Supplementary Information

Programmable photoresponsive materials based on a single molecule via distinct topochemical reactions

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Preparation of BNA.
2-(3,5-bis (trifluoromethyl) phenyl) acetonitrile (1.39 g, 5.5 mmol) and 2-naphthaldehyde (0.78 g, 5.0 mmol) were added into 50 mL of ethanol. Pyrrolidine (0.70 g, 11.0 mmol) was dropped in the previous solution. Faint yellow product precipitated after stirring 12 h at room temperature. The product was collected through filtering and washing by ethanol to give a yellow solid (1.86 g, 95%). $^1$H NMR (500 MHz, DMSO-$d_6$): $\delta$/ppm = 8.59 (s, 1H), 8.51 (s, 1H), 8.43 (s, 2H), 8.22 (s, 1H), 8.19 (d, $J = 8.7$ Hz, 1H), 8.11 (d, $J = 8.7$ Hz, 1H), 8.02 (dd, $J = 11.9$, 8.6 Hz, 2H), 7.70 - 7.60 (m, 2H); $^{13}$C NMR (126 MHz, DMSO-d6): $\delta$/ppm = 107.66, 117.74, 120.27, 122.44, 122.78, 124.61, 125.04, 126.68, 127.56, 128.17, 128.67, 129.09, 129.22, 131.12, 131.44, 131.71, 132.13, 132.88, 134.38, 137.02, 146.76; MS: m/z calculated for C$_{21}$H$_{11}$F$_6$N: 391.08; found 390.71.

Crystal growth
BNA was dissolved in dichloromethane to make a dilute solution. The green block crystals (BNA-β) were obtained with a slow evaporation rate at 16°C. To further tune molecular crystallization rate, a mixed solvent evaporation assembly method was employed for rapid crystallization. Ethanol as a poor solvent was injected into the dichloromethane solution of BNA to achieve the nearly saturated system. And then the needle-like crystals (BNA-α) quickly nucleated and precipitated in constant temperature water bath heating at 25°C.

Preparation of Adduct-α and Adduct-β.
The single crystals of BNA-α and BNA-β were ground into microcrystalline powders, and then these powders were spread into a 1 mm thin layers to receive irradiation with 365 nm OLED UV lamps (3.7 mW·cm$^{-2}$). The irradiated BNA-α (300 mg, 0.76 mmol)
was purified by column chromatography with hexane/dichloromethane mixture, 1:4 v/v, obtaining white solid Adduct-α. Yield: 204 mg, 0.26 mmol (68 %). The mixture of irradiated BNA-β (300 mg, 0.76 mmol) were purified by column chromatography with petroleum ether/dichloromethane mixture, 1:5 v/v, obtaining creamy white solid Adduct-β. Yield: 99 mg, 0.12 mmol (33 %). Purified Adduct-α and Adduct-β were dissolved in dichloromethane respectively, and their single crystals were formed after two or three days.

\[ \text{H NMR of Adduct-α (500 MHz, DMSO-}d_6\text{): } \delta/\text{ppm} = 8.22 \text{ (s, 2H), 8.09 (s, 2H), 8.04 (s, 4H), 7.92 – 7.90 (m, 2H), 7.885 (d, } J = 8.7, 2H) 7.84 – 7.82 (m, 2H), 7.70 (dd, } J = 8.7, 1.9 \text{ Hz, 2H), 7.58 – 7.54 (m, 4H), 6.49 (s, 2H).} \]

\[ \text{H NMR of Adduct-β (500 MHz, DMSO-}d_6\text{): } \delta/\text{ppm} = 8.46 \text{ (s, 1H), 8.09 (s, 1H), 8.08 –8.05 (m, 3H), 7.98 – 7.93 (m, 4H), 7.9 (s, 2H), 7.63 (s, 1H), 7.54 (dt, } J = 6.8, 3.4 \text{ Hz, 2H), 7.46 (d, } J = 7.4 \text{ Hz, 1H), 7.33 (t, } J = 7.5 \text{ Hz, 1H), 7.18 (t, } J = 7.5 \text{ Hz, 1H), 6.87 (d, } J = 7.6 \text{ Hz, 1H), 6.26 (s, 2H), 5.70 (d, } J = 8.7 \text{ Hz, 2H).} \]

**Measurements.**

\[ \text{H NMR and } ^{13}\text{C NMR spectra were recorded on a Bruker Advance 500 MHz spectrophotometer with tetramethylsilane (TMS) as the internal standard. Mass spectra was characterized by a Gas Chromatograph-Mass Spectrometer (GC-MS) (Thermo Fisher ITQ 1100\textsuperscript{TM}). The Powder X-ray diffraction (XRD) patterns were obtained with a Bruker D8 diffractometer with CuKα radiation (λ = 0.15418 nm). All PXRD results of samples are collected at room temperature. The crystal data and crystal face indices were collected on a Rigaku RAXIS-PRID diffractometer at ω-scan mode with monochromatized Mo Kα radiation (λ = 0.071073 nm). FTIR spectra were recorded with a Fourier transform infrared spectrometer (Bruker Optics VERTEX 80v). Morphology and photomechanical responses of crystal were performed with fluorescence microscopy (Vision Engineering Co., UK). Differential scanning calorimetry (DSC) was performed on a DSC Q20 instrument at a heating rate of 10}
°C/min under a nitrogen purge. Thermogravimetric analysis (TGA) thermograms were obtained on a TA instrument at a heating rate of 10 °C/min under a nitrogen purge. Three-point bending tests of crystals were performed on INSTRON 9544 universal materials tester in the displacement control mode. Nanoindentation experiments were carried out on Nano Indenter G200 equipped with a Berkovich diamond tip with ~100 nm radius at a 0.1 mN/s loading rate. Mechanical behaviors of crystals were recorded by a Nikon Coolpix P7800 digital camera coupled to a reflectivity-mode optical microscope. UV/Vis absorption spectra were characterized by a UV/Vis spectrophotometer (Shimadzu UV-2600). Fluorescence spectra were measured by an optical fiber connected to Ocean Optics QE65 Pro spectrometer. The lifetime was collected on an Edinburgh FLS 980 spectrophotometer with TCPSC technology. A 365 nm OLED UV lamps (3.7 mW·cm⁻²) and a UV pulsed laser (under power of 10 mW·cm⁻²) with an optical fiber coupled were employed as light sources in this work. The OLED UV lamp was used to monitor the process of the photocycloaddition of BNA powders, and print different patterns on the fluorescent paper. The UV pulsed laser was used to test the photomechanical responses of BNA crystals at distance of 10 mm from, and write on the fluorescence paper.

**Crystallographic data.**

The single crystal date of BNA-α, BNA-β, Adduct-α and Adduct-β have been deposited as CIF files into Cambridge Crystallographic Data Center. The publication numbers CCDC is 2032920, 2113420, 2032927 and 2032930.

**Theoretical calculation.**

Density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculation were employed to explore the processes of fluorescence change. The geometries of the π-dimers were obtained from BNA-α and BNA-β crystals structures. The ground state geometries of Adduct-α and Adduct-β were subjected to optimized
by DFT computations of B3LYP/6-31G(d) in Gaussian 09 package; The excitation energies in the n-th singlet (Sn) states were performed by TD-DFT computations of B3LYP/6-31G(d).

The energy of BNA reactants and Adduct-α and Adduct-β products were treated by utilizing B3LYP level of theory with Pople 6-31G (d) basis set.

Fabrication of Photoactuator and Photoswitching.

Two crystals of BNA-α with different thickness were fixed on the left and right sides of a capillary tip with 502 glue. This micron optic-controlled tweezer was connected to a 3-dimensional operation platform to help it gain movement. When the light source on the side of the relatively thinner crystal was turned on, the distance between the two single crystals was reduced and the object could be picked up.

The BNA was dissolved in dichloromethane, after adding ethanol, the solution was stirred overnight. And then uniform BNA-β nanocrystals precipitated. The nanocrystals were evenly spread on the transparent adhesive tape to prepare rewritable fluorescent rewritable fluorescent for photoswitching.
Preparation and Characterization of BNA.

**Scheme S1.** Synthetic route of BNA.

**Figure S1.** $^1$H NMR spectrum of BNA in DMSO-$d_6$ (500 MHz).
Figure S2. $^{13}$C NMR spectrum of BNA in DMSO-$d_6$ (500 MHz).

Figure S3. Mass spectrum of BNA.
Molecular Preorganization with Different Hierarchical Architectures.

**Figure S4.** The schematic illustrations of the crystal growth and the optical micrographs of the single crystals taken under room light. (a) needle shape crystals (BNA-α) prepared by rapid evaporation from ethanol and dichloromethane mixed solution and (b) block shape crystals (BNA-β) prepared from dichloromethane solution in a relatively sealed system. The scale bar is 200 μm.

**Figure S5.** PXRD patterns of BNA-α and BNA-β powders.
Figure S6. Thermal ellipsoid diagram of BNA-α.

Figure S7. Thermal ellipsoid diagram of BNA-β.
Table S1. Crystal data and structure refinement for BNA-α.

| Parameter                          | Value                      |
|------------------------------------|----------------------------|
| Empirical formula                  | C_{21}H_{11}F_{6}N         |
| Formula weight                     | 391.31                     |
| Temperature (K)                    | 99(2)                      |
| Crystal system                     | Triclinic                  |
| Space group                        | P-1                        |
| a (Å)                              | 7.8885(8)                  |
| b (Å)                              | 9.5215(10)                 |
| c (Å)                              | 12.4914(13)                |
| α (°)                              | 94.944(4)                  |
| β (°)                              | 94.830(4)                  |
| γ (°)                              | 110.235(4)                 |
| Volume (Å³)                        | 870.50(16)                 |
| Z                                  | 2                          |
| d_{cal} (g cm⁻³)                   | 1.493                      |
| μ (mm⁻¹)                           | 0.133                      |
| F(000)                             | 396                        |
| Crystal size (mm³)                 | 0.130 × 0.120 × 0.100      |
| Radiation                          | CuKα (λ = 1.54184)         |
| θ range for data collection (°)    | 2.904 to 27.501            |
| Index ranges                       | -10 ≤ h ≤ 10, -12 ≤ k ≤ 12, -16 ≤ l ≤ 16 |
| Reflections collected              | 26410                      |
| Independent reflections            | 3988 [R_{int} = 0.0361]    |
| Completeness to θ = 25.242°       | 99.8 %                     |
| Data / restraints / parameters     | 3988 / 0 / 259             |
| Goodness-of-fit on F²              | 1.024                      |
| Final R indices [I > 2σ (I)]       | R₁ = 0.0536, wR₂ = 0.1274  |
| R indices [all data]               | R₁ = 0.0906, wR₂ = 0.1554  |
| Largest diff. peak and hole (e Å⁻³) | 0.292 and -0.206        |
**Table S2.** Crystal data and structure refinement for BNA-β.

| Property                        | Value                          |
|---------------------------------|--------------------------------|
| Empirical formula               | C$_2$H$_{11}$F$_6$N             |
| Formula weight                  | 391.31                         |
| Temperature (K)                 | 293                            |
| Crystal system                  | monoclinic                     |
| Space group                     | P 1 21/n 1                     |
| $a$ (Å)                         | 8.4375(3)                      |
| $b$ (Å)                         | 15.1706(7)                     |
| $c$ (Å)                         | 13.3563(6)                     |
| $\alpha$ (°)                   | 90                             |
| $\beta$ (°)                     | 96.315(2)                      |
| $\gamma$ (°)                   | 90                             |
| Volume (Å$^3$)                  | 1699.23(13)                    |
| $Z$                             | 4                              |
| $d_{cal}$ (g cm$^{-3}$)         | 1.530                          |
| $\mu$ (mm$^{-1}$)               | 0.136                          |
| $F$(000)                        | 792.60                         |
| Crystal size (mm$^3$)           | 0.110 × 0.100 × 0.100          |
| Radiation                       | CuKα ($\lambda = 1.54184$)    |
| $\theta$ range for data collection (°) | 2.685 to 27.503 |
| Index ranges                    | -10 ≤ h ≤ 9, -19 ≤ k ≤ 19, -17 ≤ l ≤ 17 |
| Reflections collected           | 11085                          |
| Independent reflections         | 3894 [R$_{int} = 0.0437$]      |
| Completeness to $\theta = 25.242^\circ$ | 99.9 %                        |
| Data / restraints / parameters   | 3894 / 0 / 279                 |
| Goodness-of-fit on $F^2$        | 1.019                          |
| Final $R$ indices [$I > 2\sigma(I)$] | $R_1 = 0.0685$, $wR_2 = 0.1792$ |
| $R$ indices [all data]          | $R_1 = 0.1059$, $wR_2 = 0.2209$ |
| Largest diff. peak and hole (e Å$^{-3}$) | 0.424 and -0.270 |
**Figure S8.** Molecular configurations in (a) BNA-α and (b) BNA-β single crystals.

**Figure S9.** The parameters of geometric criteria within π-dimer. The distance between the olefin units is required within 4.2 Å. The angles (θ₁, θ₂, and θ₃) are used to judge the parallelism, and the ideal values are 0°, 90°, and 90°, respectively.

**Table S3.** Geometric parameters of BNA-α and BNA-β crystals.

|       | d (Å)     | θ₁ (degree) | θ₂ (degree) | θ₃ (degree) |
|-------|-----------|-------------|-------------|-------------|
| BNA-α | 3.607(3)  | 0.00(11)    | 86.95(16)   | 78.39(14)   |
| BNA-β | 3.651(4)  | 16.33(12)   | 100.29(18)  | 79.45(17)   |
| Ideal | < 4.2     | 0           | 90          | 90          |
Figure S10. The intra-π-dimer structure of (a) BNA-α and (b) BNA-β single crystals.

Figure S11. The inter-π-dimer packing in (a) BNA-α and (b) BNA-β single crystals.
Figure S12. Theoretical calculation of BNA π-dimer. (a) In-phase interaction between the lowest unoccupied molecular orbitals (LUMOs) of C=C bond pairs in the symmetric π-dimer of BNA-α. (b) The overlapping between the LUMOs of olefin and aromatic ring in the offset π-dimer of BNA-β single crystals.
Characterization of Photocycloaddition Products.

**Figure S13.** $^1$H NMR spectrum of **Adduct-α** in DMSO-$d_6$ (500 MHz).

**Figure S14.** $^1$H NMR spectrum of **Adduct-β** in DMSO-$d_6$ (500 MHz).
Figure S15. FT-IR spectra (KBr pellets) of BNA-α and Adduct-α.

Figure S16. FT-IR spectra (KBr pellets) of BNA-β and the Adduct-β.
Figure S17. Thermal ellipsoid diagram of Adduct-α.

Figure S18. Thermal ellipsoid diagram of Adduct-β.
Table S4. Crystal data and structure refinement for Adduct-α.

| Description                  | Value                                      |
|------------------------------|--------------------------------------------|
| Empirical formula           | C_{42}H_{22}F_{12}N_{2}                    |
| Formula weight              | 782.61                                     |
| Temperature (K)             | 98(2)                                      |
| Crystal system              | triclinic                                  |
| Space group                 | P-1                                        |
| a (Å)                       | 6.6239(3)                                  |
| b (Å)                       | 11.3191(6)                                 |
| c (Å)                       | 12.9368(7)                                 |
| α (°)                       | 67.4855(17)                                |
| β (°)                       | 84.6786(17)                                |
| γ (°)                       | 89.830(2)                                  |
| Volume (Å³)                 | 891.61(8)                                  |
| Z                           | 1                                          |
| d_cal (g cm⁻³)              | 1.458                                      |
| μ (mm⁻¹)                    | 0.129                                      |
| F (000)                     | 396                                        |
| Crystal size (mm³)          | 0.130 × 0.120 × 0.100                      |
| Radiation                   | CuKα (λ = 1.54184)                         |
| θ range for data collection (°) | 3.050 to 25.730                           |
| Index ranges                | -8 ≤ h ≤ 8, -13 ≤ k ≤ 13, -15 ≤ l ≤ 15    |
| Reflections collected       | 27462                                      |
| Independent reflections     | 3349 [R_{int} = 0.0539]                    |
| Completeness to θ = 25.242° | 99.3 %                                     |
| Data / restraints / parameters | 3349 / 0 / 310                            |
| Goodness-of-fit on F²       | 1.014                                      |
| Final R indices [I > 2σ (I)] | R₁ = 0.0539, wR₂ = 0.1292                 |
| R indices [all data]        | R₁ = 0.0789, wR₂ = 0.1448                 |
| Largest diff. peak and hole (e Å⁻³) | 0.160 and -0.161                         |
|                      | Adduct-β          |
|----------------------|-------------------|
| **Empirical formula**| C₄₂H₂₂F₁₂N₂       |
| **Formula weight**   | 782.61            |
| **Temperature (K)**  | 293(2)            |
| **Crystal system**   | monoclinic        |
| **Space group**      | P2 (1) /c         |
| **a (Å)**            | 16.3007(12)       |
| **b (Å)**            | 18.4842(13)       |
| **c (Å)**            | 12.5889(9)        |
| **α (°)**            | 90                |
| **β (°)**            | 90                |
| **γ (°)**            | 109.832(3)        |
| **Volume (Å³)**      | 3568.1(4)         |
| **Z**                | 4                 |
| **d<sub>cal</sub> (g cm⁻³)** | 1.457          |
| **μ (mm⁻¹)**         | 0.129             |
| **F(000)**           | 1584              |
| **Crystal size (mm³)** | 0.130 × 0.120 × 0.100 |
| **Radiation**        | CuKα (λ = 1.54184) |
| **θ range for data collection (°)** | 2.736 to 26.376 |
| **Index ranges**     | -20 ≤ h ≤ 20, -23 ≤ k ≤ 23, -15 ≤ l ≤ 15 |
| **Reflections collected** | 53329          |
| **Independent reflections** | 7269 [R<sub>int</sub> = 0.0472] |
| **Completeness to θ = 25.242°** | 99.8 %          |
| **Data / restraints / parameters** | 7269 / 0 / 618 |
| **Goodness-of-fit on F²** | 1.014         |
| **Final R indices [I > 2σ(I)]** | R₁ = 0.0438, wR₂ = 0.1016 |
| **R indices [all data]** | R₁ = 0.0786, wR₂ = 0.1256 |
| **Largest diff. peak and hole (e Å⁻³)** | 0.155 and -0.151 |
Thermodynamic Analysis of Irradiated BNA-α and BNA-β Samples.

Figure S19. DSC curves of (a) BNA-α and (b) BNA-β in different states. Their curves demonstrate different thermal stabilities of the irradiated BNA-α and BNA-β powders. The irradiated BNA-α is stable and there is no thermal cleavage (retrocycloaddition) before 180°C. But the irradiated BNA-β exhibits poor stability, it can undergo thermal cleavage (retrocycloaddition) at 95°C.

Figure S20. PXRD patterns of BNA-β in different states (The green, red and blue lines represent the original one, the one after irradiation and the heated one after irradiation, respectively.).
Figure S21. DSC and TGA thermogram of (a) irradiated BNA-α and (c) irradiated BNA-β. Energy profiles for (b) olefin-olefin [2+2] retrocycloaddition reactions and (d) olefin-aromatic ring [2+2] retrocycloaddition reactions.

For the DSC thermogram of irradiated BNA-α powders, following the melting endothermic peak of irradiated product (Adduct-α) at 297.1 °C, there is a broad endotherm (300.6 ~ 330.9 °C) that corresponds to a complete weight loss of the TGA thermogram (300.6 ~ 348.2 °C). This result indicates that the melted Adduct-α undergoes a decomposition and a evaporation of monomers during the broad endotherm process. The enthalpy ($\Delta H$) that involves both decomposition and phase transition is calculated to be 32.15 kcal/mol by integrating the broad endothermic zone.

The energy profiles of olefin-olefin [2+2] retrocycloadditions in BNA-α powders demonstrate that the irradiated product Adduct-α is stable with lower energy. Gibbs free energies ($\Delta G_{cal}$) of this retrocycloadditions is 5.6 kcal/mol. The enthalpy of this retrocycloadditions can calculated from $\Delta G_{cal} = \Delta H_{cal} - T\Delta S_{cal}$, where $T$ is the absolute temperature, $\Delta S_{cal}$ (55.49 cal/mol) is provided from the theoretical calculation data.
ΔH<sub>cal</sub> is calculated to be 22.1 kcal/mol. This value of ΔH<sub>cal</sub> corresponds to the olefin-olefin [2+2] retrocycloadditions, which does not involve the phase transition. Therefore, the ΔH<sub>cal</sub> from energy profiles is smaller than the ΔH from DSC thermogram.

For the DSC thermogram of irradiated BNA-β powders, there is a broad exothermic peak (86.1 ~ 127 °C). The results of ¹H NMR spectra proved that the irradiated BNA-β powders undergo retrocycloaddition during this exothermic process. Noting that the melting endothermic peak of monomer is at 145.5 °C, so the retrocycloaddition does not involve the phase transition. The enthalpy (ΔH) of retrocycloaddition is calculated to be -8.3 kcal/mol from the DSC thermogram. As shown in the energy profiles (Figure S21d), the irradiated product of Adduct-β has higher energy. ΔG<sub>cal</sub> of olefin-aromatic [2+2] retrocycloadditions is -13.1 kcal/mol. According to the equation ΔG<sub>cal</sub> = ΔH<sub>cal</sub> − TΔS<sub>cal</sub>, ΔH<sub>cal</sub> is calculated to be -7.6 kcal/mol, which is consistent with the ΔH from DSC thermogram.

In summary, irradiated product Adduct-α with lower energy demonstrates better stability. It undergoes a decomposition and a evaporation of the corresponding monomers at a very high temperature with the absorption of energy. Whereas irradiated product Adduct-β in microcrystal powders has higher energy due to the involvement of aromatic ring. Adduct-β in irradiated microcrystal powders can be thermally cleaved to monomers at lower temperature with the release of energy.
Calculated Growth Morphology and Mechanics Tests.

Figure S22. Calculated growth morphology of BNA-α.

Figure S23. Calculated growth morphology of BNA-β.

Figure S24. Crystal qualitative mechanics tests of (a) BNA-α and (b) BNA-β under mechanical stress applied through a pair of tweezers.
Figure S25. Schematic setup of three-point bending tests and nanoindentation tests.

Figure S26. Crystal quantitative mechanics tests. Load–displacement ($P–d$) curve of (a) BNA-α and (c) BNA-β crystals obtained from three-point bending tests. Load–displacement ($P–h$) curves of (b) BNA-α and (d) BNA-β crystals obtained from the nanoindentation tests. Three-point bending tests of crystals were performed in the displacement control mode. The bending elastic modulus, $E_b$, were calculated with the equation 

$$E_b = \frac{PL^3}{48I\delta},$$

where $P$ is the load applied at the center of the span length $L$, $\delta$ is the beam deflection at the center of span, and $I$ is the area moment of inertia for a rectangular cross-section. The yield strain, $\varepsilon_{\text{max}}$, were calculated by using the equation
where \( h \) is the thickness of materials. Nanoindentation experiments were utilized to measure the elastic modulus \( (E) \) and hardness \( (H) \) of crystals. The values of \( E_b \), \( E \) and \( H \) of \textbf{BNA-β} crystals are higher than those of \textbf{BNA-α} crystals, indicating that \textbf{BNA-β} crystals is inflexible and hard. In addition, the \( \varepsilon_{\text{max}} \) of \textbf{BNA-β} crystals is much smaller than that of \textbf{BNA-α} crystals, which demonstrates that the \textbf{BNA-β} crystals is easier to be fractured under the external force.

**Figure S27.** Bruker diffraction images of \textbf{BNA-α} crystal (a) before and (b) after UV irradiation. The area in (b) selected with white dotted line show a significant elongation of the diffraction spots, indicating the partially molecular displacement caused by \([2+2]\) photocycloaddition reactions. The other diffraction spots in (b) with good shape demonstrated that the periodic nature of crystal was partly retained. The scale bar is 1 mm.
Figure S28. Bruker diffraction images of BNA-α crystal (a) bended by external force and (b) after the release of external force. Their diffraction spots with good shape and intensity demonstrated that the bent and recovered crystal also remained crystalline. The scale bar is 1 mm.
The Thickness Dependence of Response Speed in BNA-α Crystal.

Figure S29. $^1$H NMR spectrum of BNA-α crystals bending at 45°, 60° and 90° with the photodimerization of 5%, 7% and 10%, respectively.

Figure S30. The bending responsive characteristics of BNA-α crystals with different thickness (from 30 to 150 μm) upon UV irradiation for different time. Dependence of the crystal curvature under continuous irradiation used to calculate the response rate ($k$) of curvature by the linear fit.
**Figure S31.** Thickness-dependent crystal deformation. (a) Dependence of the crystal curvature on irradiated time at different thicknesses. (b) Response rate of different thicknesses obtained from the linear fit of the curvature data.

**Figure S32.** Dependence of the response on the crystal thickness. By fitting the data, we obtained a model, $y = a/x^2 + b$, where $x$ is the thicknesses of crystals, $y$ is the response rate of curvature.
Photochromism Behaviors of BNA-α and BNA-β.

**Figure S33.** UV-vis absorption spectra of (a) BNA-α and (b) BNA-β at different UV irradiation time.

**Figure S34.** UV irradian time-dependent profile of UV absorption intensity and the PL intensity of (a) BNA-α and (b) BNA-β.
The Mechanism of Fluorescence Change under UV Irradiation.

Figure S35. PL spectra of irradiated BNA-α (blue line) and Adduct-α (green line).

Figure S36. PL spectra of irradiate BNA-β (blue line) and Adduct-β (green line).
Figure S37. PL spectrum and fit peaks of Adduct-β.

Figure S38. The fluorescence decay profiles of Adduct-β at 453 nm and 514 nm related to $S_2$ state and $S_1$ state shown the different average fluorescence lifetime, which further confirm the dual-state emission of Adduct-β.
The Photochromism Process of Rewritable Fluorescent Paper.

Figure S39. Fabrication of rewritable fluorescent paper based on BNA-β nanocrystals.

Figure S40. Fluorescence micrographs of BNA-β nanocrystals in rewritable fluorescent paper for different UV irradiation time. The scale bar is 20 μm.

Figure S41. The printing process of rewritable fluorescent paper.
Supplementary Videos

Supplementary Video 1. This video showed the photoinduced bending process of BNA-α crystal.

Supplementary Video 2. This video showed the rapid fluorescence change of BNA-β nanocrystal in rewritable fluorescent paper, when we wrote with a laser pen and erased by heating at 90°C.