

# Supporting Information

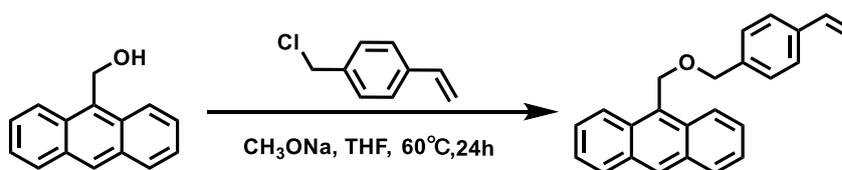
## Reversible surface dual-pattern with simultaneously dynamic wrinkled topography and fluorescence

### 1. Materials

4-(chloromethyl) styrene (St-Cl) and n-butyl acrylate (BA) were provided by TCI Chemical CO., Ltd. Anthracene-9-methanol (AN-OH) and 1,4,5,8-Naphthalenetetracarboxylic dianhydride (NDA) was purchased from J&K Scientific Ltd. Other chemicals were obtained from China National Pharmaceutical Group (Shanghai, China). BA was washed for three times by 5 wt% sodium hydroxide solution and then dried in anhydrous magnesium sulfate. All other reagents were used as received.

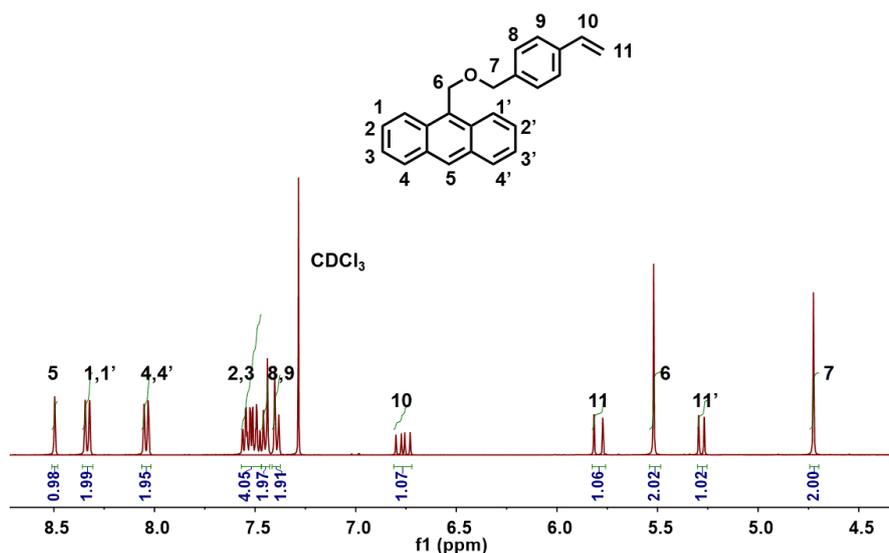
### 2. Synthesis and Characterization of Materials

#### 2.1 Synthesis of anthracene-containing styrene monomer (St-AN)



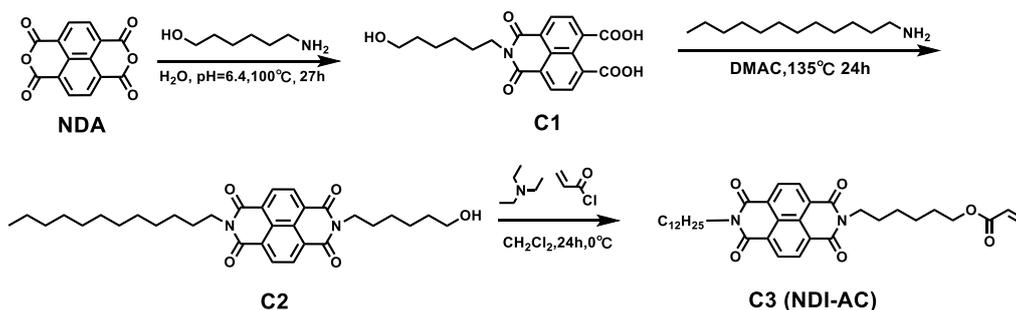
**Scheme S1.** Synthesis process of St-AN

The procedure to synthesize the anthracene-containing styrene monomer (St-AN) used in this work as shown in **Scheme S1**. A 150 mL tetrahydrofuran solution of anthracene-9-methanol (AN-OH, 4.16 g, 20 mmol) was prepared and purged with highly pure N<sub>2</sub> gas for 30 min, to eliminate oxygen. To this stirred solution, a tetrahydrofuran (7 mL) solution of sodium methoxide (CH<sub>3</sub>ONa, 5.4 g, 0.1 mol) and potassium iodide (KI, 16.7g, 0.1 mmol) was added as solids at ambient temperature. Then, the reaction system was cooled to 0 °C and added drop-wise with a tetrahydrofuran (10 mL) solution of 4-(chloromethyl) styrene (St-Cl, 3.06g, 20 mmol) in 30 min. After reacting for more than 1 day, the organic phase was collected, then precipitated in petroleum ether. The crude product was purified by column chromatography (silica gel; DCM/PE=1:1) and dried in vacuum oven at 50 °C overnight, the yellow power precursor St-AN (6.08 g) was obtained in quantitative yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.50 (s, 1H), 8.36-8.32 (m, 2H), 8.07-8.02 (m, 2H), 7.53 (dddd, J = 9.3, 7.6, 6.5, 1.2 Hz, 4H), 7.48-7.39 (m, 4H), 6.77 (dd, J = 17.6, 10.9 Hz, 1H), 5.81 (dd, J = 17.6, 0.7 Hz, 1H), 5.52 (s, 2H), 5.29 (dd, J = 10.9, 0.7 Hz, 1H), 4.73 (s, 2H). <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>) δ 138.01, 137.12, 136.58, 131.45, 131.08, 129.03, 128.64, 128.47, 128.29, 126.31, 124.97, 124.37, 113.87, 77.28, 77.05, 76.80, 72.15, 64.04.



**Figure S1.**  $^1\text{H}$  NMR spectrum for St-AN in  $\text{CDCl}_3$ .

## 2.2 Synthesis of naphthalene diimide-containing acrylate monomer (NDI-AC)



**Scheme S2.** Synthesis process of NDI monomer NDI-AC

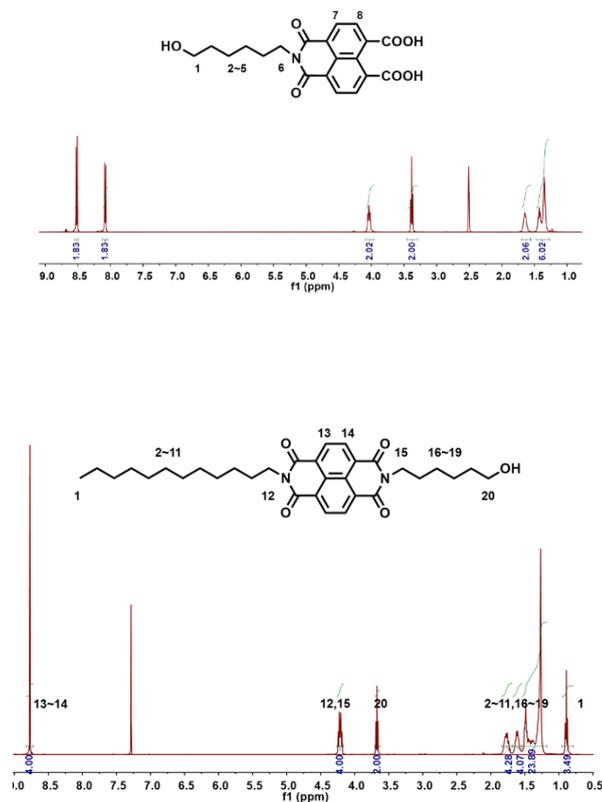
The procedure to synthesize the naphthalene diimide-containing acrylate monomer (NDI-AC) is shown in Scheme S2.

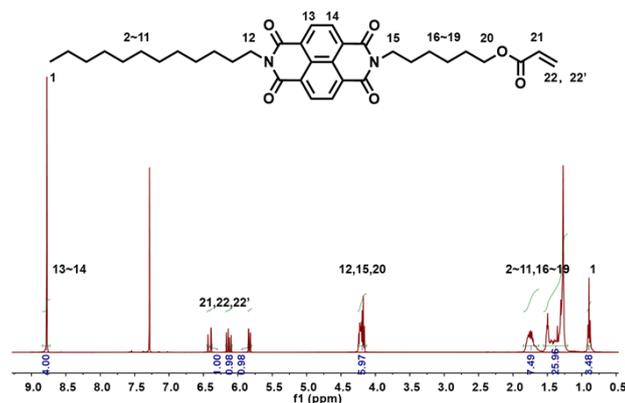
Derivative **C1**.<sup>1</sup> In a 2L flask a 1M KOH solution was added to a suspension of 1,4,5,8-Naphthalenetetracarboxylic dianhydride (6,000 g, 22.37 mmol) in deionized water (1020 ml). The mixture was ultrasonic dissolving to obtain a clear yellowish-brown solution. The mixture was acidified by addition of a 1M  $\text{H}_3\text{PO}_4$  solution to pH 6.5 and 6-aminohexan-1-ol (2.622 g, 22.37 mmol) was added. The mixture was again acidified with a 1M  $\text{H}_3\text{PO}_4$  solution to pH 6.3 and heated to  $100^\circ\text{C}$  under stirring for 24 h. The solution was cooled to room temperature after the reaction stopped. The solid precipitate separated out and was vacuum filter off. The filtrate was collected, and adequate acetic acid was dropwise added observing the formation of a precipitate. The suspension was stirred for 30 minutes and filtered and dried at  $75^\circ\text{C}$  under reduced pressure (3.742g).  $^1\text{H}$  NMR (400 MHz, DMSO):  $\delta$  8.55-8.49 (m, 2H), 8.12-8.04 (m, 2H), 4.09-3.96 (m, 2H), 3.38 (t,  $J = 6.4$  Hz, 2H), 1.64 (d,  $J = 7.1$  Hz, 2H), 1.48-1.27 (m, 6H).

Derivative **C2**. In a three-necked flask, under  $\text{N}_2$  atmosphere, a mixture of compound C1

(2.00g, 5.19 mmol), n-dodecylamine (962 mg, 5.19 mmol) in a mixture of dimethylacetamide (20ml) and toluene (3 ml) was heated to 135 °C for 24 h. The mixture was cooled to RT and precipitated in ether. The solid product was crystallized from ethanol and dried at 50°C under reduced pressure (1.563 g). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.77 (s, 4H), 4.21 (dd, *J* = 15.1, 6.5 Hz, 4H), 3.67 (t, *J* = 6.5 Hz, 2H), 1.84-1.69 (m, 4H), 1.68-1.54 (m, 4H), 1.54-1.18 (m, 24H), 0.89 (t, *J* = 6.8 Hz, 3H).

Derivative **C3**. Compound **C2** (1.32 g, 2.47 mmol) was placed into a round bottom flask and CH<sub>2</sub>Cl<sub>2</sub> was added as a solvent. The solution was cooled to 0 °C and triethylamine (0.79 mL, 5.67 mmol) was added followed by acryloyl chloride (0.55 mL, 5.67 mmol). The mixture was left at room temperature overnight. After the completion of the reaction, the mixture was extracted using saturated salt water and deionized water. Organic layer was collected and evaporated under reduced pressure at 35 °C. The crude product was purified by column chromatography using dichloromethane to afford pale yellow solid as a product (0.93g). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.78 (s, 4H), 6.41 (dd, *J* = 17.3, 1.5 Hz, 1H), 6.13 (dd, *J* = 17.3, 10.4 Hz, 1H), 5.83 (dd, *J* = 10.4, 1.5 Hz, 1H), 4.26-4.13 (m, 6H), 1.75 (tdd, *J* = 19.4, 12.5, 6.5 Hz, 7H), 1.56-1.20 (m, 26H), 0.89 (t, *J* = 6.9 Hz, 3H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>) δ 166.31, 162.83, 130.95, 130.56, 128.56, 126.61, 77.30, 77.03, 76.72, 64.50, 41.02, 40.79, 31.93, 29.83-29.15, 28.48, 28.02, 27.09, 26.69, 25.67, 22.70, 14.15.

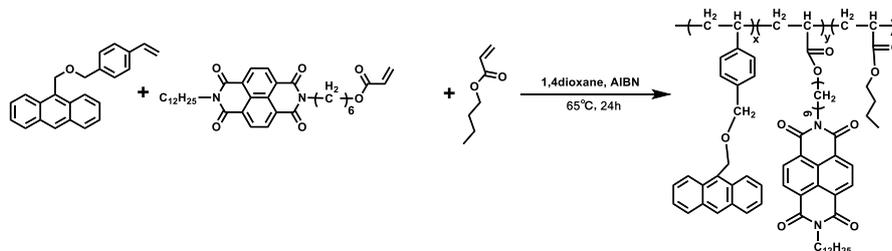




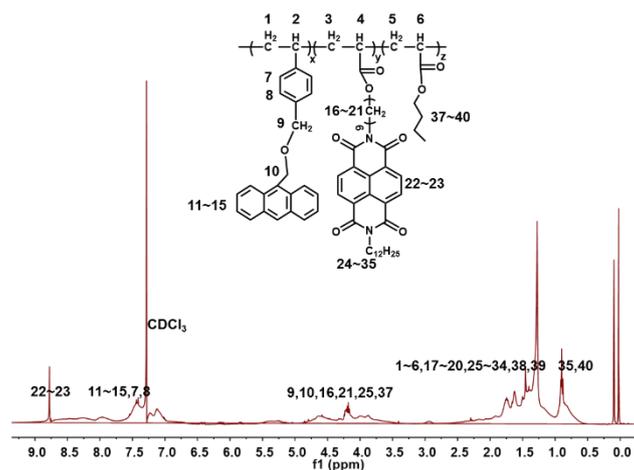
**Figure S2.**  $^1\text{H}$  NMR spectra for C1 in DMSO, C2 and C3 (NDI-AC) in  $\text{CDCl}_3$ .

### 2.3 Synthesis of co-polymer (PAN-NDI-BA)

P(AN-NDI-BA) copolymer was synthesized via the conventional free radical polymerization method according to Figure S3. NDI-AC (0.80g, 1.35mmol), St-AN (0.88g, 2.7mmol) and n-butyl acrylate (0.87g, 8.1mmol) were dissolved in 5 ml 1,4-dioxane at a feed molar ratio 1:2:6, and then 240 mg 2,2-azobisisobutyronitrile (AIBN) was added (1 wt% total monomer weight). The polymerization reaction was performed at  $65^\circ\text{C}$  for 24 hours under nitrogen protection. The reaction mixture was precipitated in cold petroleum ether when cooled to room temperature. The product was filtered and dried at  $70^\circ\text{C}$  for 24 hours. The crude product was purified by dialysis (molecular weight: 1000). At last, we could obtain deep red solid copolymer ( $M_w=9000$ ,  $M_n/M_w=1.47$ , AN:NDI=4:1 which are measured by UV-vis spectrum)



**Scheme S3.** Synthesis process of PAN-NDI-BA



**Figure S3.**  $^1\text{H}$  NMR spectrum for PAN-NDI-BA in  $\text{CDCl}_3$ .

## 2.4 Fabrication of PDMS substrate samples.

The base/crosslinking agent (Sylgard 184, Dow Corning) at a 10:1 weight ratio was put in Petri dishes and then was mixed sufficiently. After being degassed for 30 min by vacuum oven, the mixture was heat to 60 °C for 6 h to get a cross-linked PDMS elastomer sheet. Then the sample was cut into 1 cm \* 1 cm and 2cm \* 2cm square (thickness approximately 0.5mm).

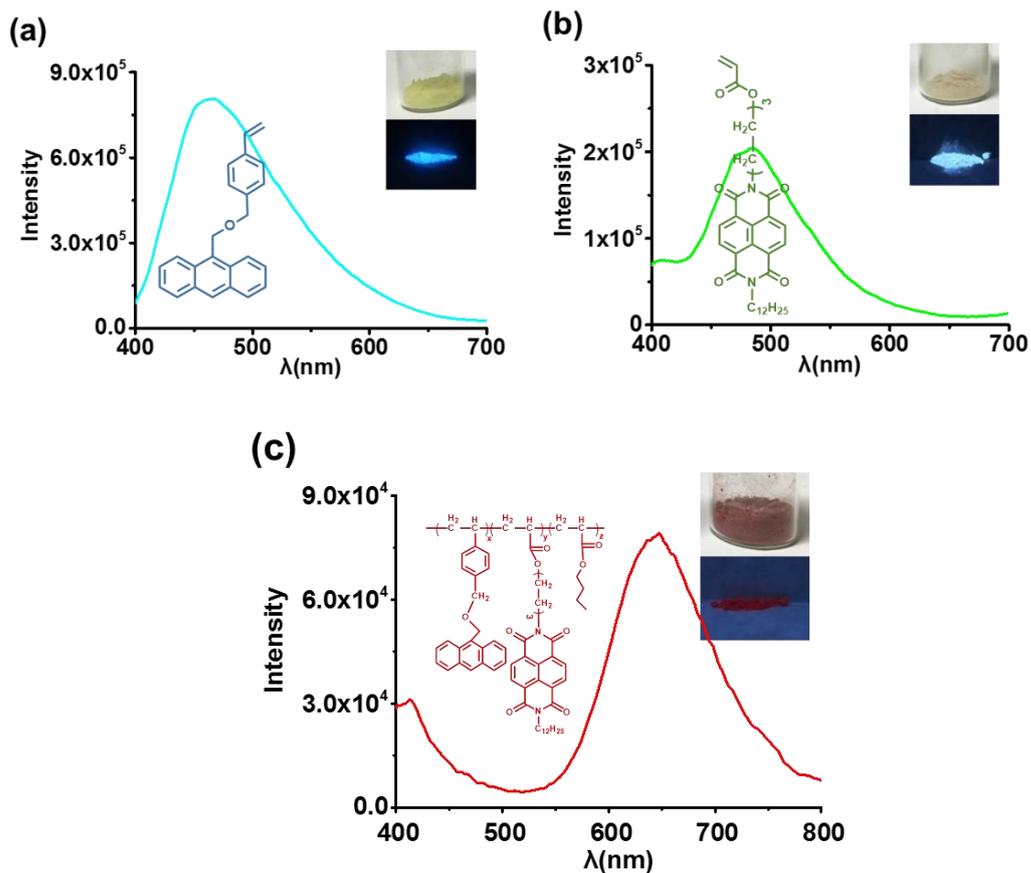
## 2.5 Preparation and erasure of patterns.

A toluene solution of PAN-NDI-BA (5wt%) was firstly spin-coated on a precast PDMS and then exposed under 365 nm UV light for the desired time forming a relatively hard top-layer film on the PDMS sheet with a thermal treatment at 70 °C. The coated PDMS sheet was cooled to room temperature to generate the wrinkle pattern. As for erasure of the wrinkle pattern, the wrinkled PDMS bilayer underwent heating at 150 °C or exposure under 254 nm UV light for the desired duration for de-cross-linking of the top-layer to make the surface wrinkle-free and fluorescence recovery. All processes underwent in the  $\text{N}_2$  atmosphere.

**Characterization.**  $^1\text{H}$  NMR spectra and  $^{13}\text{C}$  NMR spectra were recorded on a Varian Mercury Plus spectrometer (400 MHz). Average molecular weight was measured by gel permeation chromatography (GPC, LC-20A, Shinadzu, Japan) using tetrahydrofuran as an eluent. The surface patterns and the modulus of top films were measured by atomic force microscope (Dimension Icon & FastScan Bio America). Surface patterns were also recorded by profile measurement microscope (VF-7501, KEYNCE, Japan). The anthracene dimerization and decrosslinking process were traced by ultraviolet-visible spectroscopy using TU-1091 spectrophotometer (Persee, China). The fluorescence spectra were recorded using an LS-55B fluorescence meter (Perkin-Elmer, Inc., USA). The excitation wavelength is 365 nm. Fluorescence images (STED images) of coating were viewed with Super-Resolution Multiphoton Confocal Microscope. The excitation wavelength is 405 nm. The UV light source is LED and the intensity of 365nm UV light is  $15\text{mW}\cdot\text{cm}^{-2}$ .

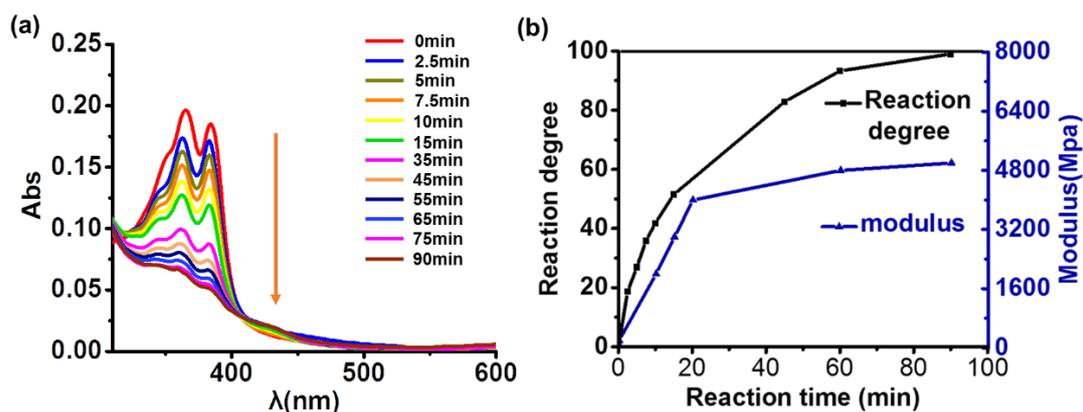
## 3. Results and Discussion

### 3.1 The formation of charge transfer interaction



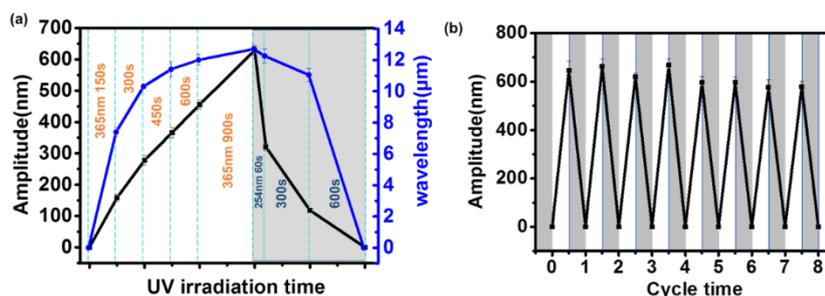
**Figure S4.** Fluorescence spectra of (a)St-AN, (b)NDI-AC and (c)PAN-NDI-BA. Inset pictures are corresponding photographs taken under natural light and UV light.

### 3.2 UV-Vis spectra and dynamics of dimerization



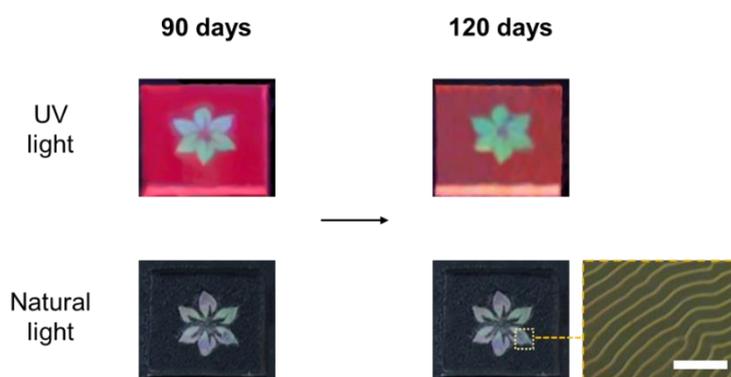
**Figure S5.** (a) Evolution of UV-Vis spectra of dimerization reaction among AN when exposed to 365nm UV for desired time. (b) Photodimerization reaction degree (black square, left vertical axis) and surface Young's modulus  $E_f$  (blue triangle, right vertical axis) as a function of 365 nm UV light irradiation time.

### 3.3 Variation of wrinkle characteristic with UV irradiation time



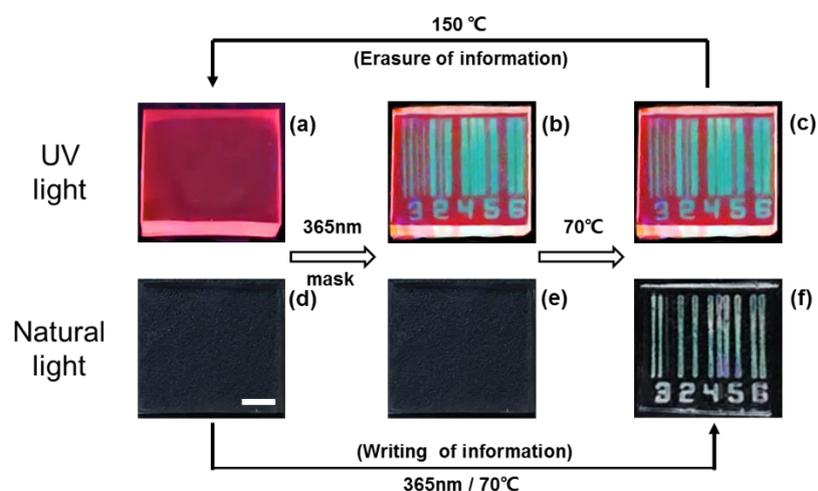
**Figure S6.** (a) Amplitude (A, black square, left vertical axis) and wavelength ( $\lambda$ , blue, right vertical axis) of wrinkles as a function of UV light irradiation time. (b) Process of formation and erasing of wrinkles via exposure to different UV light. The gray regions represented formation process exposed to 365 nm UV light. The white regions represented erasure process exposed to 254 nm UV light.

### 3.4 The long-term stability for dual-patterns



**Figure S7.** Photographs illustrating the long-term stability for the photodimerization based on dual-patterns with wrinkles and fluorescence. The scale bar represents 50  $\mu\text{m}$ .

### 3.5 Application for information storage and smart display



**Figure S8.** Photographs illustrating application of patterns with wrinkles and fluorescence for information storage: (a-c) under 365nm UV, (d-f) under natural light. Selective exposure of the bilayer was executed through photomask “bar code” which represented the writing of information. Heating at 150°C represents the erasure of information. The scale bar represents 500µm.

### References

[1] Sassi, M.; Salamone, M. M.; Ruffo, R.; Mari, C. M.; Pagani, G. A.; Beverina, L., Gray to Colorless Switching, Crosslinked Electrochromic Polymers with Outstanding Stability and Transmissivity From Naphthalenediimide-Functionalized EDOT. *Adv. Mater.* **2012**, 24, 2004-2008.