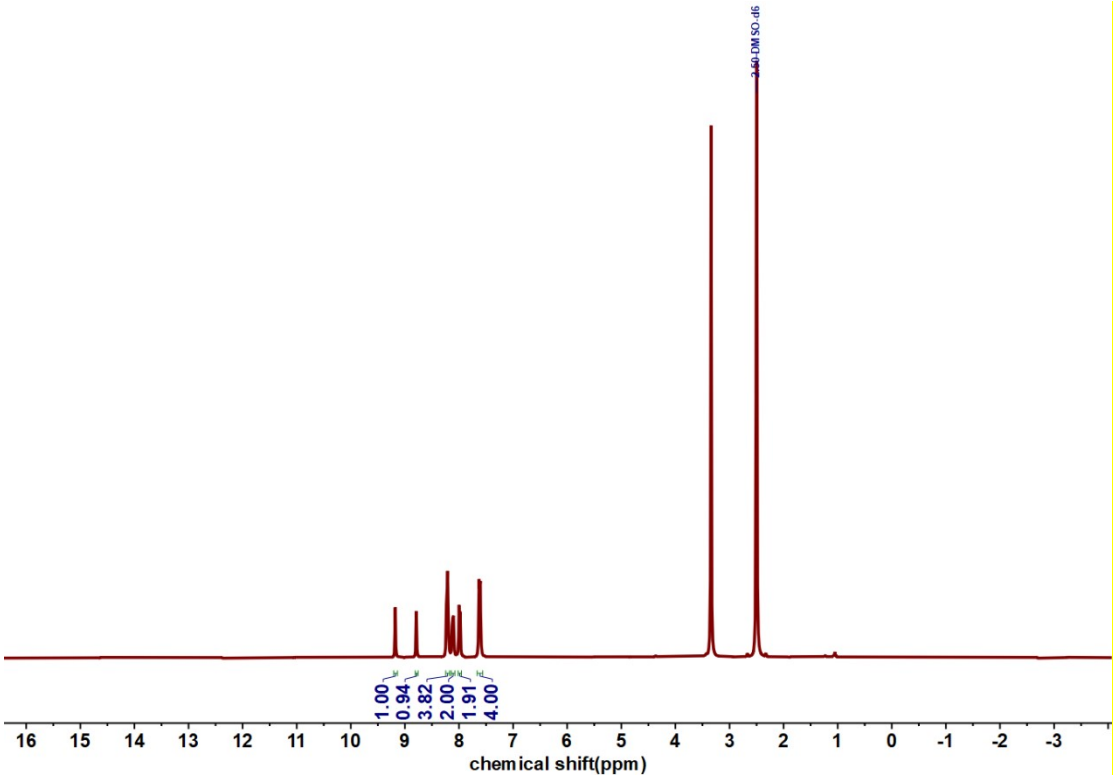

Fig. S2. 1H NMR spectrum (400 MHz, DMSO-d_6) of **Z-3AN2PA-CF_3.**

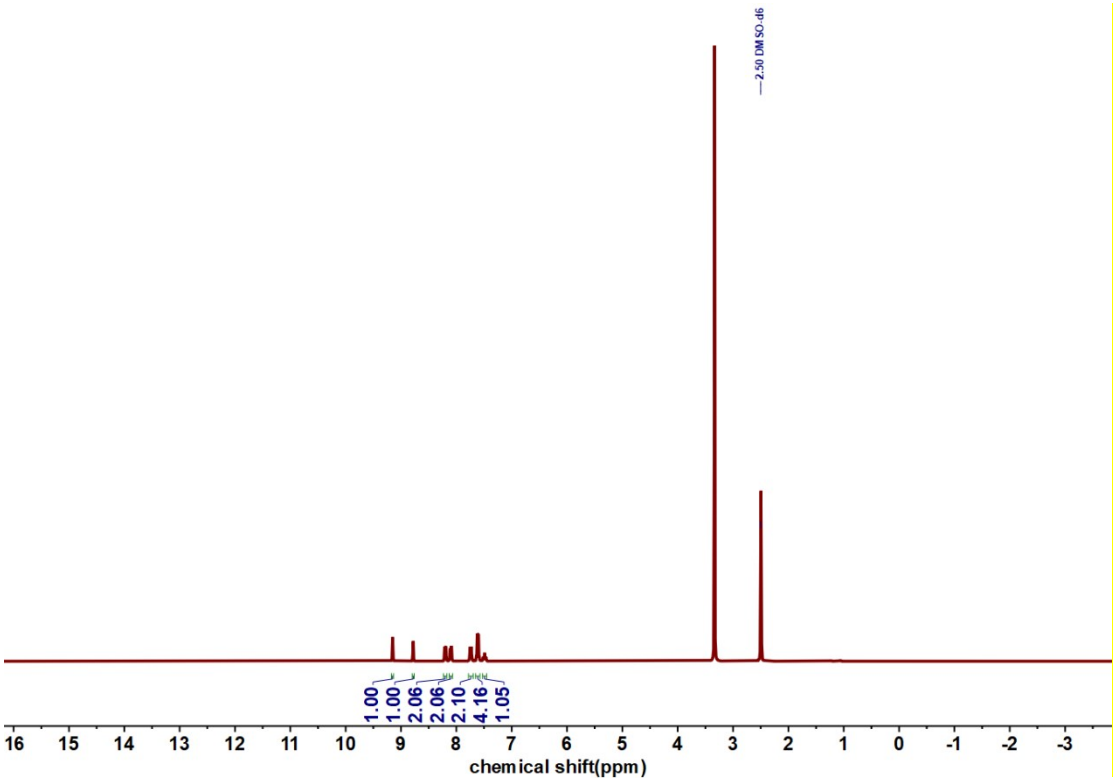

Fig. S3. 1H NMR spectrum (400 MHz, DMSO-d_6) of **Z-3AN2PA-2F.**

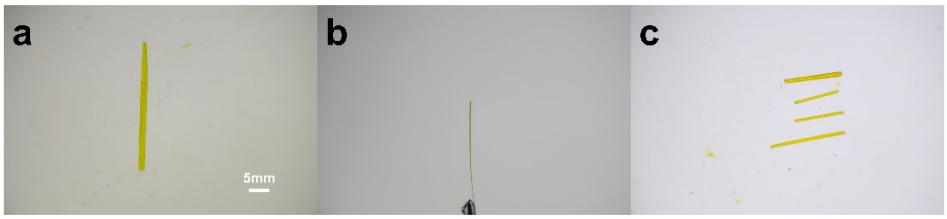

Fig. S4. The morphology pictures of **Z-3AN2PA** (a), **Z-3AN2PA-CF₃** (b) and **Z-3AN2PA-2F** (c).

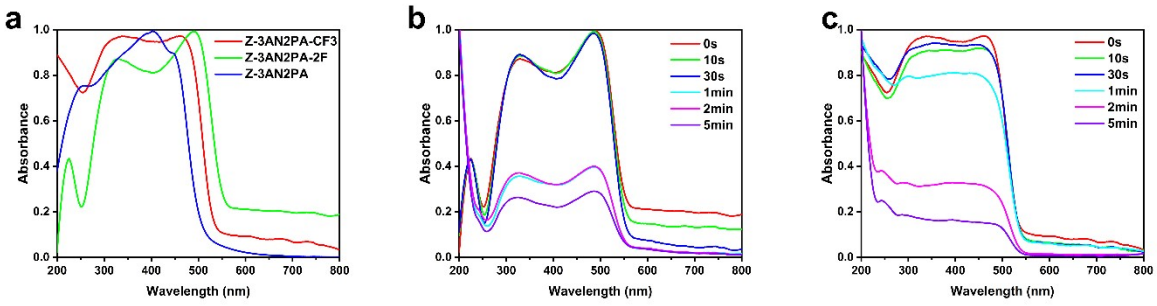

Fig. S5. UV–vis absorption spectra of **Z-3AN2PA**, **Z-3AN2PA-CF₃** and **Z-3AN2PA-2F** (a). Time-dependent UV-Vis spectra for **Z-3AN2PA-CF_3** (b) and **Z-3AN2PA-2F** (c) by 450 nm irradiation.

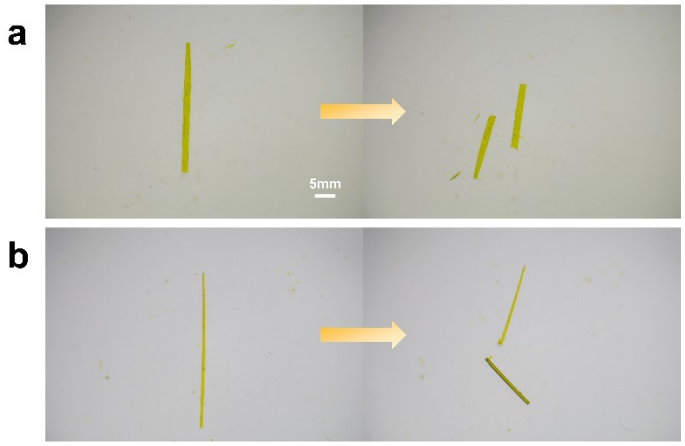

Fig. S6. Brittle fracture occurs in **Z-3AN2PA** (a) and **Z-3AN2PA-2F** (b) under external force.

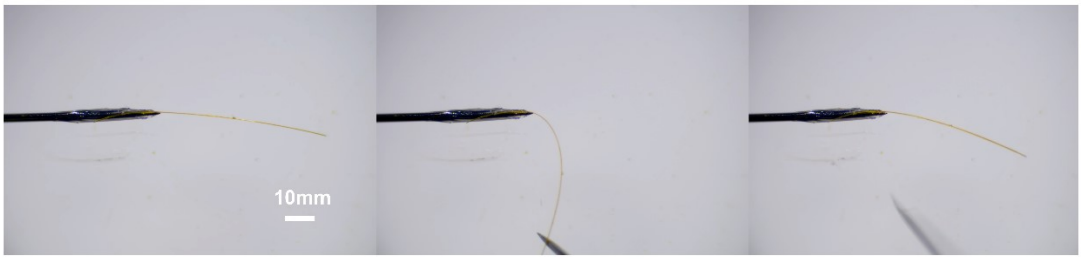

Fig. S7. The process of elastic bending of **Z-3AN2PA-CF_3** crystals.

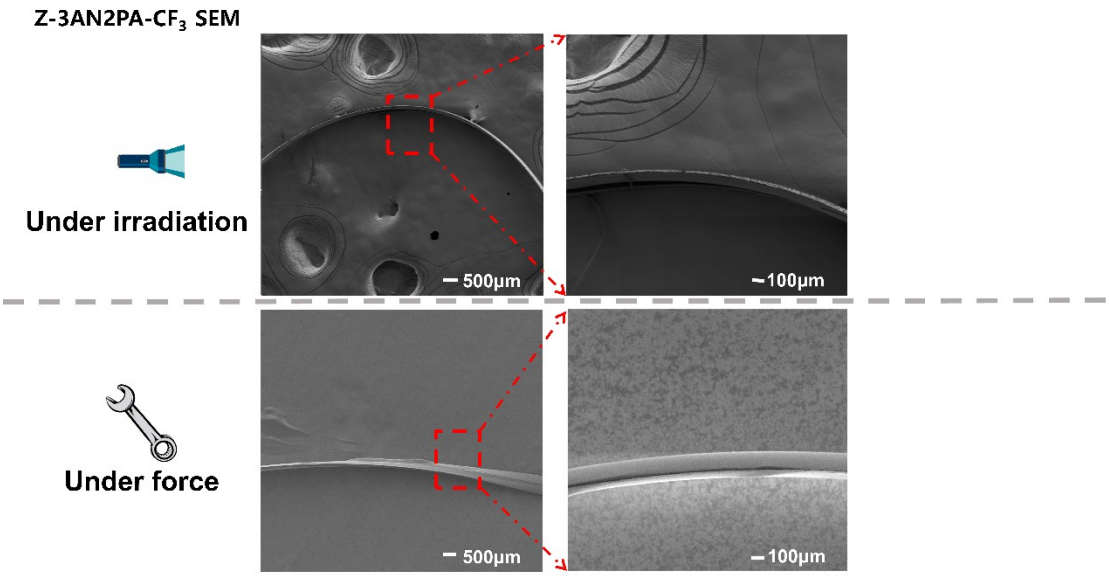

Fig. S8. Scanning electron microscopy images of **Z-3AN2PA-CF_3** crystals after irradiation and mechanically induced bending.

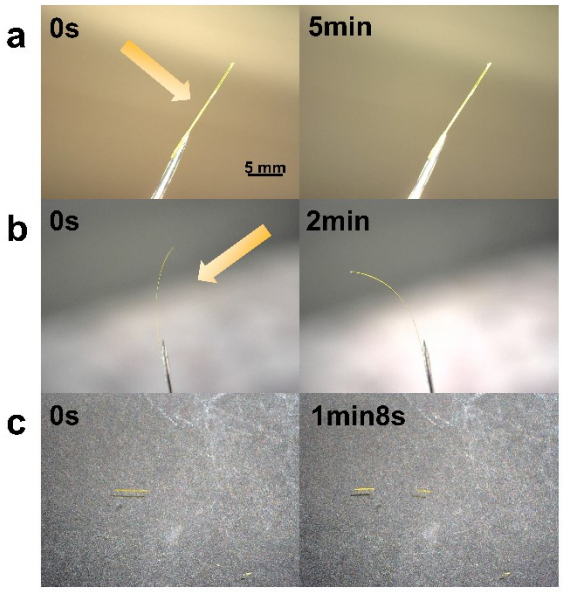

Fig. S9. The photomechanical behaviors of **Z-3AN2PA** (a), **Z-3AN2PA-CF₃** (b), and **Z-3AN2PA-2F** (c) under sunlight irradiation.

Fig. S10. The photomechanical behaviors of **Z-3AN2PA** under 365 nm irradiation.

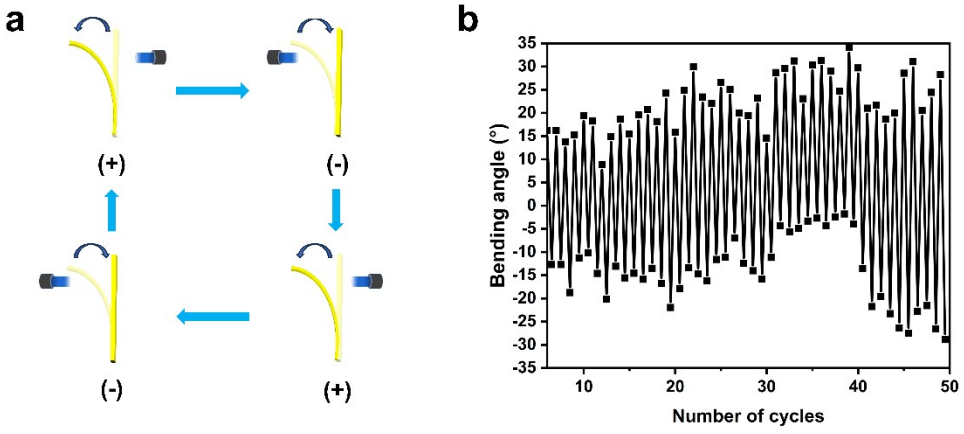

Fig. S11. Schematic illustration of the bending cycle test for **Z-3AN2PA-CF₃** crystal. A positive bending (+) angle means that the light source is on the right of the crystal for 0.1 s and the crystal is bent to the left. A negative bending (-) angle means that the light source is irradiated for 0.1 s on the left of the crystal and the crystal is bent to the right (a). The bending angles of the **Z-3AN2PA-CF$_3$** crystal during the 50th bending cycle. The irradiation time is 0.1 s for the first 40 irradiation durations, and 0.2 s for the last 10 irradiation durations (b).

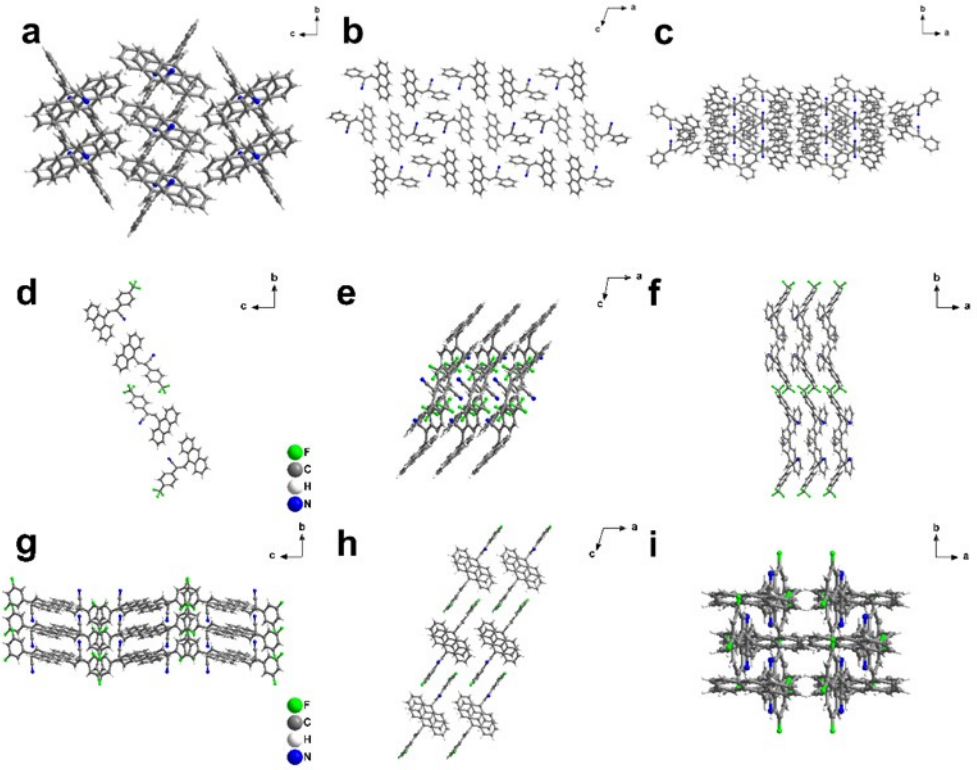

Fig. S12. The packing structures of **Z-3AN2PA** (a-c), **Z-3AN2PA-CF$_3$** (d-f) and **Z-3AN2PA-2F** (g-i) viewed along the *a*-axis, *b*-axis, and *c*-axis.

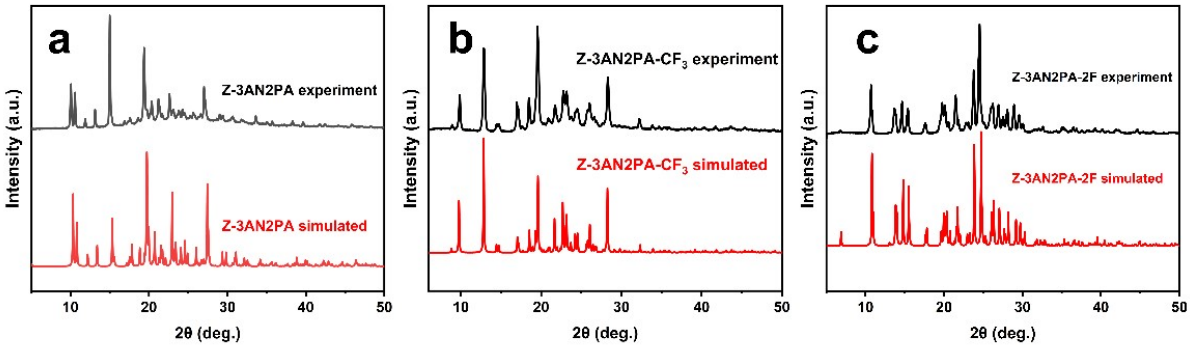

Fig. S13. PXRD patterns of **Z-3AN2PA** (a), **Z-3AN2PA-CF₃** (b), and **Z-3AN2PA-2F** (c).

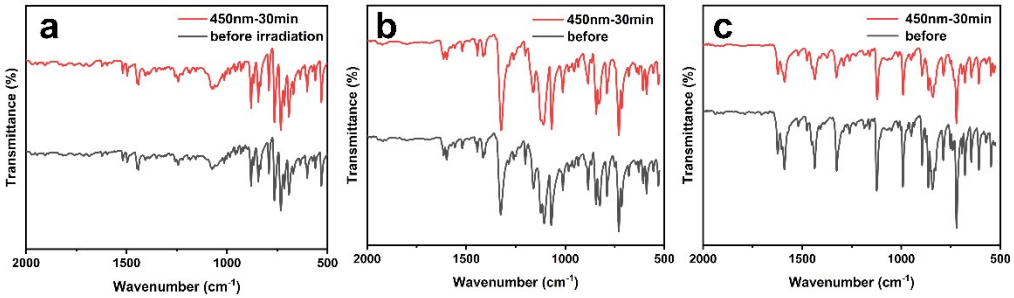

Fig. S14. FT-IR spectra of **Z-3AN2PA** (a), **Z-3AN2PA-CF₃** (b), and **Z-3AN2PA-2F** (c) before and after irradiation.

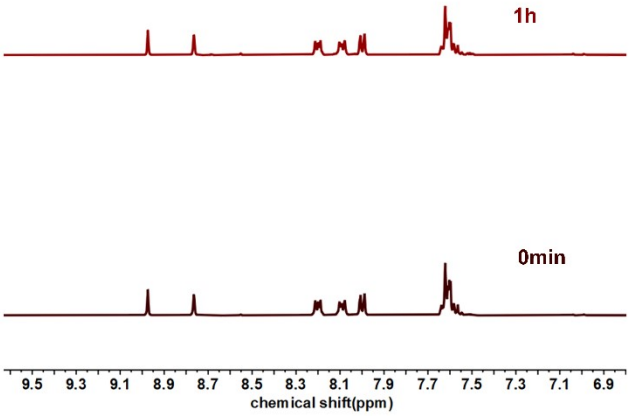

Fig. S15. Time-dependent ^{1}H NMR (400 MHz, DMSO-d6) spectra of **Z-3AN2PA**.

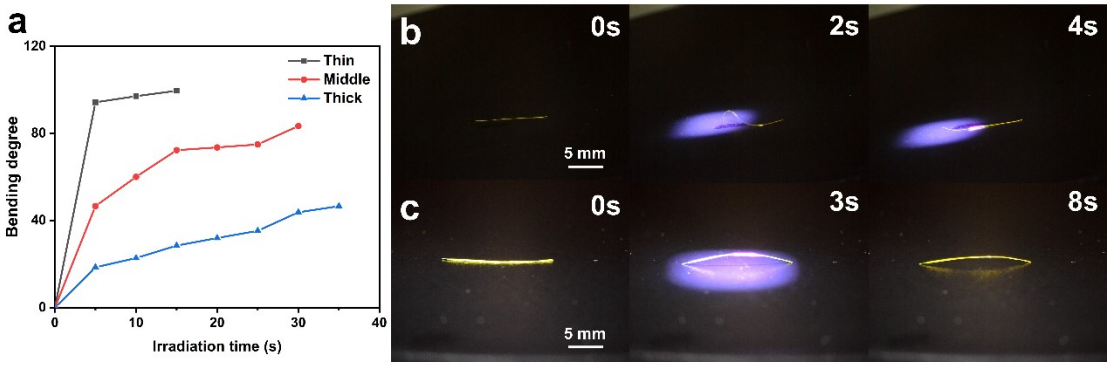

Fig. S16. Bending degree of **Z-3AN2PA-CF_3** crystals with different thicknesses(a). Photomechanical behavior of thinner **Z-3AN2PA-CF_3** crystal on the Plane (b). Photomechanical response behavior of Thicker **Z-3AN2PA-CF_3** Crystal on the Plane (c). (thinner size: 0.018 mm; middle size: 0.064 mm; thick size: 0.108 mm)

Table S1. The temperature variation measured by Infrared thermal imager under 450 nm light irradiation.

Irradiation time	0s	10s	60s	180s	300s
Temperature	22.8℃	23.3℃	26.2℃	30.4℃	32.9℃

Table S2. Crystallographic information for the crystals of **Z-3AN2PA**, **Z-3AN2PA-CF_3** and **Z-3AN2PA-2F**.

	Z-3AN2PA	**Z-3AN2PA-CF_3**	**Z-3AN2PA-2F**
Formula	$C_{23}H_{15}N$	$C_{24}H_{14}F_3N$	$C_{23}H_{13}F_2N$
CCDC number	2469131	2429964	2429965
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$C2/c$
a/Å	18.3518(3)	4.67530(10)	17.2254(6)
b/Å	5.28900(10)	36.9040(11)	7.4849(2)
c/Å	17.3164(3)	10.6315(3)	26.9940(7)
α/°	90	90	90
β/°	109.188(2)	100.522(3)	107.221(3)
γ/°	90	90	90
Volume/Å3	1587.40(5)	1803.49(9)	3324.32(18)
Z	4	4	8
ρ_{calc}/g cm^{-3}	1.278	1.375	1.364
μ/mm^{-1}	0.567	0.850	0.781
F (000)	640.0	768.0	1408.0
R_{int}	0.214	0.291	0.293
GoF	1.066	1.082	1.069
R_1, wR_2 [$I > 2\sigma(I)$]	$R_1 = 0.0355$	$R_1 = 0.0651$	$R_1 = 0.0623$
	$wR_2 = 0.0967$	$wR_2 = 0.1772$	$wR_2 = 0.1780$
R_1, wR_2 [all data]	$R_1 = 0.0389$	$R_1 = 0.0857$	$R_1 = 0.0856$
	$wR_2 = 0.0997$	$wR_2 = 0.1895$	$wR_2 = 0.1946$