

Supporting Information

**A solar actuator based on hydrogen-bonded azopolymers for electricity generation**

*Yubing Xiong,<sup>a,c†</sup> Lidong Zhang,<sup>b,d†</sup> Philipp Weis,<sup>a</sup> Pance Naumov,<sup>b\*</sup> and Si Wu<sup>a\*</sup>*

<sup>a</sup> Max Planck Institute for Polymer Research, Ackermannweg 10, Mainz 55128, Germany

<sup>b</sup> New York University Abu Dhabi PO Box 129188, Abu Dhabi, United Arab Emirates

<sup>c</sup> Department of Chemistry, Zhejiang Sci-Tech University, Hangzhou 310018, Zhejiang Province, China

<sup>d</sup> Department of Chemistry and Molecular Engineering, East China Normal University, Shanghai 200241, China

## Experimental

### Materials

2,6-Difluoro-4-bromoaniline, agarose (AG), 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (Xantphos),  $\text{KMnO}_4$ ,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , dichloromethane (DCM), hexane, celite, acetamide,  $\text{Cs}_2\text{CO}_3$ , dioxane, ethyl acetate,  $\text{MgSO}_4$ , dimethyl formamide (DMF),  $\text{D}_2\text{O}$ ,  $\text{CDCl}_3$ ,  $\text{DMSO}-d_6$ , and tetrahydrofuran (THF) were purchased from Sigma-Aldrich and used without further purification. Tris(dibenzylideneacetone) dipalladium ( $\text{Pd}_2\text{dba}_3$ ) was purchased from TCI and used as received. Microscopy glass slides (25.4 mm  $\times$  76.2 mm  $\times$  1.0 mm) from T&Q industries were washed with ethanol and water and dried at 50 °C before casting of the films.

### Synthesis

2,2',6,6'-Tetrafluoro-4,4'-diacetamidoazobenzene (F-Azo) was synthesized according to the reported method with minor modifications.<sup>[1]</sup> The synthesis route of F-Azo is illustrated in **Figure S2**.

*Synthesis of 1,2-bis(4-bromo-2,6-difluorophenyl)diazene:* A flask was charged with 2,6-difluoro-4-bromoaniline (5.0 g, 24 mmol) and a freshly ground mixture of  $\text{KMnO}_4$  (10.0 g) and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (10.0 g). Then, DCM (120 mL) was added into the flask and the solution was refluxed overnight. After that, the mixture was filtered through celite and dried using  $\text{MgSO}_4$ . After removing  $\text{MgSO}_4$  by filtration, the filtrate was concentrated under reduced pressure. The crude residue was purified by column chromatography (DCM/hexanes, 1/1, v/v) to obtain the product as an orange/red solid (0.88 g, 18%).  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ) (*trans*-isomer)  $\delta$  ppm 7.29–7.26 (m, 4 H); (*cis*-isomer) 7.11–7.08 (m, 4 H).

*Synthesis of 2,2',6,6'-tetrafluoro-4,4'-diacetamidoazobenzene (F-Azo)*

A flask was charged with 1,2-bis(4-bromo-2,6-difluorophenyl)diazene (49 mg, 0.12 mmol), acetamide (43 mg, 0.72 mmol),  $\text{Cs}_2\text{CO}_3$  (137 mg, 0.42 mmol) and dioxane (1.0 mL). The resulting mixture was subjected to three freeze-pump-thaw cycles. After that,  $\text{Pd}_2\text{dba}_3$  (5 mg, 0.006 mmol) and 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (Xantphos) (14 mg, 0.024 mmol) were quickly added to the top of the frozen solution. The flask was then allowed to warm to room temperature under argon and heated

at 90 °C for 1 h. Then, the mixture was diluted with ethyl acetate and washed with brine for several times. The two phases were separated, and the organic phase was dried using MgSO<sub>4</sub>, filtered, and concentrated under reduced pressure. The resulting mixture was purified by column chromatography (ethyl acetate/hexane, 1/3, v/v) to obtain F-Azo as orange crystals (26.8 mg, 62%). <sup>1</sup>H NMR (250 MHz, DMSO - d<sub>6</sub>) (*trans*-isomer) δ ppm 10.65 (s, 2H), 7.52–7.47 (d, *J* = 12.5 Hz, 4 H), 2.12 (s, 6 H). (*cis*-isomer) 10.48 (s, 2H), 7.36–7.31 (d, *J* = 12.5 Hz, 4 H), 2.05 (s, 6 H).

## Methods

*<sup>1</sup>H NMR spectroscopy:* Proton nuclear magnetic resonance (<sup>1</sup>H NMR) spectra were recorded at 25 °C on Bruker Avance 250 spectrometer (250 MHz). All chemical shifts are reported in ppm relative to the signals corresponding to the residual non-deuterated solvents (CHCl<sub>3</sub> = 7.26 ppm, DMSO = 2.50 ppm).

*Light irradiation:* A solar simulator (Model: Osram UV light, E27) and LEDs at 470 nm and 530 nm (device types LCS-0470-03-22 and LCS-0530-03-22 Mightex Systems) were used as light sources for photoisomerization. The output intensities of the LEDs were controlled by an LED controller (device type SLC-MA04-MU, Mightex Systems) and were calibrated by an optical powermeter (Model 407A, Spectra-Physics Corporation).

*UV-vis absorption spectroscopy:* UV-vis spectra were recorded on a Lambda 900 spectrometer (Perkin Elmer). To study photoisomerization using absorption spectroscopy, the samples were irradiated using light from a solar simulator or LED. The spectra before and after irradiation were recorded. The spectra were recorded with different time periods until the spectrum did not change anymore, indicating the sample reached the photostationary state.

*Tensile testing:* Ultimate tensile testing was conducted on a HY-0580 universal testing machine (Shanghai, China). The specimens were cut from the obtained films into a dumbbell shape and the measurements were conducted at a crosshead speed of 20 mm min<sup>-1</sup> at RT.

*Differential scanning calorimetry (DSC) measurement:* DSC measurements were performed on DSC Q2000 V24.11 Build 124 () between 20 and 150 °C at a heating/cooling rate of 10 °C/min in a sealed aluminum pan.

*Fabrication of F-Azo@AG film:* To 10 mL of DMF, 1.0 g of AG was added under vigorous stirring to obtain a homogenous mixture. AG was dissolved by heating the mixture at 110 °C. Then, 11 mg F-Azo in 1.0 mL DMF was added into the above solution using a syringe. The stirring was terminated when there were no bubbles any longer. After that, the as-obtained solution was casted onto pre-cleaned glass slides. Films were obtained after drying in air at room temperature for 2 days. Film thickness was controlled using glass molds. Dry F-Azo@AG film was kept in vacuum overnight at 50 °C for equilibration.

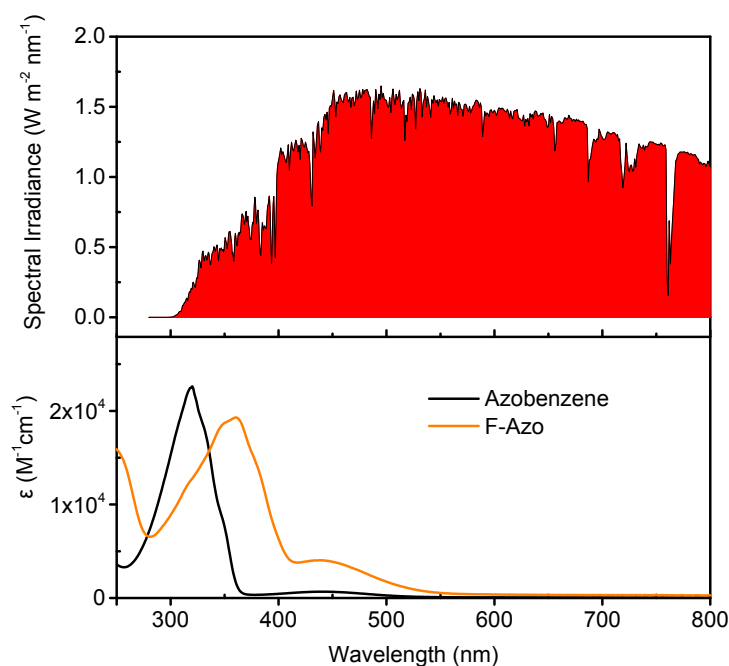
*Effects of irradiation power on bending performance:* F-Azo@AG films were dried at 40 °C in a vacuum oven for 2 hours before cutting to strips (L = 7.0 mm; W = 1.0 mm). The strip was fixed on a support with one side being exposed to simulated sunlight at various power intensities (Solar simulator, 91160, Newport Oriel), and the responsive processes were recorded with Apple Iphone-6 plus, and the recorded movies were analyzed with the software HotShot Link (ver.1.2).

*Effects of width on the bending performance:* The dried F-Azo@AG films were cut to 7 mm long strips with the width from 1.0 mm to 5.0 mm. The strip was fixed on a support with one side being exposed to simulated sunlight at 76.6 mW/cm<sup>2</sup>. The bending processes were recorded by Apple Iphone-6 plus, and the recorded movies were analyzed with the software HotShot Link(ver.1.2).

*Kinematics analysis for sunlight-driven bending of the strips:* The software HotShot Link (ver. 1.2) was used for the kinematic analysis. We first determined (x,y) coordinates of a point with respect to the origin (0,0) on the program window. Inclination of the tip at different times were extracted as (x,y) by selecting a point on the tip. The first point (inclination = 0, time = 0) corresponds to the first frame immediately after the sunlight was switched on. The (x,y) coordinates were extracted at different times. The deflection of the strip relative to the position in the first frame was calculated in pixels as  $d = [(x^2 - x^1)^2 + (y^2 - y^1)^2]^{1/2}$ , where  $x_{1,2}$  and  $y_{1,2}$  are the coordinates of two consecutive points.

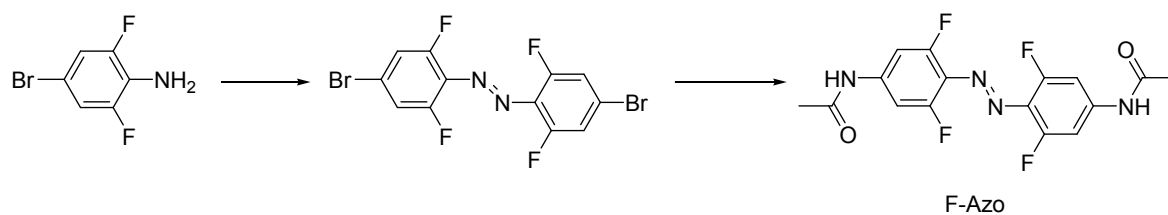
*Thermographic imaging:* A strip (10 mm × 1 mm × 40 μm) of F-Azo@AG was fixed and imaged with thermal camera using infrared lens (Image IR camera, Germany). Simulated sunlight at 76.6 mW/cm<sup>2</sup> was applied horizontally from one side of the film.

*Sunlight-powered generation of electricity:* The PVDF piezoelectric transducer (Model: LDT0-028K, purchased from Seeed Studio Shenzhen, China) as the generator was connected to one end of F-Azo@AG film (22 mg) by glue. A weight (125 mg) was combined at the other end of the F-Azo@AG film to keep the film straight. The distance between the F-Azo@AG film and the solar simulator was 18 cm. A dam-board was placed in front of the PVDF piezoelectric transducer to avoid photothermal effect. A multimeter (Agilent 34401A) was used to measure generated alternating voltage. The sunlight was supplied by a solar simulator equipped with a shutter (Model: Osram UV light, E27).

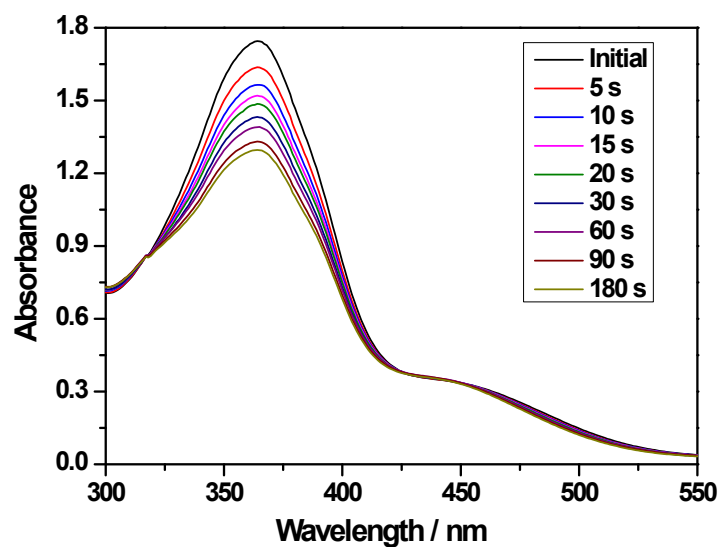


**Figure S1.** UV-vis absorption spectra of Azobenzene and F-Azo in DMSO.

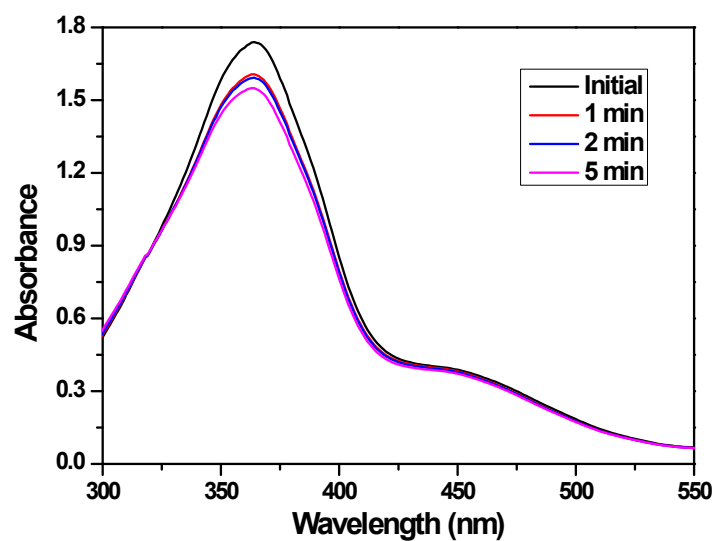
F-Azo has a more intense and red-shifted absorption band in the visible range compared with azobenzene, which makes F-Azo better suited than azobenzene for sunlight harvesting.



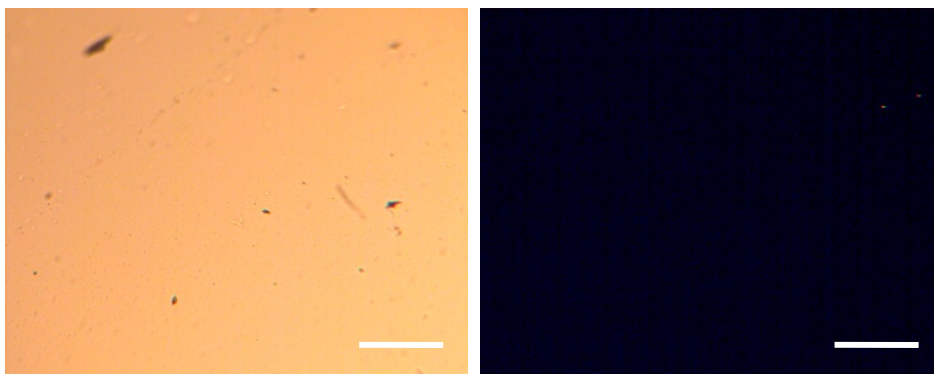
**Figure S2.** Synthesis of 2,2',6,6'-Tetrafluoro-4,4'-diacetamidoazobenzene (F-Azo).



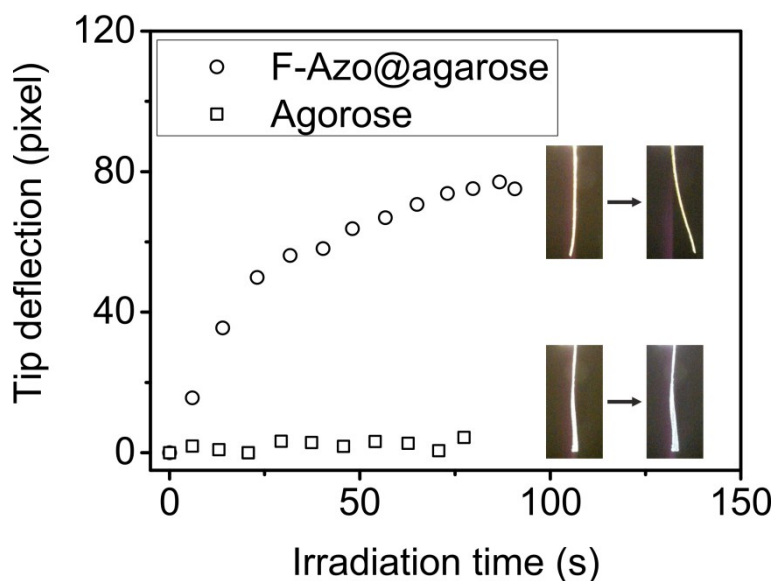
**Figure S3.** UV-Vis spectra of F-Azo@AG film irradiated by green light (530 nm, 4.94 mW/cm<sup>2</sup>).



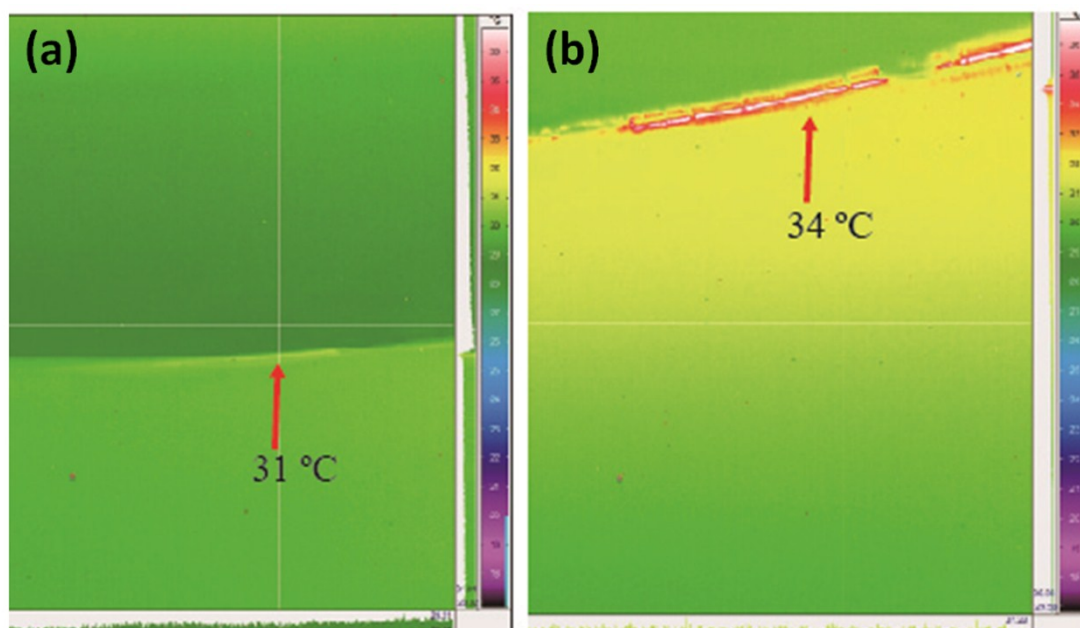
**Figure S4.** UV-Vis spectra of F-Azo@AG film irradiated by a solar stimulator (76.6 mW/cm<sup>2</sup>).



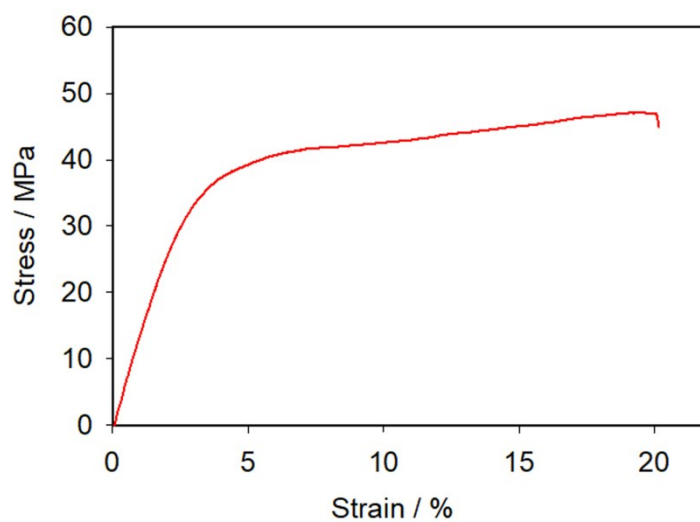
**Figure S5.** Optical (left) and polarized optical (left) microscopy images of a F-Azo@AG film. The images were captured on an optical microscope (Zeiss) equipped with a CCD camera. (Scale bar is 200  $\mu\text{m}$ ). The polarized optical microscopy image indicates that F-Azo molecules did not have preferred orientation in the films.



**Figure S6.** Comparison of bending performance of an agarose stripe and a F-Azo@AG stripe under simulated sunlight irradiation ( $76.6 \text{ mW}/\text{cm}^2$ ). The strips are  $7 \text{ mm} \times 1.0 \text{ mm}$  with a thickness of  $\sim 40 \mu\text{m}$ . Insets the snapshots of the stripes before and after irradiation. The snapshots are from Movies 4 and 10. This result suggests that the bending is due to incorporating AG with F-Azo.

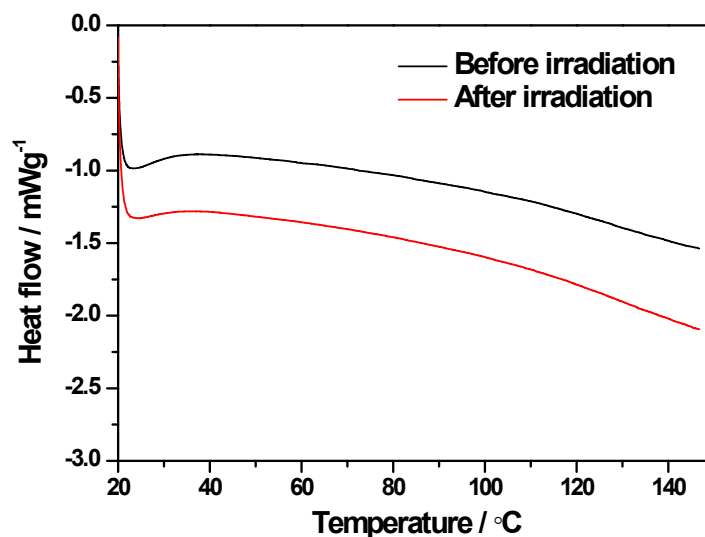


**Figure S7.** Infrared thermography images of a F-Azo@AG film (a) without and (b) under the exposure of simulated sunlight ( $76.6 \text{ mW/cm}^2$ ).

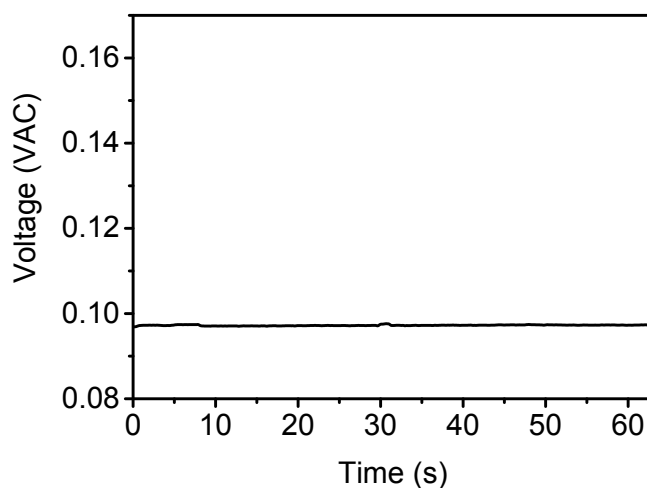


**Figure S8.** Stress-strain curve of F-Azo@AG film.





**Figure S9.** DSC curves of F-Azo@AG film before and after green light irradiation (530 nm, 4.94 mW/cm<sup>2</sup>).



**Figure S10.** Output voltage-time signal by the generator showing only base alternating voltage, where no light was applied to the actuator.

### Movies

Movie 1. A F-Azo@AG film (20 mm × 20 mm × 40 μm) under simulated sunlight irradiation (76.6 mW/cm<sup>2</sup>).

Movie 2. A F-Azo@AG stripe (7 mm × 1 mm × 40 μm) under simulated sunlight irradiation (76.6 mW/cm<sup>2</sup>).

Movie 3. A F-Azo@AG stripe (7 mm × 3 mm × 40 μm) under simulated sunlight irradiation (76.6 mW/cm<sup>2</sup>).

Movie 4. A F-Azo@AG stripe (7 mm × 5 mm × 40 μm) under simulated sunlight irradiation (76.6 mW/cm<sup>2</sup>).

Movie 5. A F-Azo@AG stripe (7 mm × 1 mm × 40 μm) under simulated sunlight irradiation (65.0 mW/cm<sup>2</sup>).

Movie 6. A F-Azo@AG stripe (7 mm × 1 mm × 40 μm) under simulated sunlight irradiation (56.9 mW/cm<sup>2</sup>).

Movie 7. A F-Azo@AG stripe (7 mm × 1 mm × 40 μm) under simulated sunlight irradiation (23.6 mW/cm<sup>2</sup>).

Movie 8. A pure AG stripe (7 mm × 1 mm × 40 μm) under simulated sunlight irradiation (76.6 mW/cm<sup>2</sup>).

Movie 9. A F-Azo@AG stripe (40 mm × 5 mm × 20 μm) under green light irradiation (530 nm, 16.5 mW/cm<sup>2</sup>).

Movie 10. A F-Azo@AG stripe (40 mm × 5 mm × 30 μm) under blue light irradiation (470 nm, 14.8 mW/cm<sup>2</sup>).

## References

[1] D. Bleger, J. Schwarz, A. M. Brouwer, S. J. Hecht, *J. Am. Chem. Soc.* **2012**, *134*, 20597–20600.

[2] L. D. Zhang, P. Naumov, *Angew. Chem. Int. Ed.* **2015**, *54*, 8642–8647.

[3] L. D. Zhang, H. Liang, J. Jacob, P. Naumov, *Nat. Commun.* **2015**, *6*, 7429.