

Supporting Information

Visible light activated dendrimers for solar thermal energy storage and release below 0 °C

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1. Materials

2-Chloro-6-fluoroaniline (98%), 3-chloro-5-fluorophenol (98%), 12-bromo-1-hexanol (99%) were purchased from Energy Chemical Co. Ltd. Sodium acetate (98%), potassium carbonate (98%), potassium iodide (98%) and sodium sulphate (99%) were purchased from Beijing Chemical Plant. Poly(amidoamine) dendrimers (ethylenediamine core, generation 3.0) were purchased from Sigma-Aldrich Chemical Co. Acryloyl chloride (stabilized with phenothiazine) (98%), trichloromethane (98%), and triethylamine (Et₃N) were purchased from Sinopharm Chemical Reagent Co. Ltd. Tetrahydrofuran (THF), acetone, ethyl acetate and other organic solvents were purchased from Beijing Chemical Plant. Acryloyl chloride (stabilized with phenothiazine) (98%) was distilled under reduced pressure before use. Deionized water was obtained from a Millipore water purification system. Quartz substrates (20 × 40 mm, 1.5 mm thickness) was purchased from Chutian Co., Ltd.

2. Characterization methods and instruments

¹H-NMR spectra were recorded with a Bruker DMX-400 spectrometer in deuterated solvent at 298 K. Fourier transform infrared (FT-IR) spectra were recorded on PerkinElmer spectrophotometer at room temperature. UV-vis absorption spectra (UV-vis) were recorded on a JASCO V-570 spectrophotometer. All reactions were monitored by thin-layer chromatography (TLC) using Merck silica gel 60 F254 plates (0.25 mm). TLC plates were visualized using UV light (254 nm). Silica column chromatography was performed using Merck Silica Gel 60 (200-300 mesh). Mass spectrometric analyses were conducted using an LCQ Advantage from Thermo Scientific via electrospray ionization (ESI). The average molecular weight and molecular weight distribution of the photochromic dendrimer was measured by Gel Permeation Chromatography GPC (Waters 1515) with styragel columns relative to polystyrene standards using DMF (HPLC grade) as the mobile phase. Thermogravimetric analysis (TGA) was carried out using METTLER TGDSC 1 at a heating rate of 10 °C min⁻¹ from 30 °C to 700 °C in a nitrogen stream. Differential scanning calorimetry (DSC) curves were obtained using a DSC 8000 (PerkinElmer Inc.). Optical microscopy images were captured on an optical microscope (Zeiss) equipped with a SLR camera. Infrared thermometer images were captured by an infrared camera (FLUKE Tis20+). Solar radiation was simulated using a solar simulator (94023A) and used in conjunction with a filter (JB490, EXFSJ-45°-F15*15-THONGLV-FLAN-GY) that allows wavelengths ≥ 490 nm to pass through.

3. Experimental section

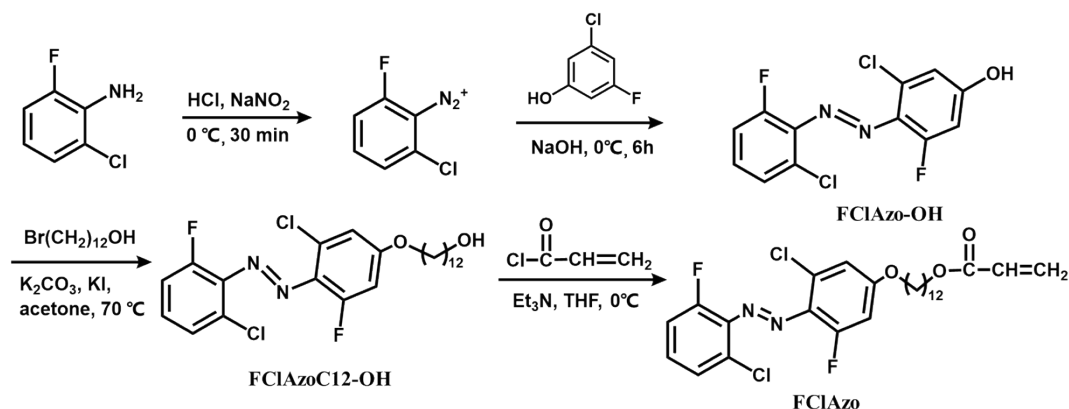


Figure S1. Synthesis route of fluorochloroazobenzene derivatives.

Synthesis of FCIAzo-OH

2-Chloro-6-fluoroaniline (4.35 g, 30.00 mmol), 11 mL of concentrated hydrochloric acid and 50 mL of deionized water were added to a 250 mL flask, stirred and cooled to 0 °C, then slowly added dropwise 10 mL of sodium nitrate (2.27 g, 33.00 mmol) in water. The mixed liquid was stirred at 0 °C for 30 min to obtain a diazonium salt solution. 3-Chloro-5-fluorophenol (4.82 g, 33.00 mmol) was added to another flask containing deionized water (50 mL) and sodium hydroxide (4.00 g, 100 mmol) with stirring and after cooling to 0 °C, the above diazonium salt solution was slowly added dropwise. During the dropwise addition, saturated aqueous sodium carbonate solution was added to maintain the pH value of the mixed solution at 9-10. After the dropwise addition, the mixed liquid was stirred at 0 °C for 12 h. After the reaction, the pH value of the mixture was adjusted to 3-5 with 0.5 M hydrochloric acid, and the mixture was extracted with dichloromethane after stirring for 30 min. The organic layer was dried with anhydrous sodium sulfate and concentrated to obtain the crude product. The crude product was purified by column chromatography (ethyl acetate/petroleum ether=1/2, V/V) to obtain high-purity FCIAzo-OH. Yield 38.9%. ¹H NMR (400 MHz, CDCl₃, δ): 7.43-7.25 (m, 2H, Ar-H), 7.16 (t, 1H, Ar-H), 6.92 (s, 1H, Ar-H), 6.66 (d, 2H, Ar-H). MS (ESI): [M - H]⁺=300.96.

Synthesis of FCIAzoC12-OH

FCIAzo-OH (4.00 g, 13.00 mmol), potassium carbonate (18.00 g, 130.43 mmol), and potassium iodide (1.66 g, 10.00 mmol) were added to a solution containing 150 mL of anhydrous acetone. The flask was stirred at room temperature for 30 min, and then a mixed

solution (10 mL) of 12-bromo-1-hexanol (5.30 g, 22.50 mmol) and acetone was added. The mixture was heated to 65 °C and stirred at reflux for 24 h. After the reaction, the mixed solution was filtered to remove inorganic salts, and then the filtrate was concentrated to obtain crude product. The crude product was purified by column chromatography (ethyl acetate/petroleum ether=1/3, V/V) to obtain FClAzoC12-OH. Yield: 70.3%. ¹H NMR (400 MHz, CDCl₃, δ): 7.42-7.32 (m, 2H, Ar-H), 7.17 (t, 1H, Ar-H), 6.69 (s, 1H, Ar-H), 6.67 (d, 1H, Ar-H), 4.03 (t, 2H, CH₂), 3.65 (t, 2H, CH₂), 1.46-1.21 (m, 20H, CH₂). MS (ESI): [M + H]⁺=486.97.

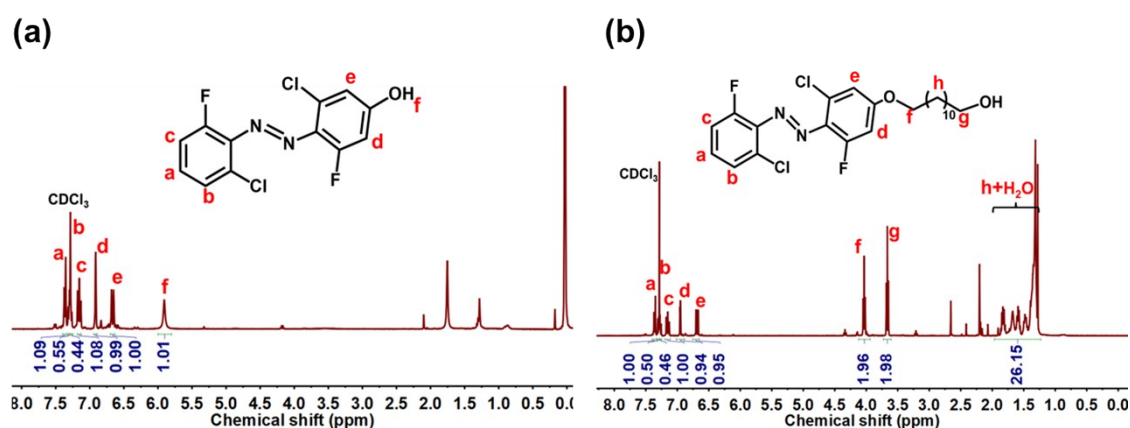


Figure S2. ¹H NMR spectra of (a) FClAzo-OH and (b) FClAzoC12-OH.

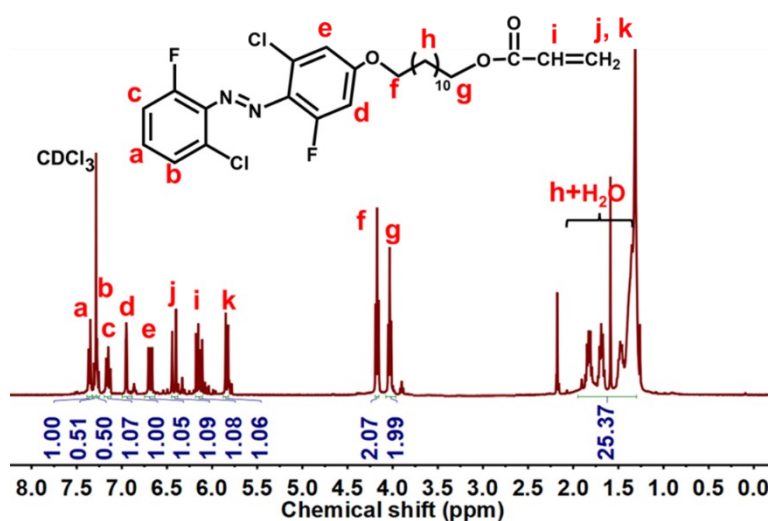


Figure S3. ¹H NMR spectra of FClAzo.

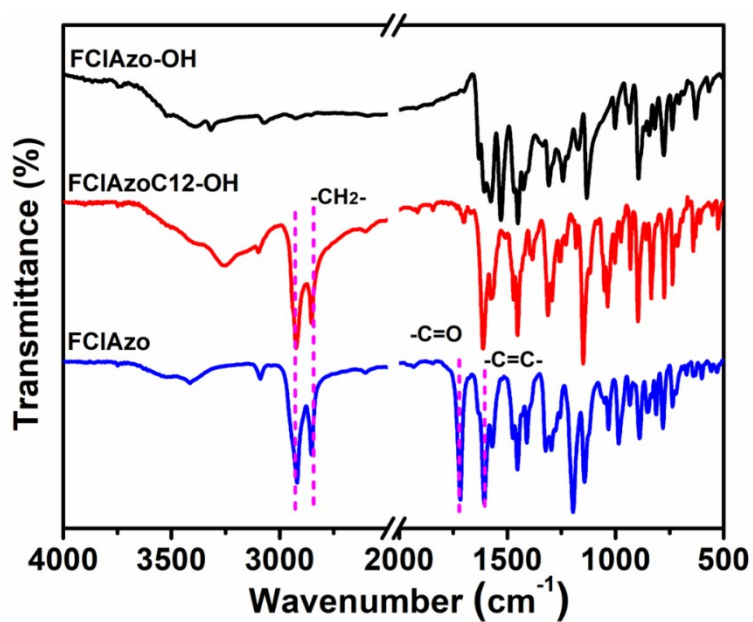


Figure S4. FT-IR spectra of FCIAzo-OH, FCIAzoC12-OH and FCIAzo.

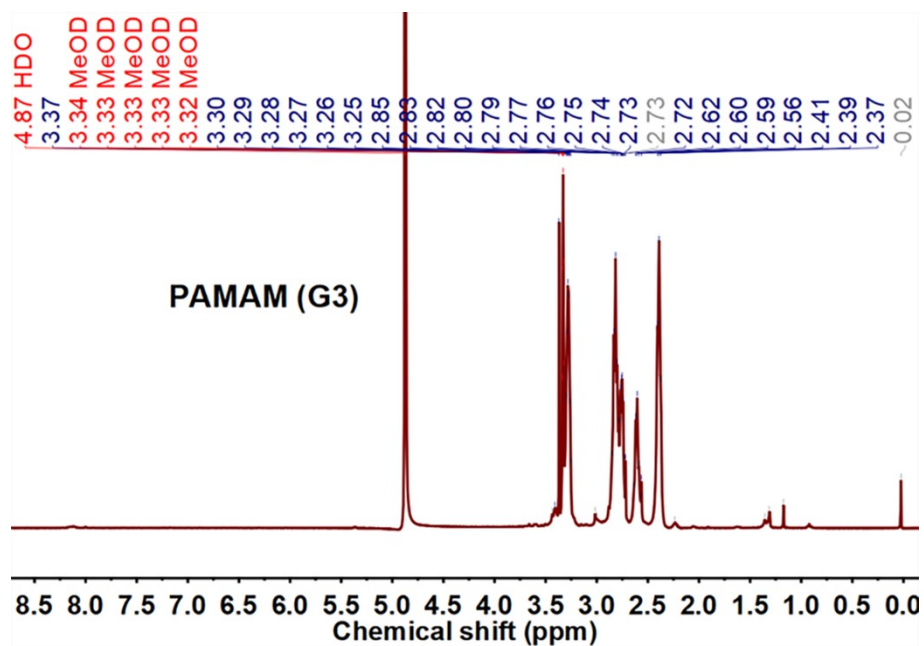


Figure S5. ^1H NMR spectrum of PAMAM (G3).

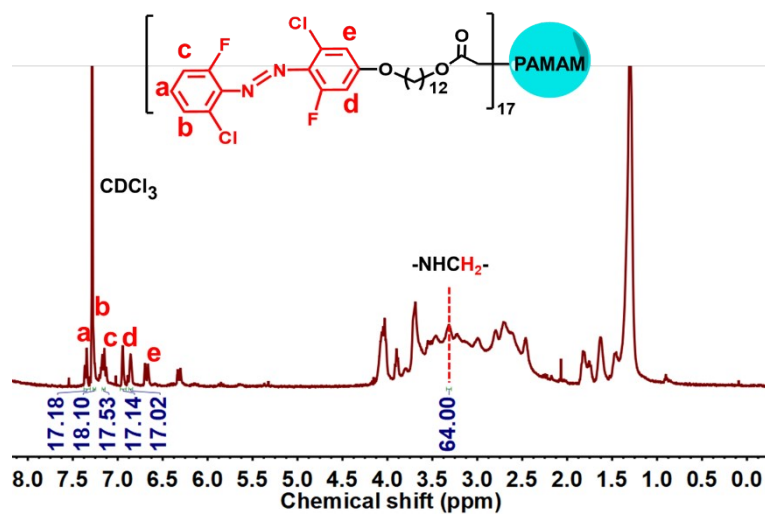


Figure S6. ^1H NMR spectrum of G3-FCIAzo.

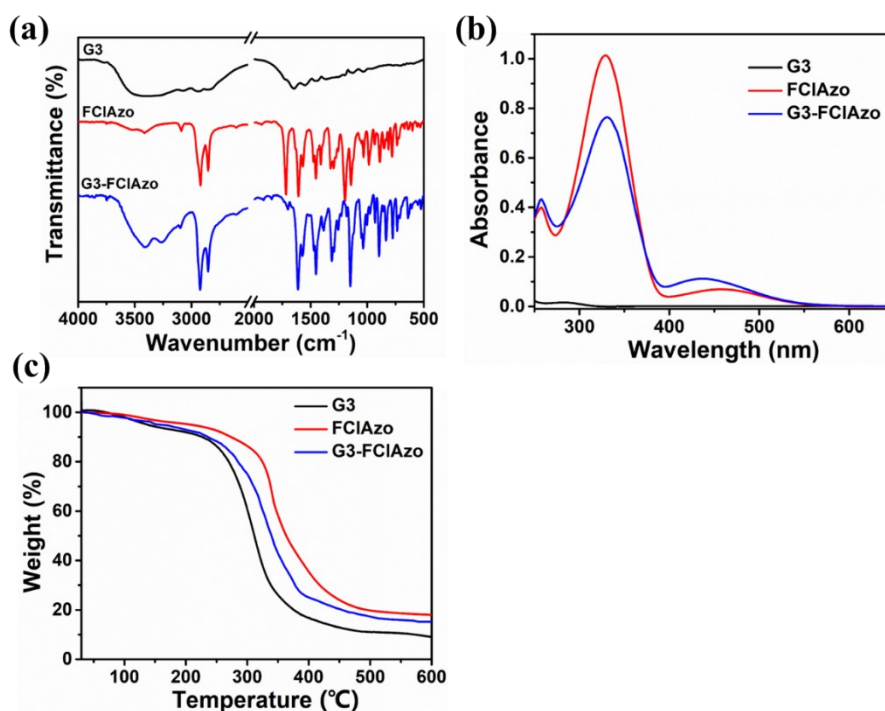


Figure S7. (a) FT-IR spectra of G3, FCIAzo and G3-FCIAzo. (b) UV-vis spectra of G3, FCIAzo and G3-FCIAzo in ethyl acetate. (c) TGA curves of G3, FCIAzo and G3-FCIAzo.

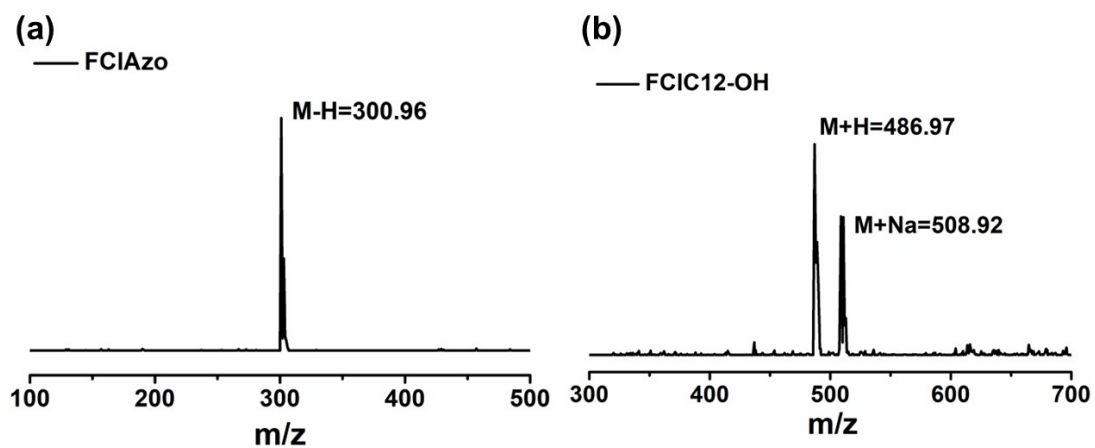


Figure S8. Mass spectra of (a) FCIAzo-OH and (b) FCIAzoC12-OH.

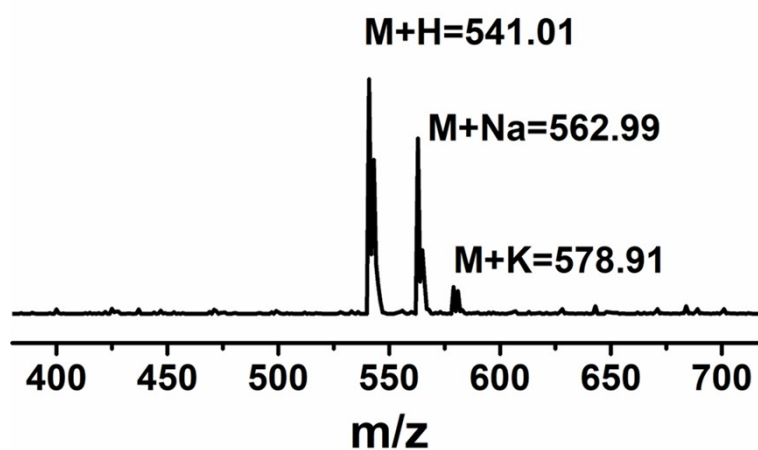


Figure S9. Mass spectrum of FCIAzo.

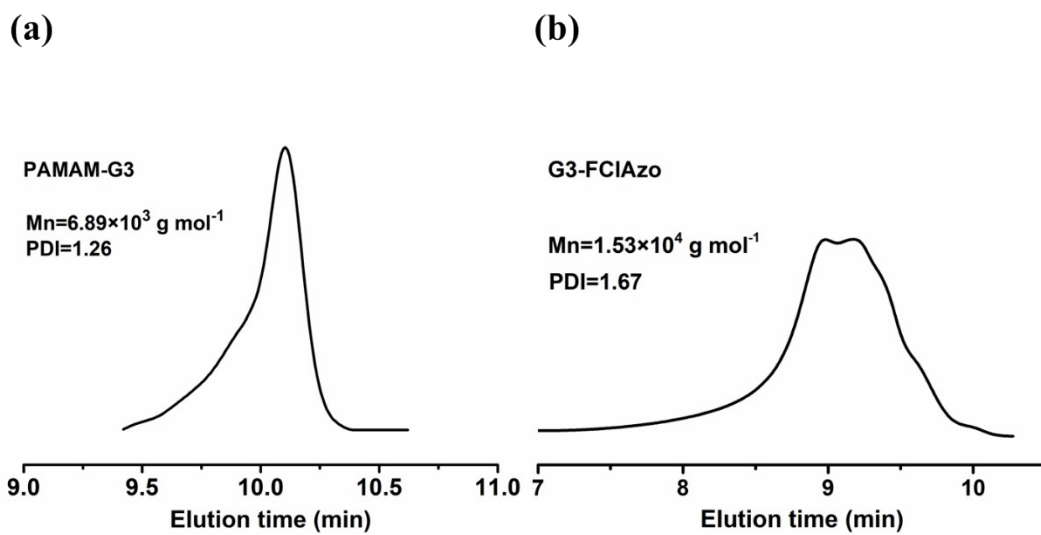


Figure S10. GPC traces of (a) PAMAM-G3 and (b) G3-FCIAzo.

4. Photoisomerization properties of MOSTs

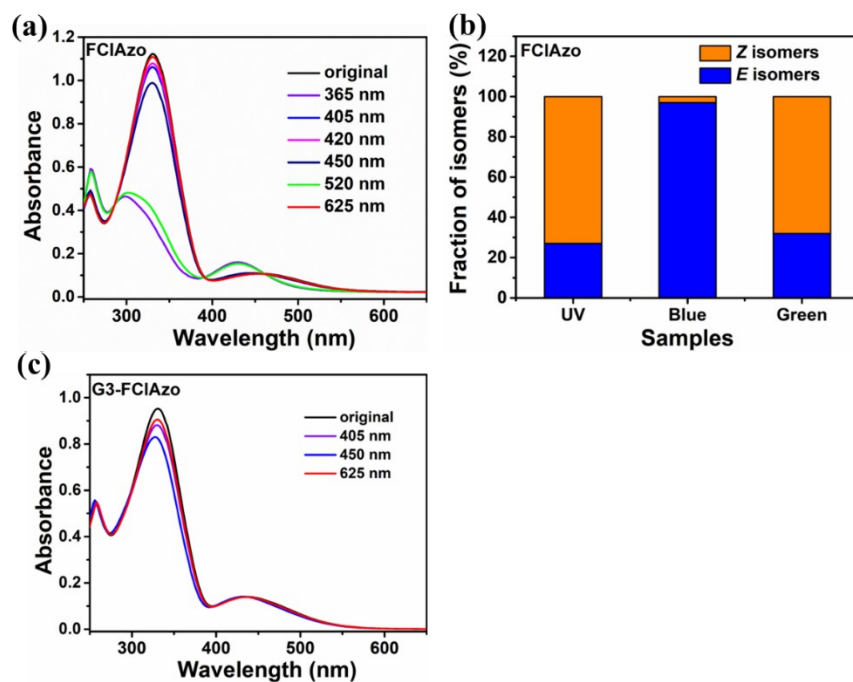


Figure S11. (a) UV-vis spectra of FClAzo in ethyl acetate irradiated by different wavelengths of light. (b) Fraction of Z-isomers of FClAzo in ethyl acetate irradiated by different wavelengths of light. (c) UV-vis spectra of G3-FClAzo in ethyl acetate irradiated by different wavelengths of light.

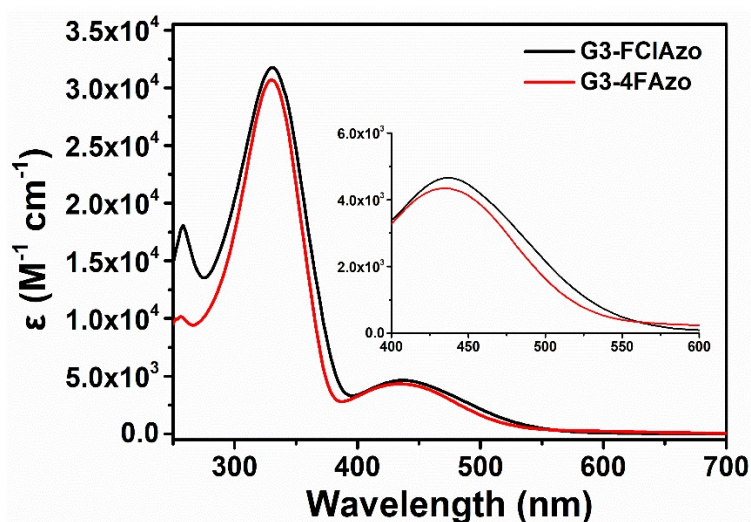


Figure S12. UV-visible absorption spectra of previously reported G3-4FAzo and G3-FClAzo in ethyl acetate (3×10^{-5} M). G3-FClAzo exhibits stronger absorption capacity of green light.

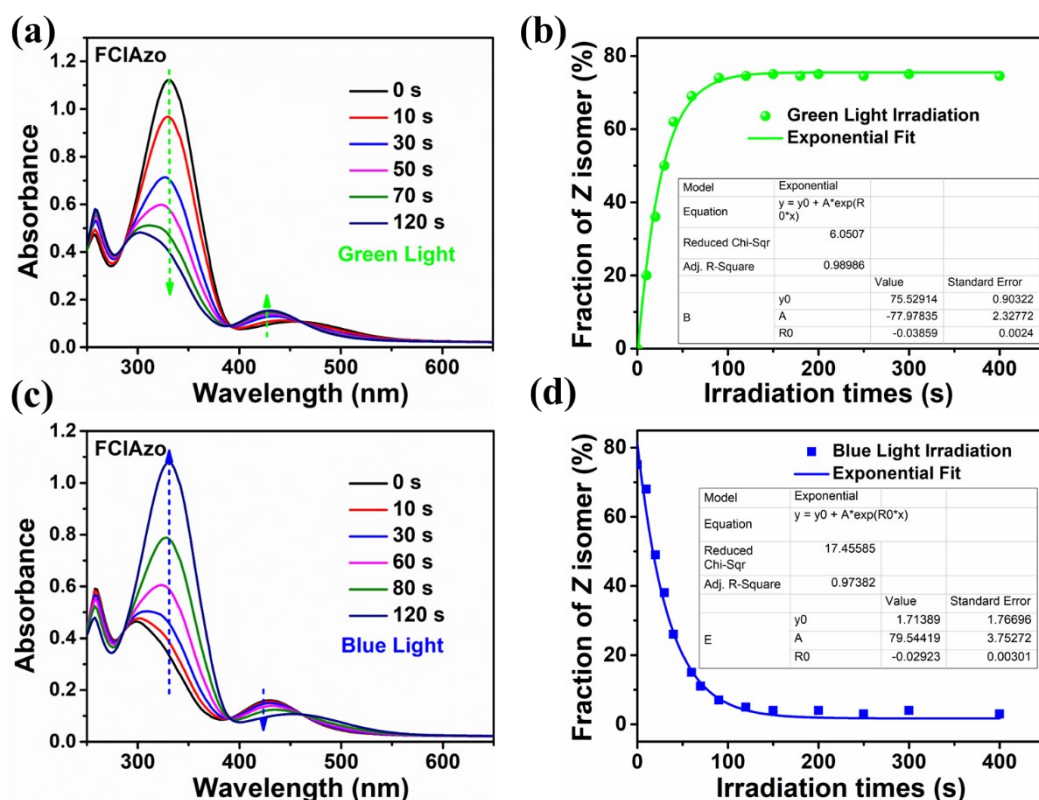


Figure S13. UV-vis spectra of FClAzo in ethyl acetate (3×10^{-5} M) irradiated by (a) green (520 nm, 20 mW cm^{-2}) and (c) blue light (420 nm, 20 mW cm^{-2}). The fitting results of Z-isomer fractions of FClAzo solution after (b) green light irradiation (520 nm, 20 mW cm^{-2}) and (d) blue light irradiation (420 nm, 20 mW cm^{-2}).

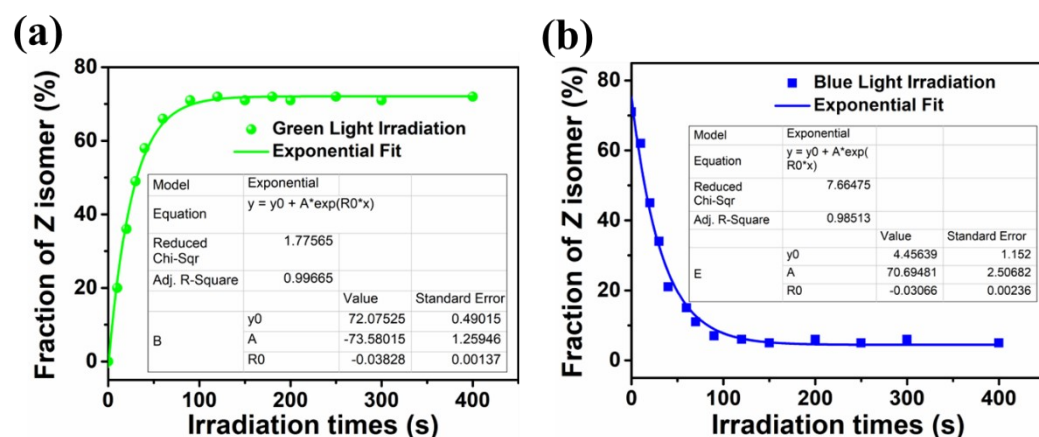


Figure S14. The fitting results of Z-isomer fractions of G3-FClAzo solution after (a) green light irradiation (520 nm, 20 mW cm^{-2}) and (b) blue light irradiation (420 nm, 20 mW cm^{-2}).

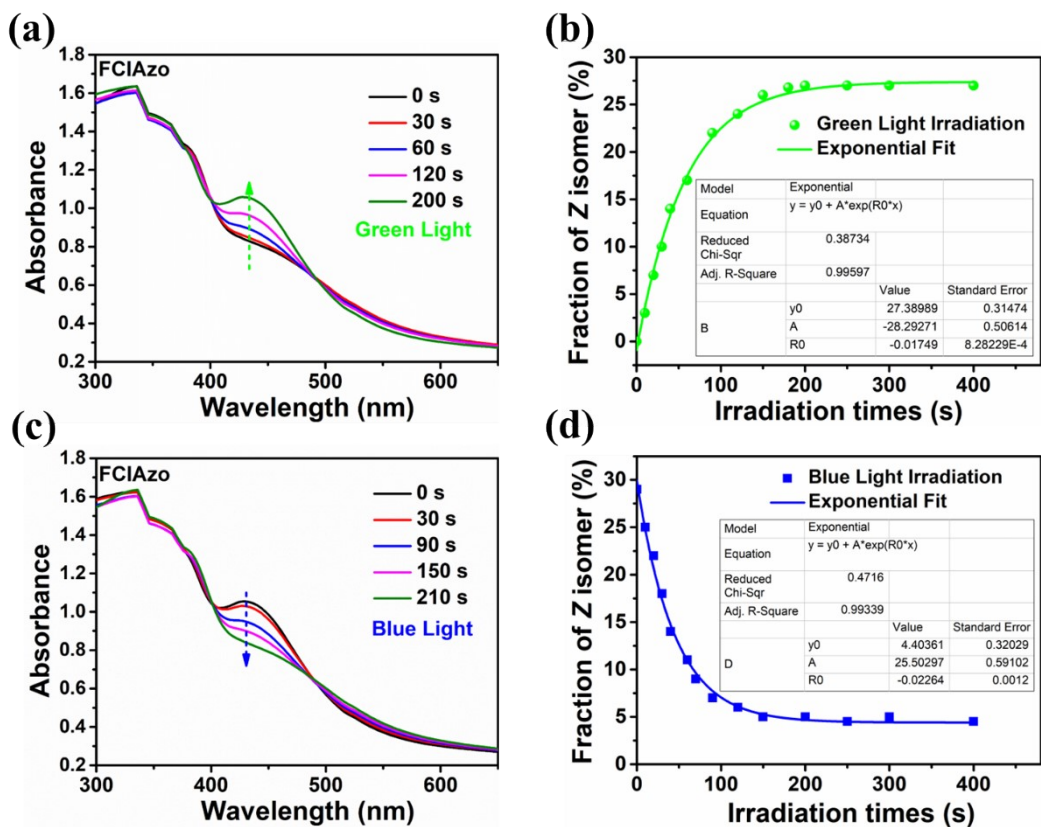


Figure S15. UV-vis spectra of FCIazo film irradiated by (a) green (520 nm, 20 mW cm⁻²) and (c) blue light (420 nm, 20 mW cm⁻²). The fitting results of Z-isomer fractions of FCIazo film after (b) green light irradiation (520 nm, 20 mW cm⁻²) and (d) blue light irradiation (420 nm, 20 mW cm⁻²).

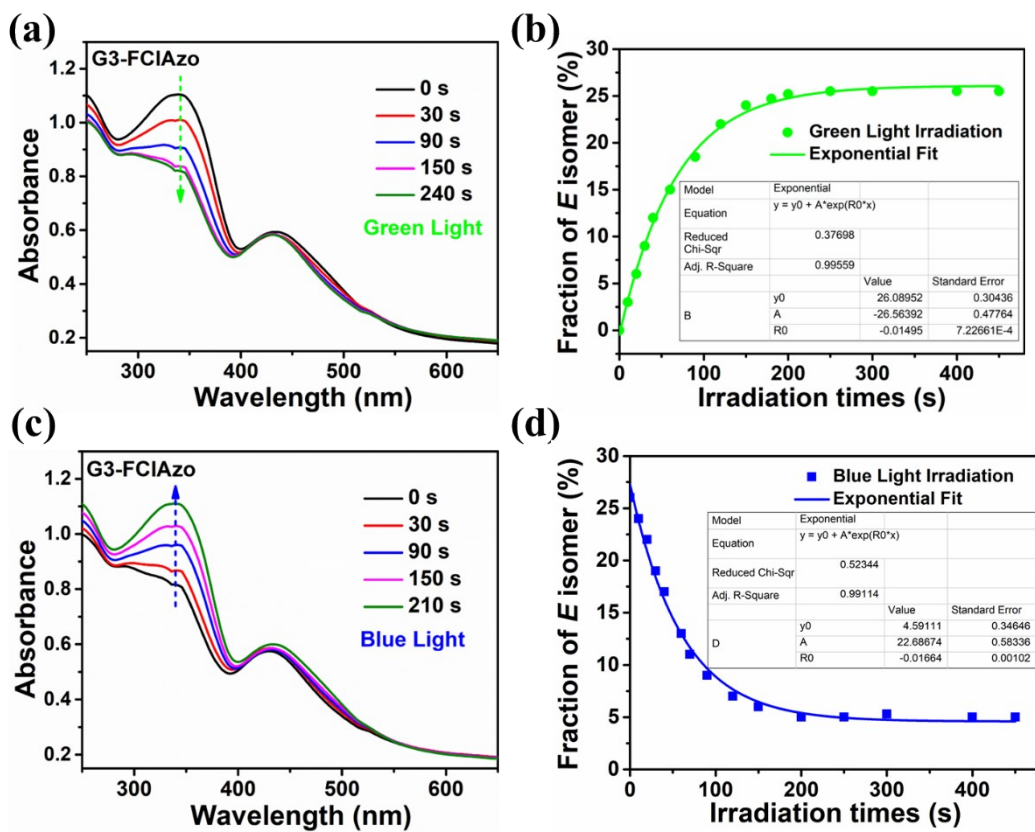


Figure S16. UV-vis spectra of G3-FCIAzo film irradiated by (a) green (520 nm, 20 mW cm⁻²) and (c) blue light (420 nm, 20 mW cm⁻²). The fitting results of Z-isomer fractions of G3-FCIAzo film after (b) green light irradiation (520 nm, 20 mW cm⁻²) and (d) blue light irradiation (420 nm, 20 mW cm⁻²).

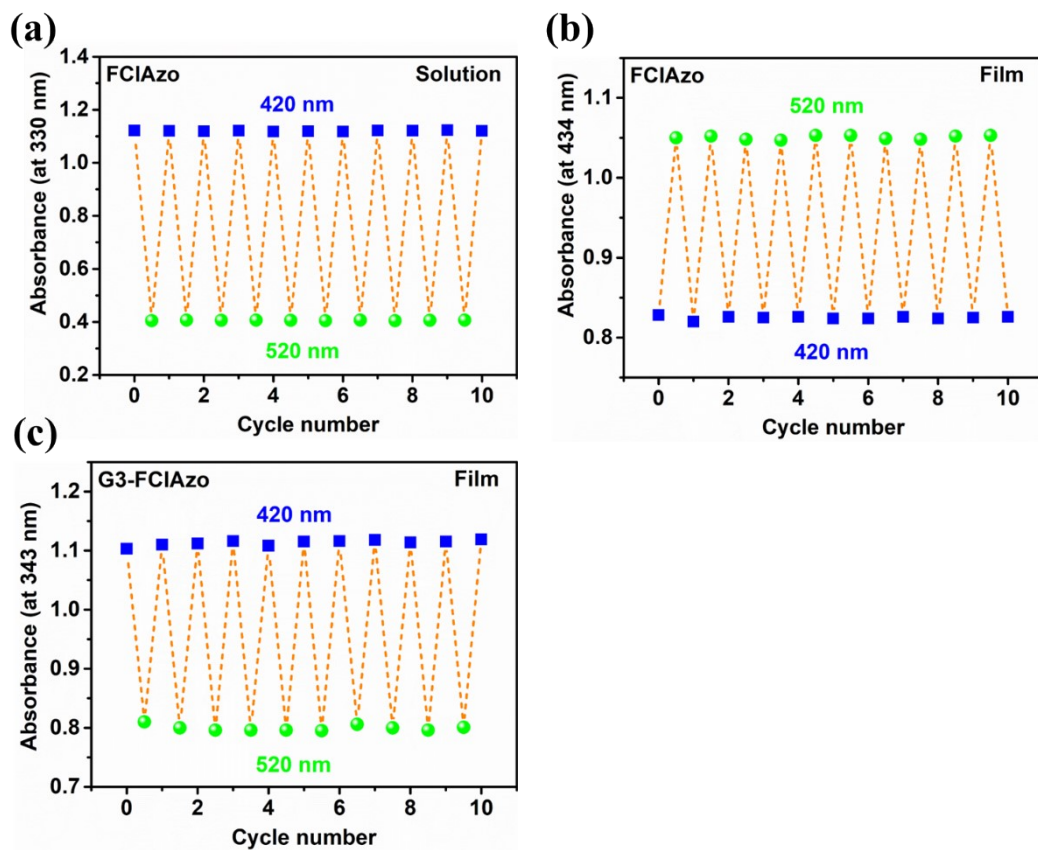


Figure S17. Cycling stability of (a) FClAzo solution, (b) FClAzo film and (c) G3-FClAzo film under the alternative green light and blue light irradiation.

5. Thermal relaxation behavior of MOSTs

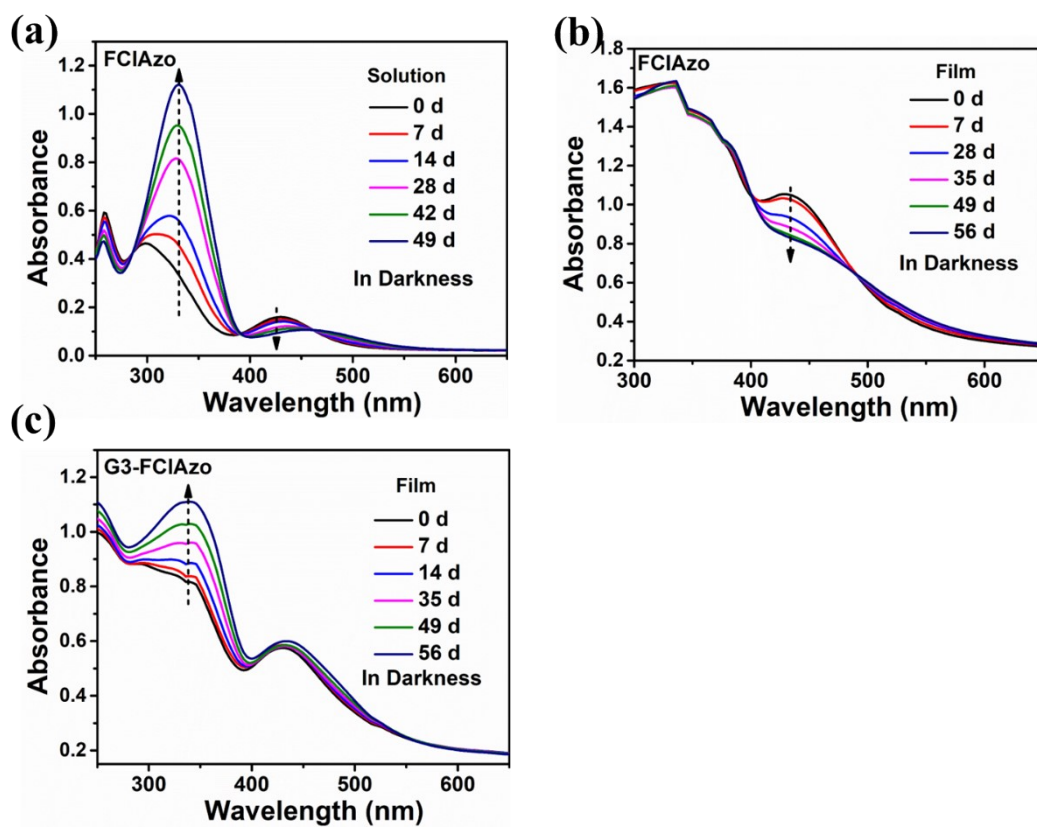


Figure S18. UV-vis spectra of a) FClAzo solution, b) FClAzo film and c) G3-FClAzo film under dark conditions at room temperature.

6. Storage performances of MOSTs

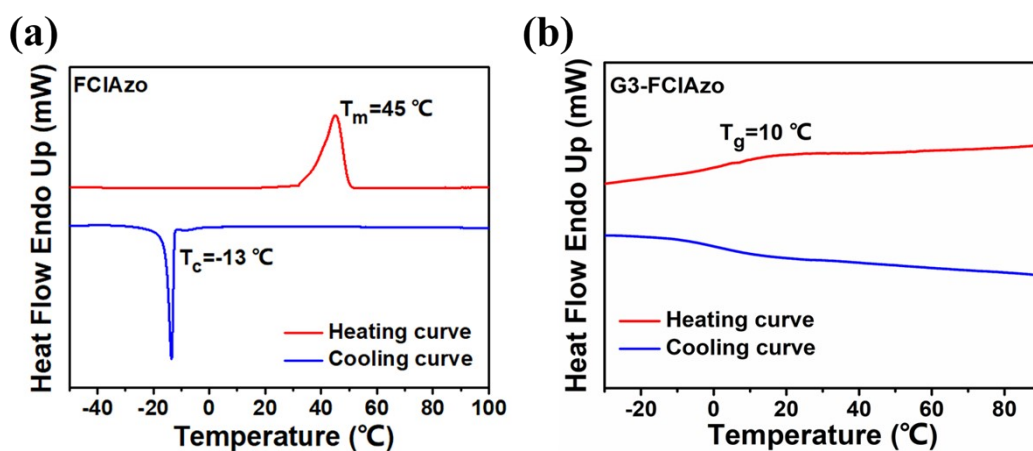


Figure S19. DSC heating and subsequent cooling curves of (a) FCIAzo and b) G3-FCIAzo after UV light irradiation in solution with the rate of $10\text{ }^\circ\text{C min}^{-1}$.

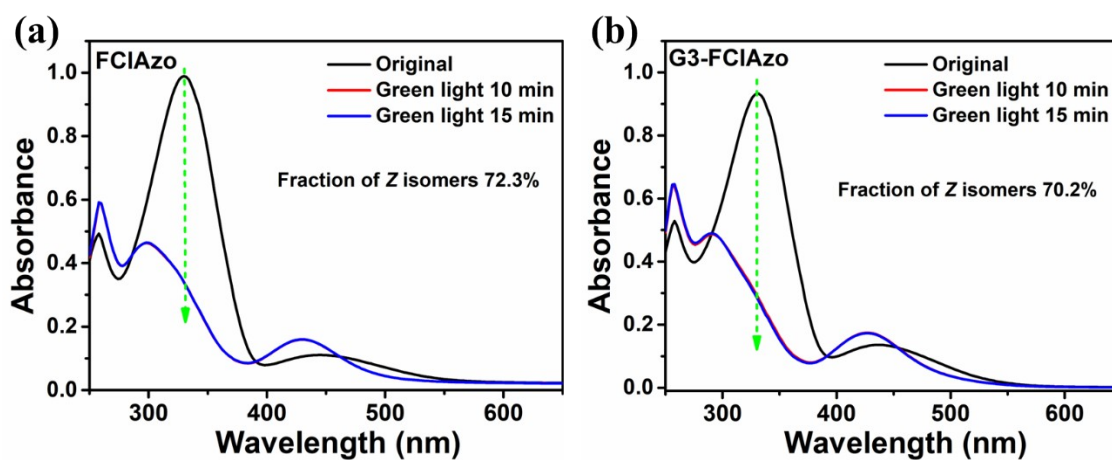


Figure S20. (a) UV-vis spectra of FCIAzo used for DSC testing after green light (520 nm , 50 mW cm^{-2}) irradiation to photostationary state. The fraction of Z isomers is about 72.3%. (b) UV-vis spectra of G3-FCIAzo used for DSC testing after green light (520 nm , 50 mW cm^{-2}) irradiation to photostationary state. The fraction of Z isomers is about 70.2%.

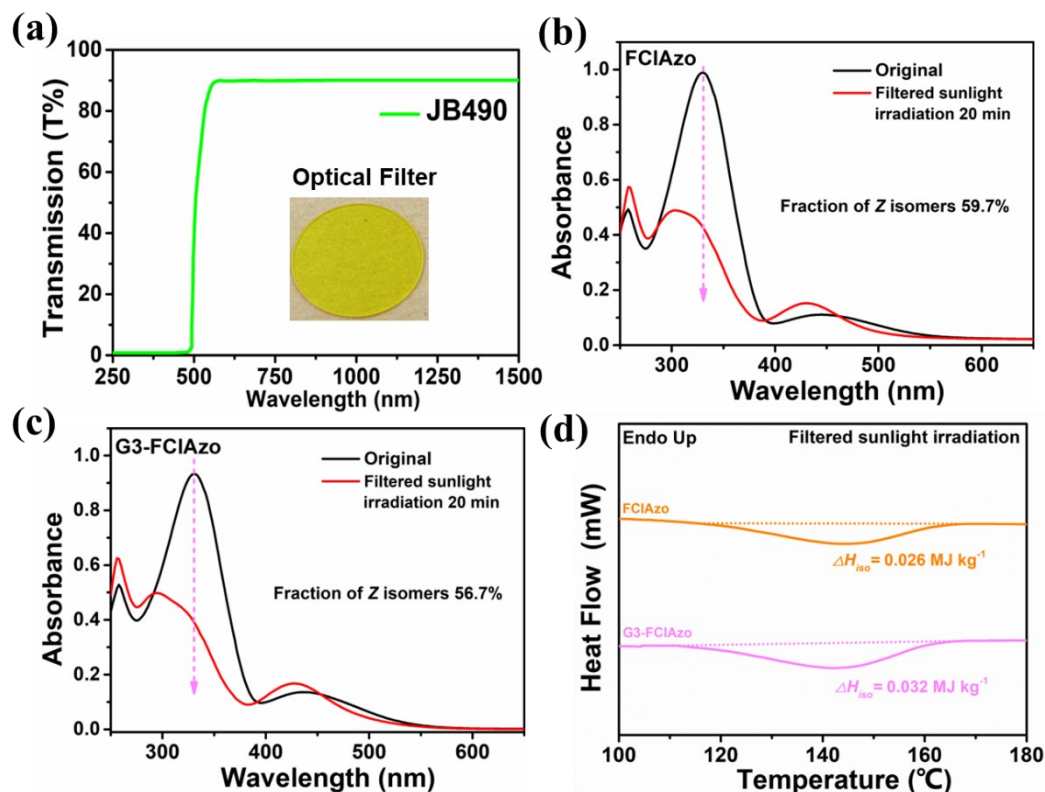


Figure S21. (a) UV-vis transmission spectrum of optical filter. (b) UV-vis spectra of FClAzo after filtered sunlight irradiation (100 mW cm^{-2} , 20 min). The fraction of Z isomers is about 59.7%. (c) UV-vis spectra of G3-FClAzo after filtered sunlight irradiation (100 mW cm^{-2} , 20 min). The fraction of Z isomers is about 56.7%. (d) The DSC heating curves of FClAzo and G3-FClAzo after filtered sunlight irradiation (100 mW cm^{-2} , 20 min) in solution with the heating and cooling rate of $10 \text{ }^\circ\text{C min}^{-1}$.

7. Heat release and applications of MOST films

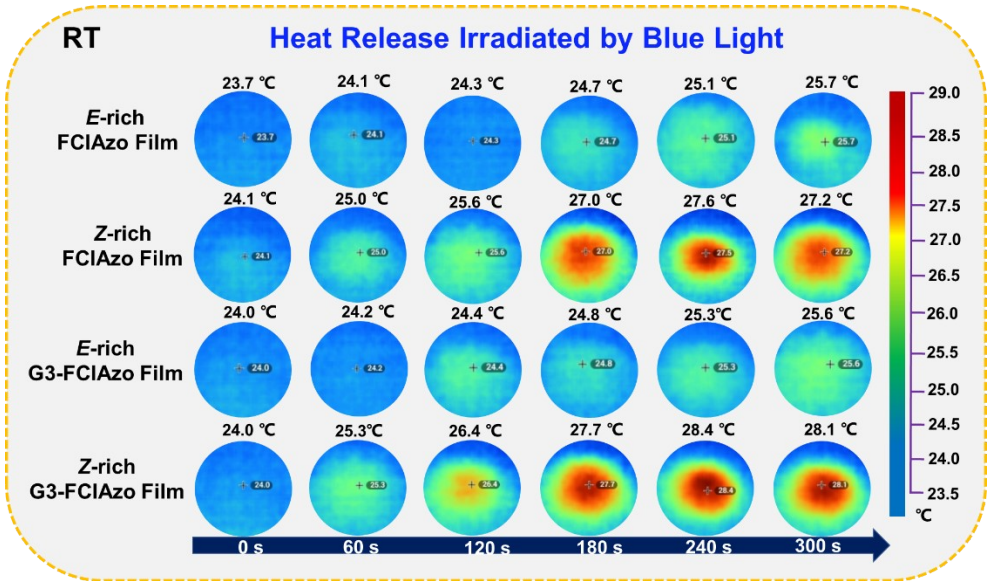


Figure S22. IR thermal images of *E*-rich FCIAzo film, *Z*-rich FCIAzo film, *E*-rich G3-FCIAzo film and *Z*-rich G3-FCIAzo film during blue light irradiation at room temperature for different times.

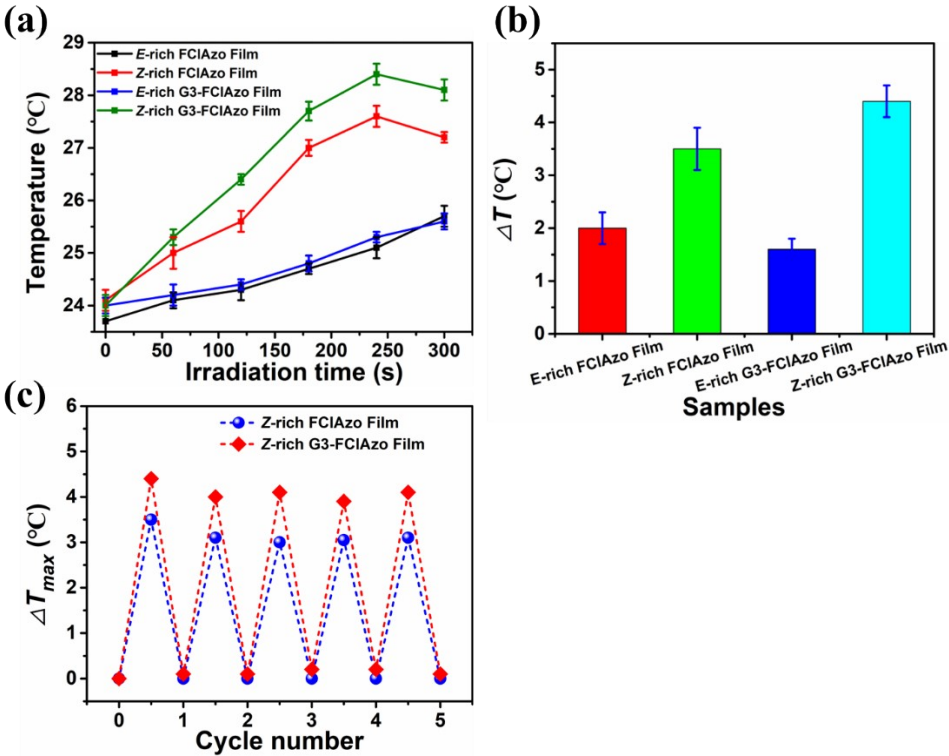


Figure S23. (a) Temperature changes of MOST films during under blue light irradiation for different times. (b) Histogram of highest temperature differences of MOST films during blue light irradiation. (c) Temperature difference of *Z*-rich solar thermal films upon five cycles of heat release.

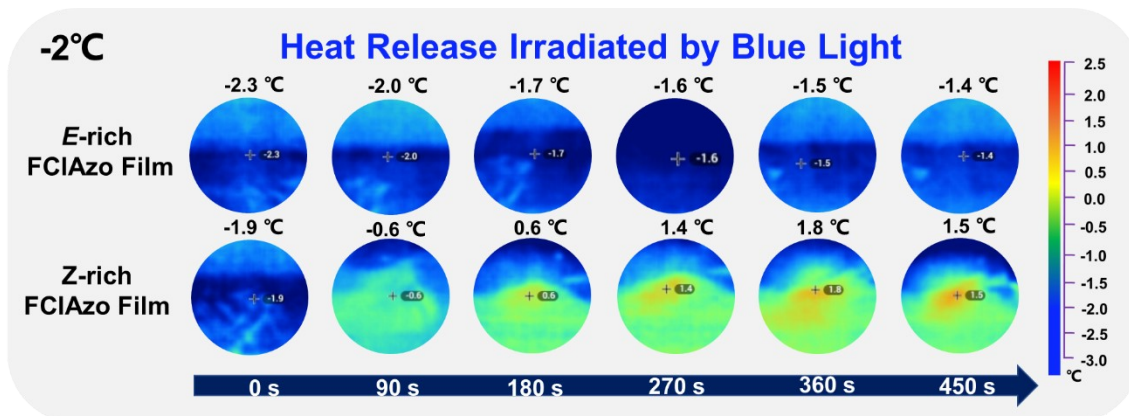


Figure S24. IR thermal images of *E*-rich FCIAzo film and *Z*-rich FCIAzo film during blue light irradiation at low-temperature for different times.

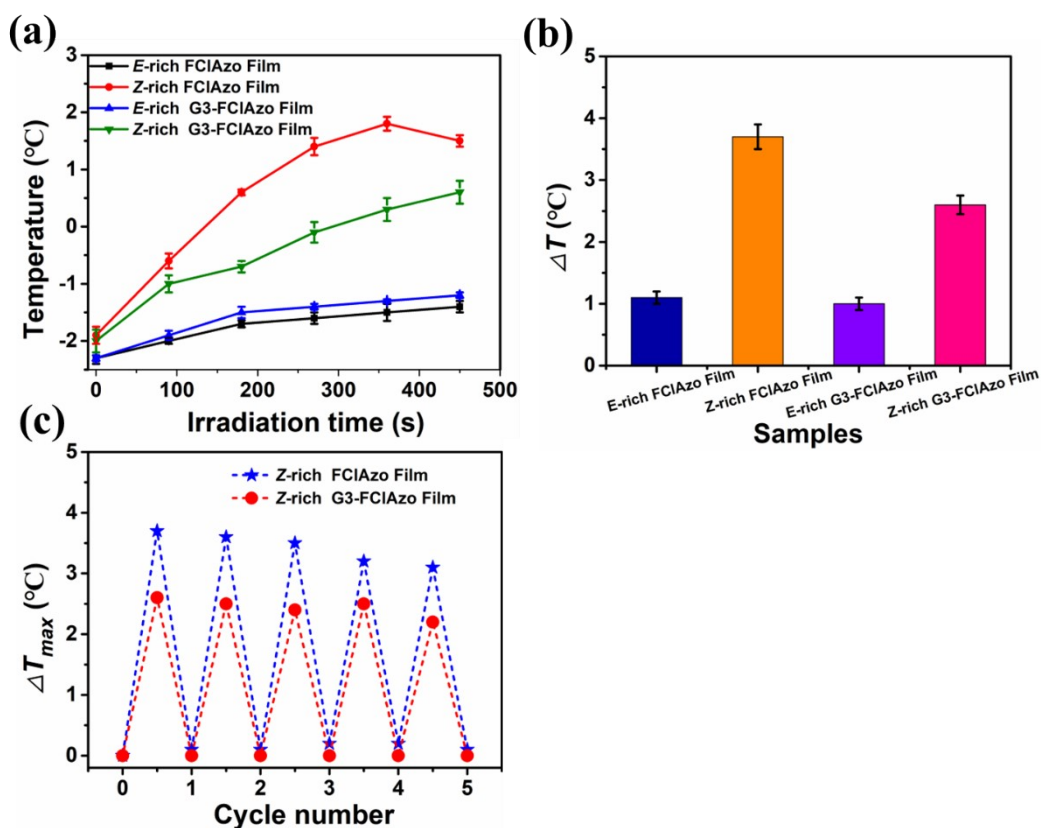


Figure S25. (a) Temperature changes of MOST films during under blue light irradiation for different times. (b) Histogram of highest temperature differences of MOST films during blue light irradiation. (c) Temperature difference of *Z*-rich solar thermal films upon five cycles of heat release.

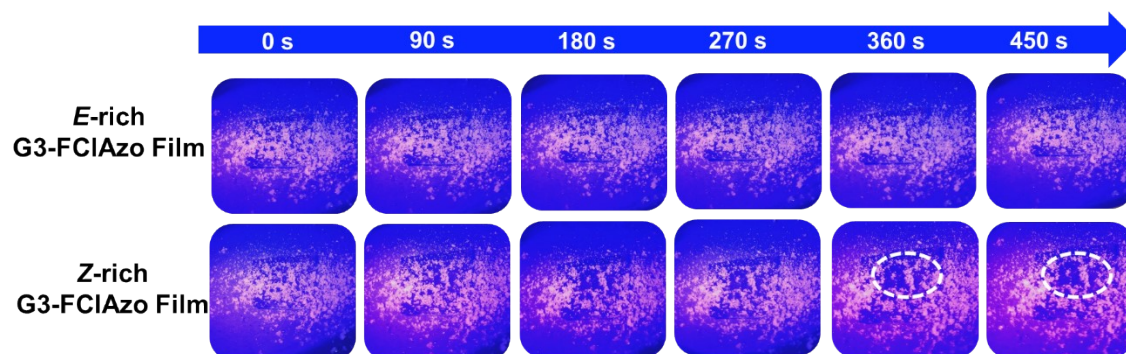


Figure S26. IR thermal images of the deicing effect of *E*-rich G3-FCIAzo film and *Z*-rich G3-FCIAzo film during blue light irradiation at low-temperature for different times.

8. Theoretical calculation

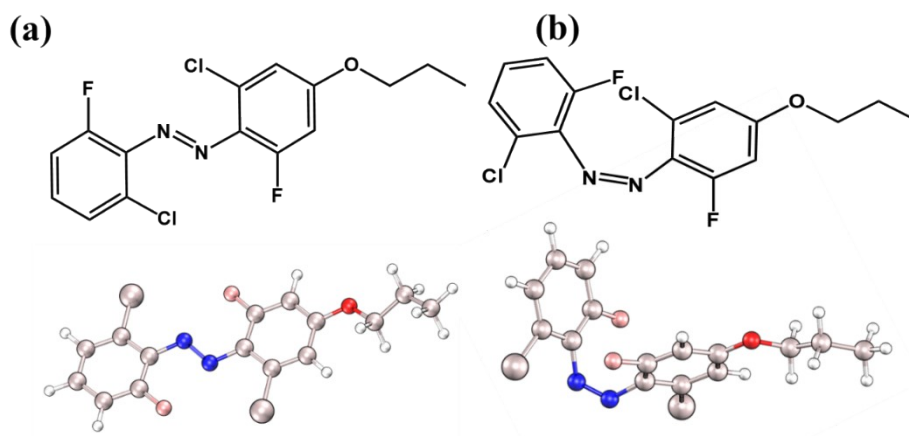
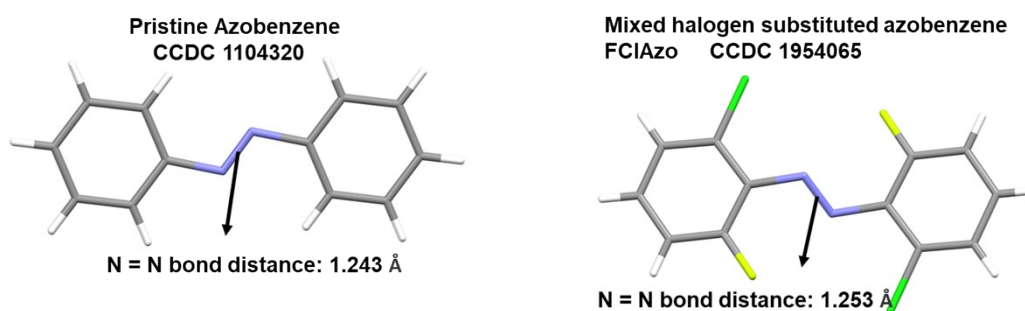


Figure S27. Chemical structures of (a) FClAzo *E* precursor and (b) FClAzo *Z* precursor for energy density calculations

(a) Crystal structure



(b) Theoretical calculation

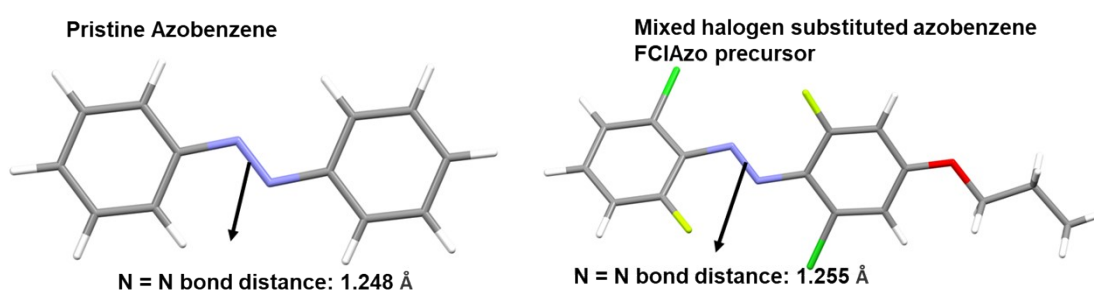


Figure S28. (a) Crystal structures and N=N bond distances of pristine azobenzene and mixed halogen azobenzene (FClAzo). Crystal structure data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. (b). Theoretically calculated values of N=N bond distances for pristine azobenzene and mixed halogen azobenzene (FClAzo precursor).

9. Equations

Determination of the fraction of isomers by UV–vis Spectroscopy.

The isomerization properties were investigated by irradiating sample solutions in quartz cuvettes with UV, blue, green and red light, respectively. The fraction of isomers at the photostationary state (PSS) is estimated based on the Equation S1:

Equation S1. Fraction of isomers

$$A = \frac{A_0 - A_t}{A_0} \times 100\% \quad (1)$$

Wherein, A is the fraction of Z -isomers, A_0 is the absorbance of samples before undergoing Z -to- E isomerization, A_t is the absorbance of samples at the time of “ t ”.

Equation S2. Thermal isomerization half-life ($\tau_{1/2}$)

$$\tau_{1/2} = \frac{\ln 2}{k} \quad (2)$$

Where k is the first-order kinetics constant calculated by Equation 1.

Equation S3. Measurement of storage energy density

The most commonly used thermal analysis technique for measuring the storage energy densities (ΔH) of MOST fuels is differential scanning calorimetry (DSC), which has been performed in this work to measure the differences in heat flow when a sample absorbs or releases heat due to the thermal effect. The observed heat flows were converted to ΔH using Equation 3:

$$\Delta H = \frac{qM\omega_{cis}}{m}$$

where q is the heat released (J), as determined by the integration of the DSC exothermic peak area, m is the mass of the sample, M is the molecular weight of sample, and ω_{cis} is the mole fraction of the Z isomers present. Herein, ΔH is the actually measured storage enthalpy of samples, whose value often shows a difference with the theoretical maximum value.

10. Tables

Table S1. The fraction of *Z* isomers (*Z*%) of MOST sample in ethyl acetate under different wavelength light irradiation calculated by UV-vis absorption spectra.

Sample	Fraction of <i>Z</i> isomers		
	365 nm	420 nm	520 nm
	<i>Z</i> %	<i>Z</i> %	<i>Z</i> %
FCIAzo	72%	3%	70%
G3- FCIAzo	70%	5%	66%

The fraction of *Z* isomers of MOST fuels were calculated by UV-vis absorption spectra after different wavelength light irradiation to the photo-stationary state.

Table S2. A comparison of excited state energy levels, wavelengths, and oscillator intensities of 4FAzo precursor and FCIAzo precursor.


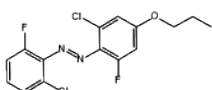
	State	Energy (eV)	Wavelength (nm)	fosc
	S1	2.524	495.60	0.00032
	S1	2.502	491.28	0.05242

Table S3. Residual energy densities of MOST samples in darkness for different times.

Dark time (day)	FCIAzo		G3-FCIAzo	
	Residual energy density (MJ kg ⁻¹)	Residual proportion (%)	Residual energy density (MJ kg ⁻¹)	Residual proportion (%)
0	0.031	100	0.040	100
7	0.025	80	0.027	75
14	0.017	54	0.019	52
21	0.014	45	0.016	44
28	0.009	29	0.011	30

Table S4. Gibbs free energy and energy difference of *E* and *Z* isomers of FClAzo precursor.

	<i>E</i> isomers energy (G^0)	<i>Z</i> isomers energy (G^0)	Energy difference	
	eV	eV	eV	kJ mol ⁻¹
FClAzo precursor	-51244.459	-51244.198	0.261	25.2

Table S5. XYZ coordinates optimized molecular geometry of *E* FClAzo precursor.

C	-4.62315	-3.26027	0.093817
C	-4.45122	-4.63584	0.027707
C	-3.17634	-5.18486	0.016403
C	-2.0706	-4.34952	0.072533
C	-2.20138	-2.9531	0.170096
C	-3.51167	-2.44431	0.168948
F	-3.71988	-1.12036	0.18791
Cl	-0.47945	-5.0657	0.047506
N	-1.02645	-2.17981	0.153143
C	2.443721	0.122256	0.509851
C	2.233029	1.502869	0.554369
C	0.940774	2.00483	0.71078
C	-0.12457	1.121452	0.781633
C	0.034582	-0.26817	0.663329
C	1.364578	-0.72634	0.551664
F	1.619075	-2.04068	0.526339
Cl	-1.72111	1.794185	0.986757
N	-1.11777	-1.0622	0.710651
O	3.336615	2.272983	0.44497
C	3.171763	3.675562	0.202088
C	4.499888	4.238089	-0.26027
C	4.370567	5.705537	-0.66345
H	-5.60307	-2.80334	0.084056
H	-5.31608	-5.28331	-0.02426
H	-3.03077	-6.25369	-0.04287
H	3.443532	-0.27794	0.423057
H	0.747168	3.063025	0.780475
H	2.409586	3.819411	-0.5691
H	2.830652	4.168607	1.117823
H	5.238606	4.120437	0.535885
H	4.850301	3.643318	-1.10697
H	5.32945	6.104127	-0.9963
H	3.660488	5.828211	-1.48452

H	4.022031	6.320746	0.169752
H	4.850301	3.643318	-1.10697
H	5.32945	6.104127	-0.9963
H	3.660488	5.828211	-1.48452
H	4.022031	6.320746	0.169752

Table S6. XYZ coordinates optimized molecular geometry of Z FClAzo precursor.

C	-2.67088	-2.61005	0.108908
C	-3.35501	-2.82665	1.298303
C	-2.75704	-3.52701	2.337887
C	-1.46461	-4.00215	2.187065
C	-0.73475	-3.7706	1.017286
C	-1.38077	-3.08688	-0.01354
F	-0.72966	-2.90169	-1.18093
Cl	-0.70431	-4.83977	3.514453
N	0.552148	-4.36117	0.8607
C	1.248059	-0.06349	1.377571
C	1.854707	0.50905	0.25781
C	2.31033	-0.30676	-0.77821
C	2.172101	-1.68228	-0.66928
C	1.547262	-2.28885	0.422963
C	1.110001	-1.42832	1.43675
F	0.57316	-1.95747	2.551822
Cl	2.750297	-2.68161	-1.97555
N	1.551002	-3.70842	0.522753
O	1.965325	1.855153	0.280676
C	2.728277	2.525352	-0.72999
C	3.079226	3.902034	-0.19924
C	3.913364	4.69915	-1.1983
H	-3.11812	-2.08027	-0.72061
H	-4.36118	-2.44844	1.416359
H	-3.28047	-3.70304	3.266687
H	0.911604	0.555799	2.196439
H	2.77051	0.103241	-1.66243
H	3.639364	1.960708	-0.94697
H	2.134591	2.58852	-1.64803
H	2.158323	4.43658	0.045813
H	3.629286	3.776791	0.736265
H	4.205569	5.662229	-0.77859
H	4.827822	4.165042	-1.46686
H	3.35786	4.891165	-2.11855