

Electronic Supplementary Material (ESI) for New Journal of Chemistry
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Supporting Information

A facile way to achieve all-photonic logic functions and photo-printing based on donor-acceptor Stenhouse adduct

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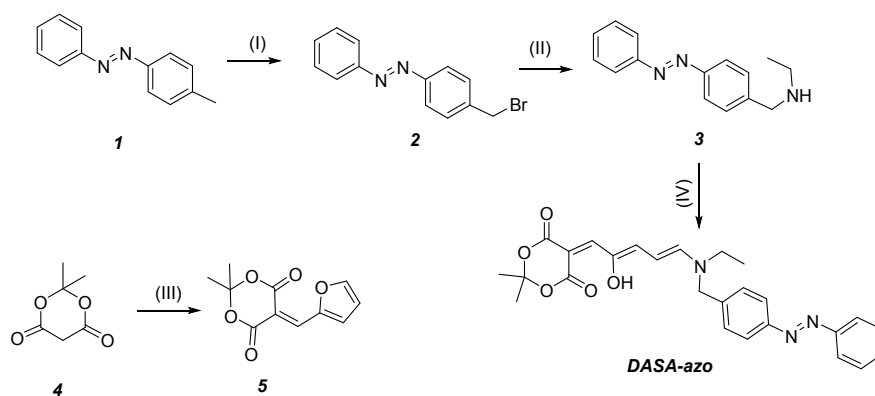
1. Experimental Section

1.1. Materials and instrumentations

4-Methylazobenzene, 2,2-dimethyl-1,3-dioxane-4,6-dione and 2-fural-dehyde were purchased from Heowns Biochemical Technology (Tianjin, China). Ethylamine (EA), *N*-bromosuccinimide (NBS) and benzoyl peroxide (BPO) were obtained from Sino-Pharm Chemical Reagent (Beijing, China).

UV-vis absorption and fluorescence spectra were recorded with UV-2450 (Shimadzu, Japan) and F-4600 (Hitachi, Japan), respectively. ¹H NMR and ¹³C NMR spectra in chloroform-*d* were recorded on Bruker 400M and 500M NMR spectrometers (Bruker, Germany) with tetramethylsilane (TMS) as the internal standard. MS spectra were recorded on MS spectrometry Compact™ (Bruker, Germany). Irradiation experiments were carried out by using halogen lamp of visible light XD-302 (150 W) (Wence, China), 430 nm and 525 nm optical filters, 365 nm UV light WFH-204B(8 W) (Qiwei, China).

1.2. Synthesis of *DASA-azo*



Scheme S1. Synthesis of *DASA-azo*. (I) NBS, BPO, 80 °C, CCl₄; (II) EA, K₂CO₃, 80°C, DMF; (III) 2-furaldehyde, 75°C, H₂O; (IV) **5**, RT, THF.

Synthesis of 4-bromomethylazobenzene (2):

A mixture of 4-methylazobenzene (**1**) (2.14 g, 10.9 mmol), BPO (100 mg, 0.413 mmol), NBS (2.00 g, 11.2 mmol) and tetrachloromethane (50.0 mL) was refluxed for 16 h. After reaction completed, the solution was concentrated under reduced pressure. The residue was separated by column chromatography on silica gel (petroleum ether: dichloromethane=3:1). Yield: (2.12 g, 70.3%), a red solid. ¹H NMR (400 MHz, chloroform-*d*) δ: 8.05–7.82 (m, 4H), 7.66–7.38 (m, 5H), 4.58 (s, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ: 152.61, 152.35, 140.54, 131.25,

129.90, 129.14, 123.30, 122.96, 32.79. HR-MS (ESI+, m/z): $[M+H]^+$ calcd for $[C_{13}H_{12}BrN_2]^+$, 275.0106; found, 275.0118.

Synthesis of 4-(ethylamino-N-ethyl)-azobenzene (3):

A mixture of compound **2** (0.5 g, 1.8 mmol), ethylamine (0.18 g, 4 mmol), K_2CO_3 (0.573 g, 4.2 mmol) and *N,N*-dimethylformamide (DMF, 15 mL) was refluxed for 10 h under N_2 atmosphere. After the reaction finished, the solution was concentrated under reduced pressure, then diluted by dichloromethane, washed by water for 3 times. The organic layer was collected. After removing the dichloromethane under reduced pressure, the produce was obtained by column chromatography on silica gel (dichloromethane: methanol=10:1). Yield: 0.35g. 1H NMR (400 MHz, chloroform-*d*) δ : 7.96–7.88 (m, 4H), 7.57–7.46 (m, 5H), 3.91 (s, 2H), 2.75 (q, $J=7.1$ Hz, 2H), 1.19 (t, $J=7.2$ Hz, 3H). ^{13}C NMR (126 MHz, chloroform-*d*) δ : 151.81, 143.07, 130.91, 129.08, 128.90, 122.98, 122.80, 53.35, 43.56, 15.03. HR-MS (ESI+, m/z): $[M+H]^+$ calcd for $[C_{15}H_{18}N_3]^+$, 240.1495; found, 240.1472.

Synthesis of 5-(furan-2-ylmethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione (5):

Compound **5** was synthesized according to the method of Alaniz et al^[1]. 1H NMR (500 MHz, chloroform-*d*) δ : 8.49 (d, $J=3.9$ Hz, 1H), 8.38 (s, 1H), 7.87 (d, $J=1.6$ Hz, 1H), 6.77 (ddd, $J=3.9, 1.7, 0.8$ Hz, 1H), 1.79 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ : 163.21, 160.18, 150.41, 150.21, 141.18, 128.07, 115.27, 107.55, 104.50, 27.56. HR-MS (ESI+, m/z): $[M+Na]^+$ calcd for $[C_{11}H_{10}O_5Na]^+$, 245.0420; found, 245.0453.

Synthesis of DASA-azo:

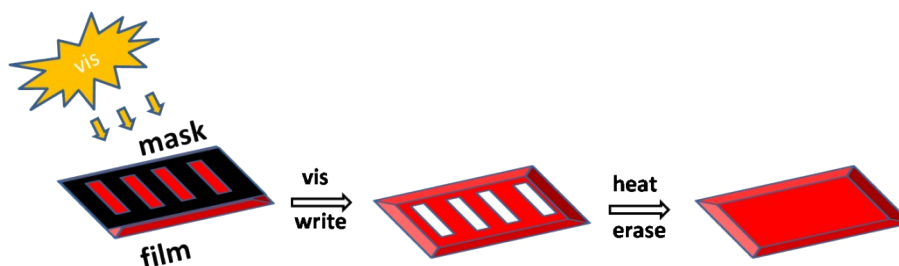
A mixture of compound **3** (0.35 g, 1.5 mmol), compound **5** (0.33 g, 1.5 mmol) and tetrahydrofuran (THF, 10 mL) was stirred at room temperature for 5 h, then removing the solvent. The residue was purified by flash column (ethylacetate: dichloromethane=1:10). Yield: 0.25g. 1H NMR (500 MHz, chloroform-*d*) δ : 11.35 (d, $J=42.7$ Hz, 1H), 7.97 (dd, $J=14.5, 7.7$ Hz, 4H), 7.55 (d, $J=8.4$ Hz, 3H), 7.40 (d, $J=7.8$ Hz, 2H), 7.34 (d, $J=12.5$ Hz, 1H), 7.24 (s, 1H), 6.74 (dd, $J=12.2, 1.6$ Hz, 1H), 6.17 (dt, $J=33.9, 12.3$ Hz, 1H), 4.68 (d, $J=27.5$ Hz, 2H), 3.49 (dq, $J=14.3, 7.1$ Hz, 2H), 1.75 (d, $J=3.8$ Hz, 6H), 1.31–1.19 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ : 166.98, 165.00, 156.58, 152.50, 150.22, 150.00, 145.37, 136.92, 131.49, 131.38, 129.17, 128.59, 127.94, 123.65, 122.99, 103.66, 102.19, 101.82, 92.32, 60.13, 51.95, 51.66, 43.96, 26.77, 14.34, 11.78. HR-MS (ESI+, m/z): $[M+H]^+$ calcd for

$[\text{C}_{26}\text{H}_{28}\text{N}_3\text{O}_5]^+$, 462.2023; found, 462.2078. HR-MS (ESI-, m/z): $[\text{M}-\text{H}]^-$ calcd for $[\text{C}_{26}\text{H}_{26}\text{N}_3\text{O}_5]^+$, 460.1878; found, 460.1867.

1.3. Preparation of photo-printing device and operation of photo-printing

Putting polystyrene (PS, 1.5 g), *DASA-azo* (2 mg) and styrene (3 mL) in a vessel, then stirring and heating the mixture until it became uniform. Afterwards, 7 mL dichloromethane was added to dilute the polymer solution. A solution of *DASA-azo* and PS in dichloromethane and styrene solvents was casted on a glass substrate. After complete evaporation of the solvents, a translucent thin PS film with corresponding colors was formed.

Cover the film with hollow-out photo-mask of different pattern, then exposure to visible light for 4 min, the image of PS film can be erased in 5 min by heating at 80 °C. The procedure of photo-printing (write/erase) was displayed in Scheme. S2.



Scheme S2. Illustrations of photo-printing operation.

References:

- [1] S Helmy, F A Leibfarth, S. Oh, J E Poelma, C J Hawker and J R de Alaniz. *J. Am. Chem. Soc.*, **2014**, 136, 8169-8172.

2. Supplementary Figures

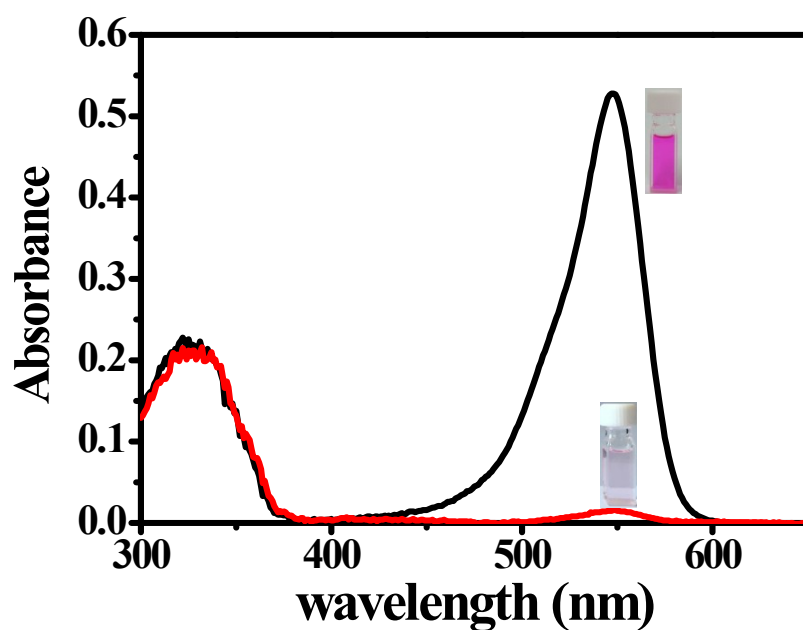


Fig. S1. Absorption spectra changes of *DASA-azo* (10 μM) and the corresponding photographs. Initial state without light (black line); under irradiation with 525 nm light for 30 s (red line).

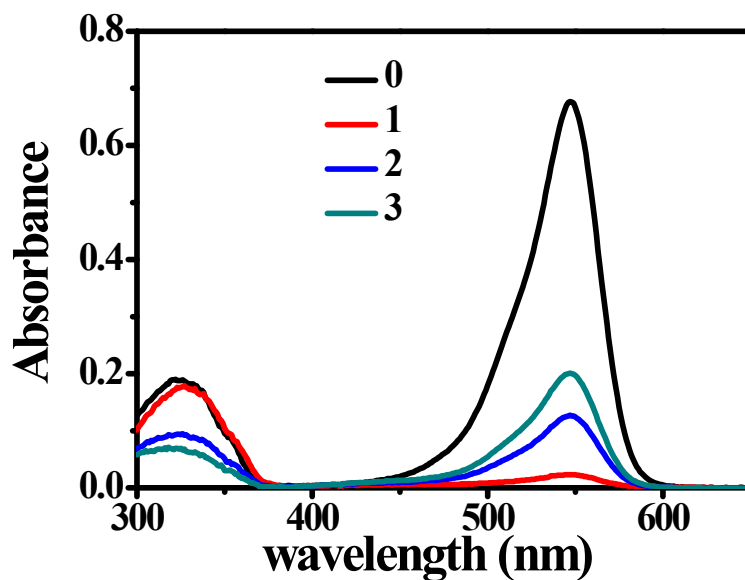


Fig. S2. Absorbance changes of *DASA-azo* toluene solution with different photo-operations (0: 13 μM solution of *DASA-azo* in toluene; 1: light sample 0 at 525 nm for 30 s; 2: light sample 1 at 365 nm (8 W) for 3 min; 3: light sample 1 at 365 nm for 5 min).

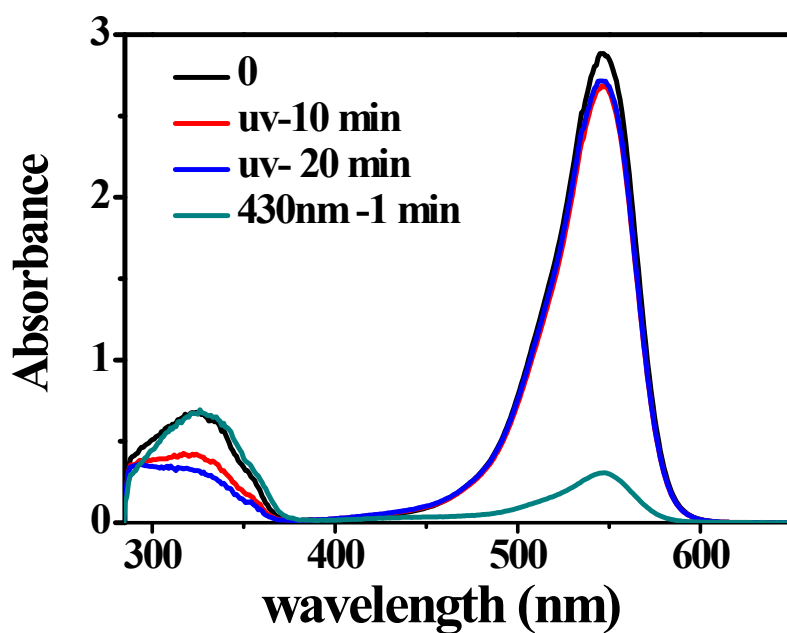


Fig. S3. Absorption spectra changes of *DASA-azo* (40 μM in toluene). Initial state without light (black line); under 365 nm UV irradiation for 10 min (red line); 20 min (blue line); and followed by 430 nm irradiation for 1 min (cyan line).

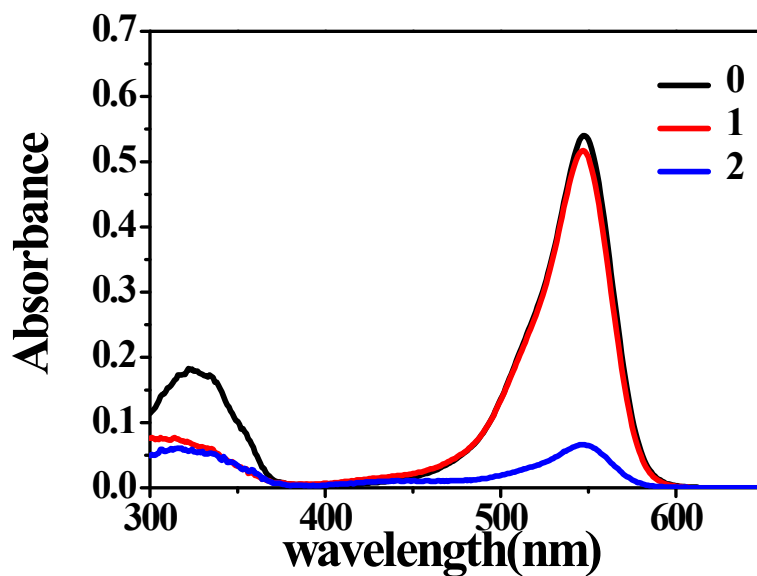


Fig. S4. Absorption spectra changes of *DASA-azo* (10 μM in toluene). Initial state without light (black line, 0); under 365 nm UV irradiation for 4 min (red line, 1); and followed by 525 nm irradiation for 30 s (blue line, 2).

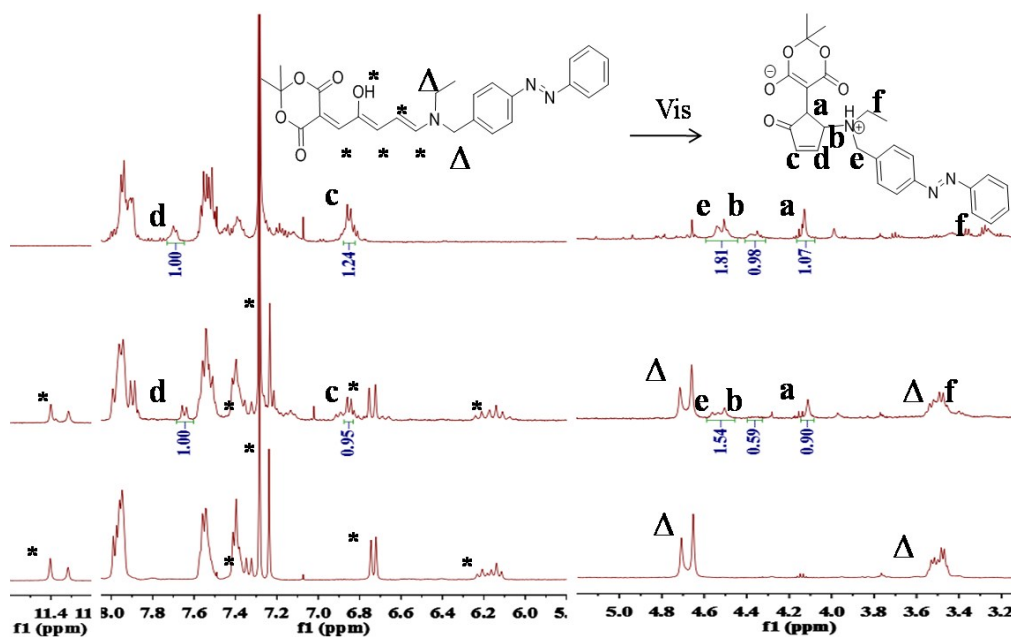


Fig. S5. ^1H NMR spectra changes of *DASA-azo* in chloroform-*d* under irradiation with visible light. Initial state without light (bottom); under irradiation with visible light for 12 h (middle) and 48 h (top).

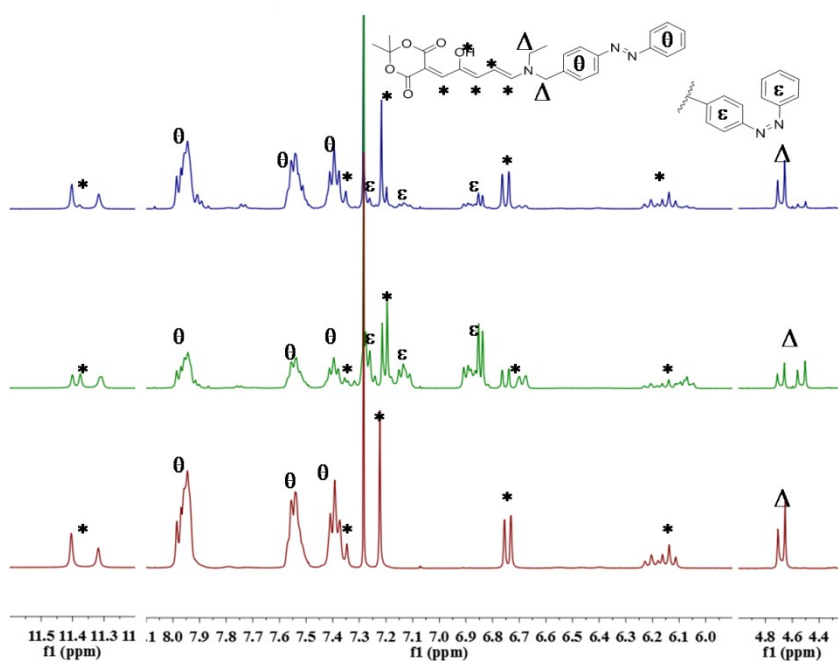


Fig. S6. ^1H NMR spectra changes of *DASA-azo* in chloroform-*d* after irradiation at 365 nm. Initial state: without light (bottom); irradiate at 365 nm for 24 h (middle); irradiate at 430 nm for 1h (top).

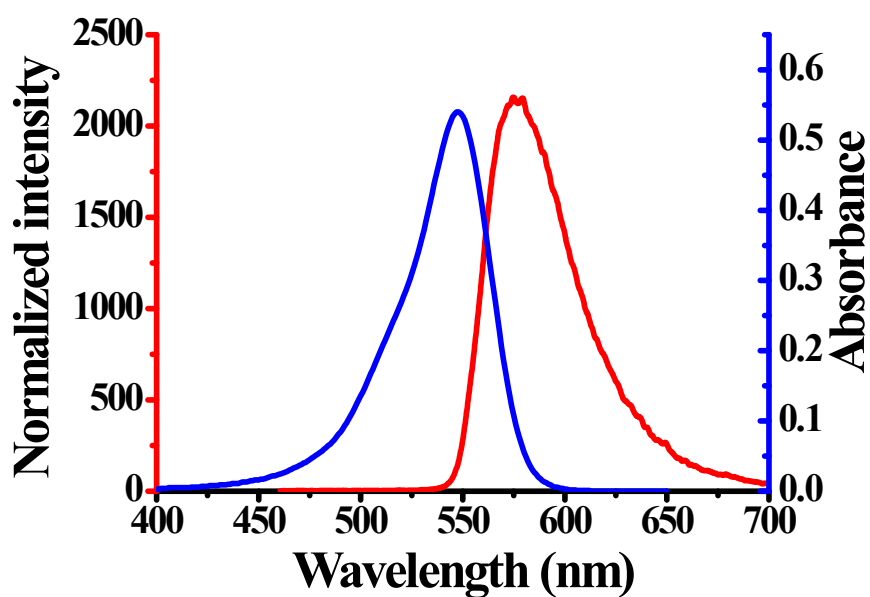


Fig. S7. Absorbance spectra (blue line) and emission (red line) fluorescent spectra of *DASA-azo* at toluene solution (excited at 540 nm).

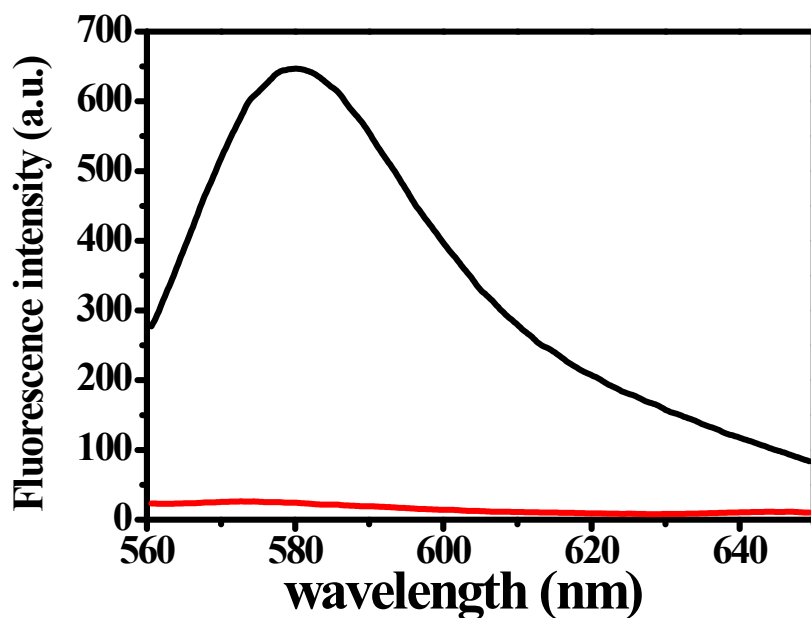


Fig. S8. Changes of fluorescence before (black line) and after (red line) irradiation with 525 nm for 30 s (10 μ M *DASA-azo* in toluene).

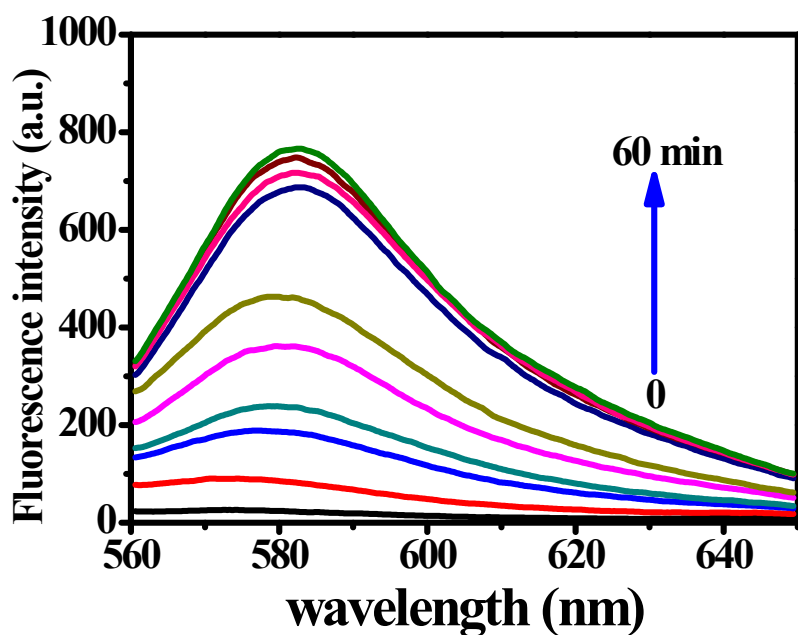


Fig. S9. Fluorescence spectra changes after removing the visible light for different time. (0: fluorescence of 10 μM *DASA-azo* in toluene after lighting at visible light for 30 s).

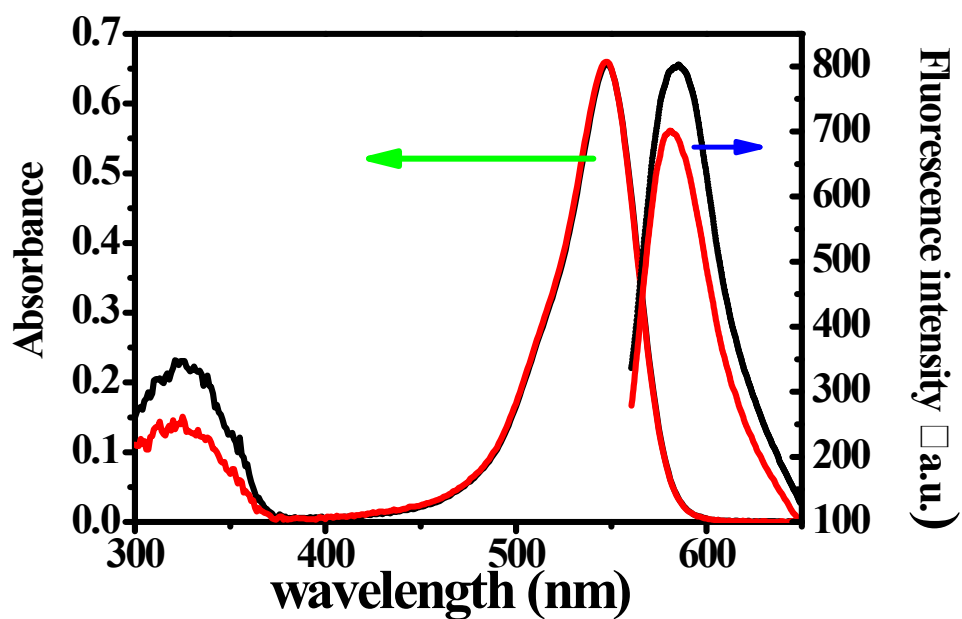


Fig. S10. Changes of fluorescence and absorption spectra before and after irradiation with 365 nm (10 μM *DASA-azo* in toluene). Initial state without light (black line); light at 365 nm for 3 min (red line).

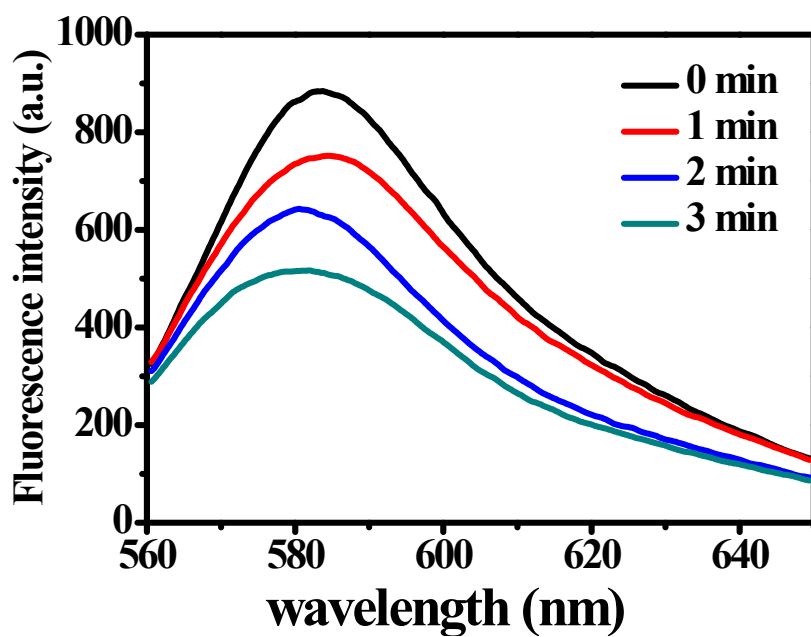


Fig. S11. Fluorescence spectra changes of *DASA-azo* (10 μ M in toluene) after irradiation at 365 nm for 0 min (black line), 1 min (red line), 2 min (blue line) and 3 min (cyan line).

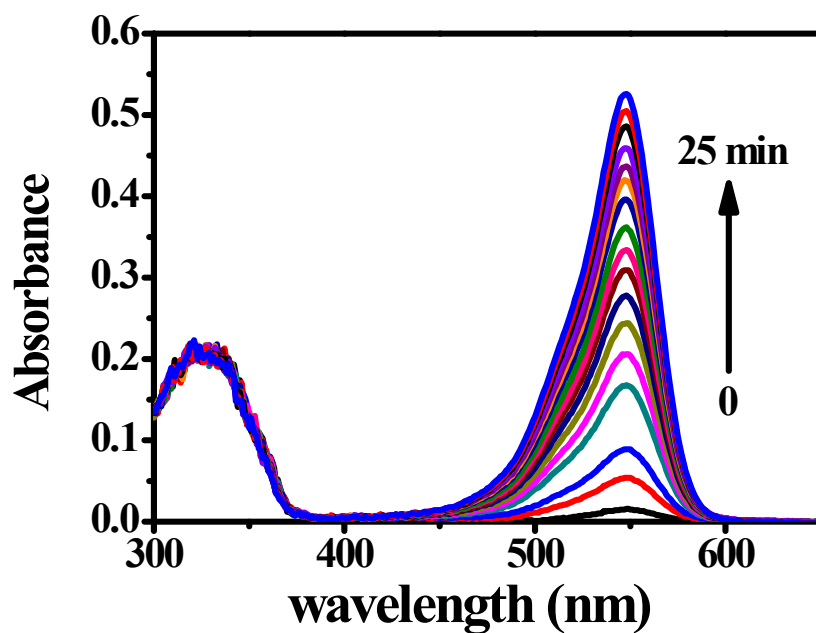


Fig. S12. Changes of absorption of *DASA-azo* in toluene (10 μ M) in dark for different time.

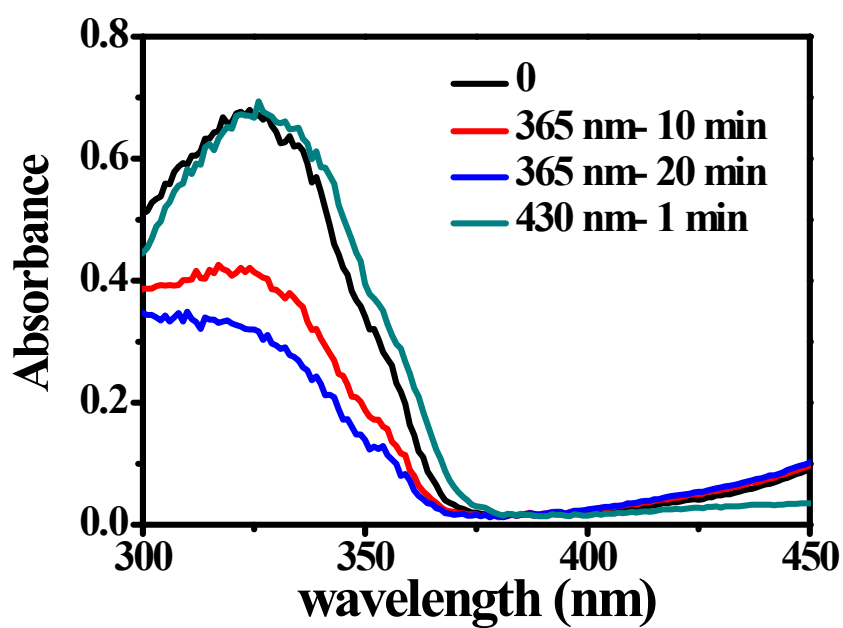


Fig. S13. Changes of absorption under irradiation with different wavelengths of light (*DASA-azo* 40 μM in toluene). Initial state without light (black line); irradiation at 365 nm for 10 min (red line); irradiation at 365 nm for 20 min (blue line); irradiation at 430 nm for 1 min (cyan line).

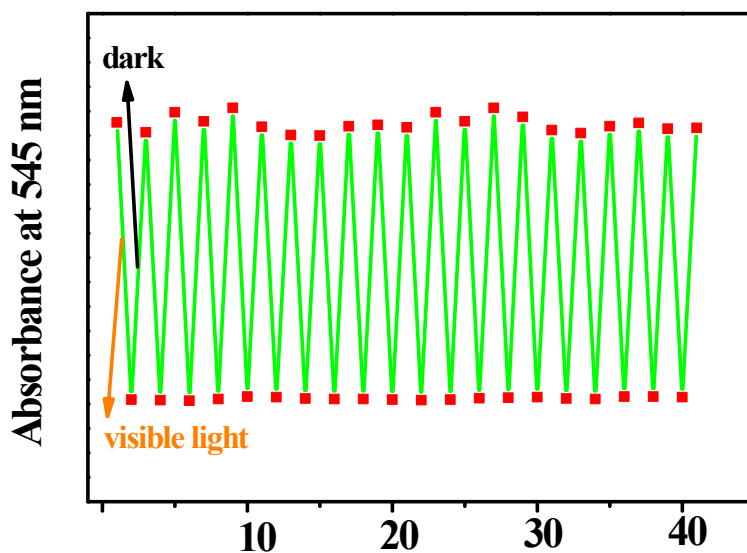


Fig. S14. Multi-photoswitching cycles of *DASA-azo* in toluene (10 μM), alternately irradiate at 525 nm for 30 s and in dark for 10 min (40 °C).

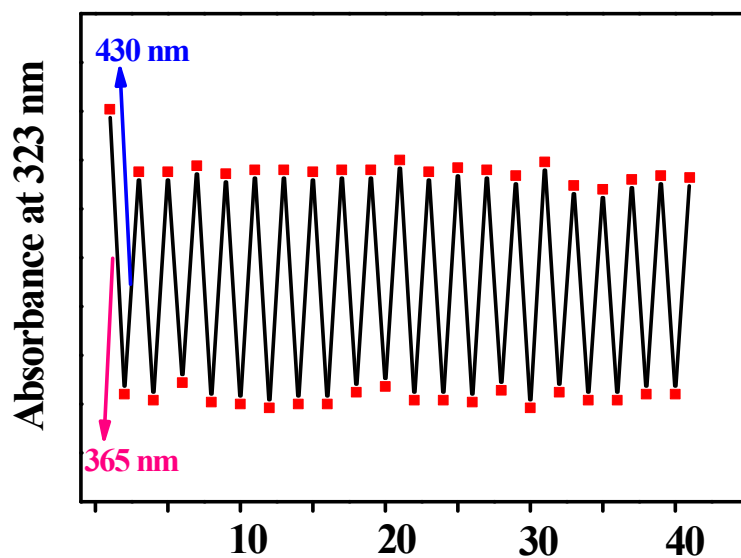


Fig. S15. Multi-photoswitching cycles of *DASA-azo* in toluene (10 μM), alternately irradiate at 365 nm for 4 min and 430 nm for 1 min.

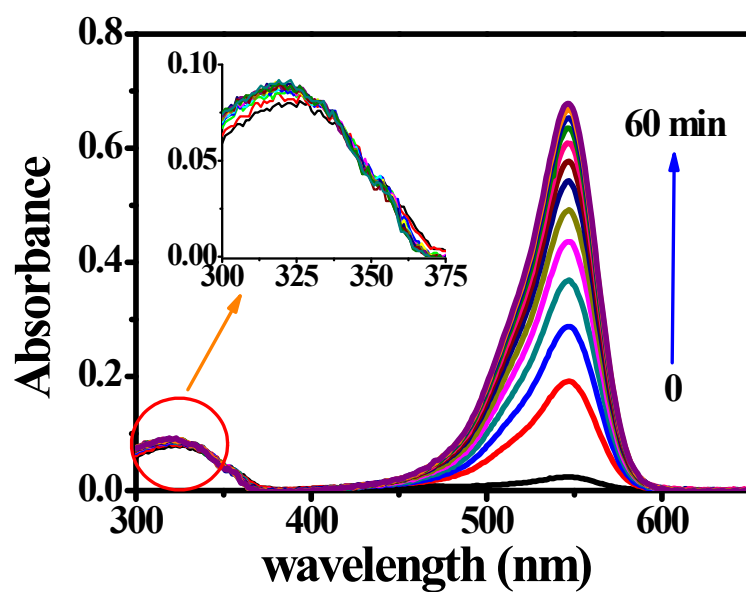


Fig. S16. Absorbance changes of *DASA-azo* toluene solution which was irradiated at 525 nm and 365 nm for 4 min in dark from 0 min to 60 min (initial state: 13 μM *DASA-azo* toluene solution after lighting at 525 nm and 365 nm for 4 min; absorbance was recorded in every 5 min).

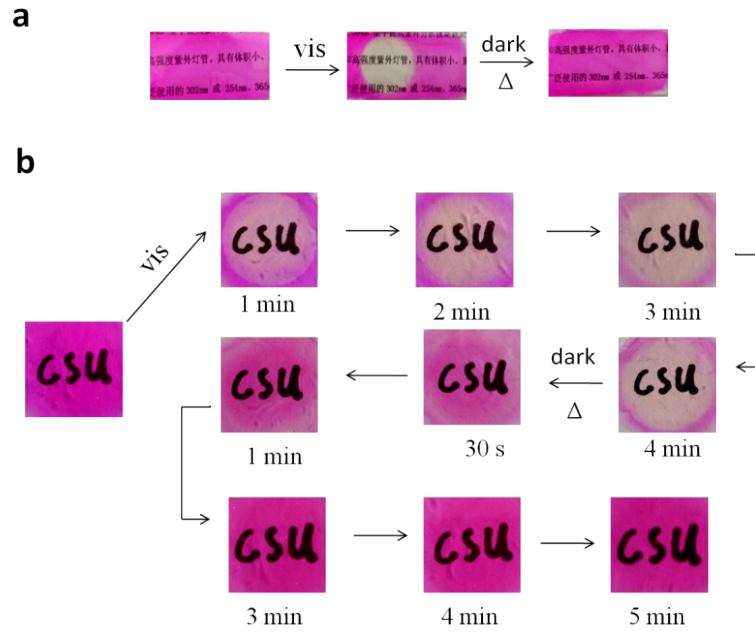


Fig. S17. (a) Photographs of the photochromic performance of the film device (irradiation at visible light for 4min; heating at 80 °C for 5 min); (b) Photochromic process of film device (irradiation under visible light with different time: 0 – 4 min; by removing the light and heating in dark 80 °C for different time: 30 s – 5min).

3. NMR data

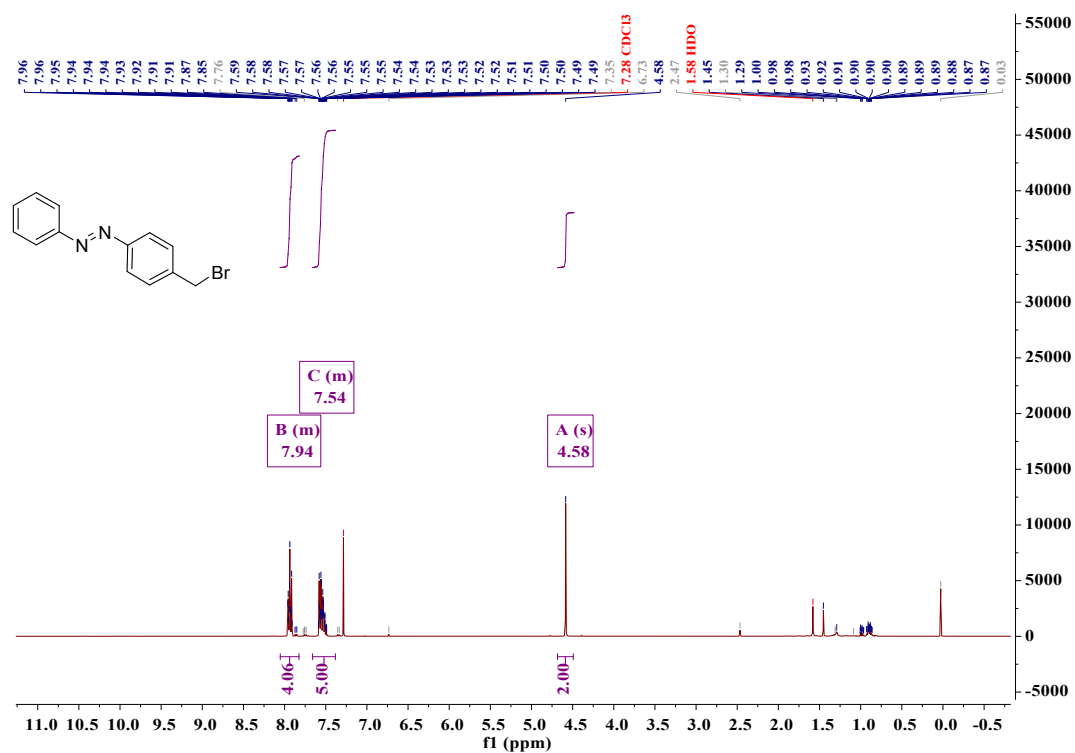


Fig. S18. ¹H NMR spectra of compound 2.

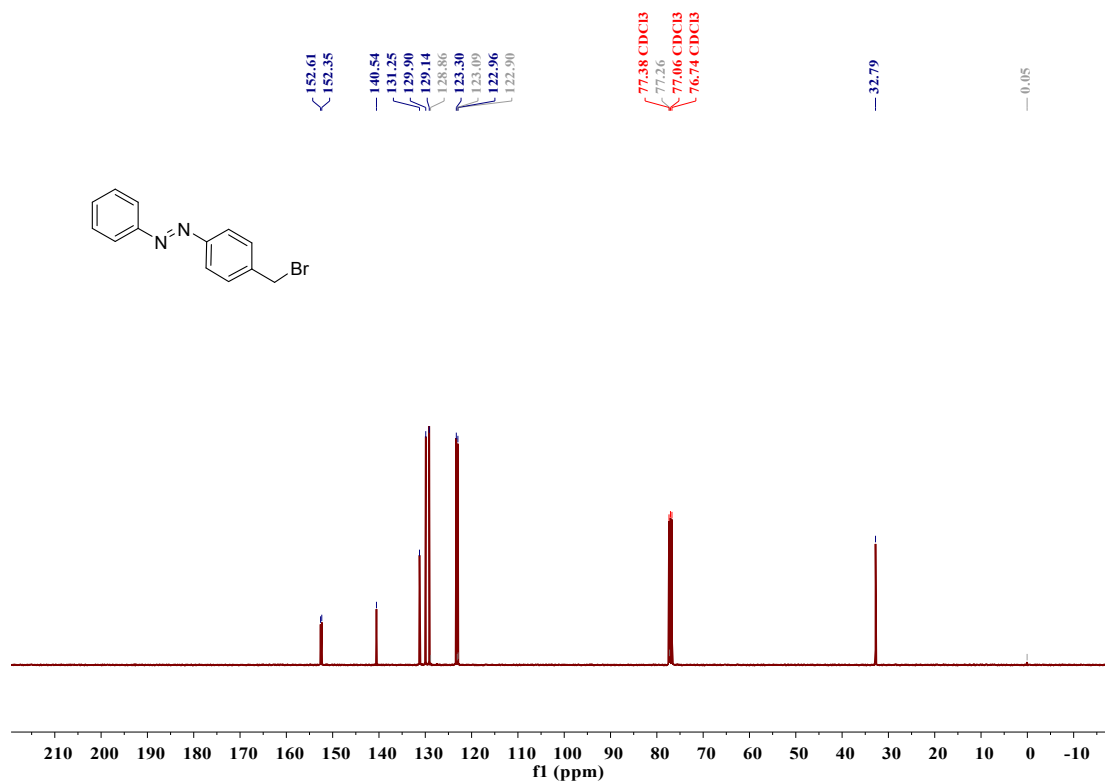


Fig. S19. ¹³C NMR spectra of compound 2.

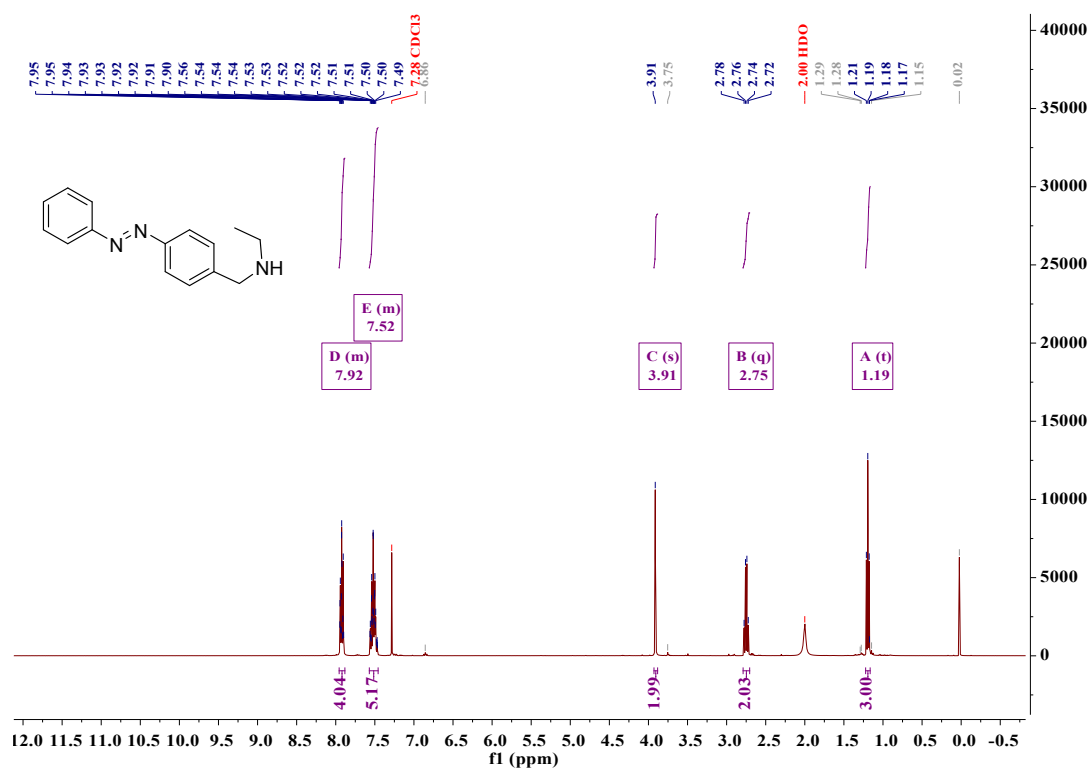


Fig. S20. ¹H NMR spectra of compound 3.

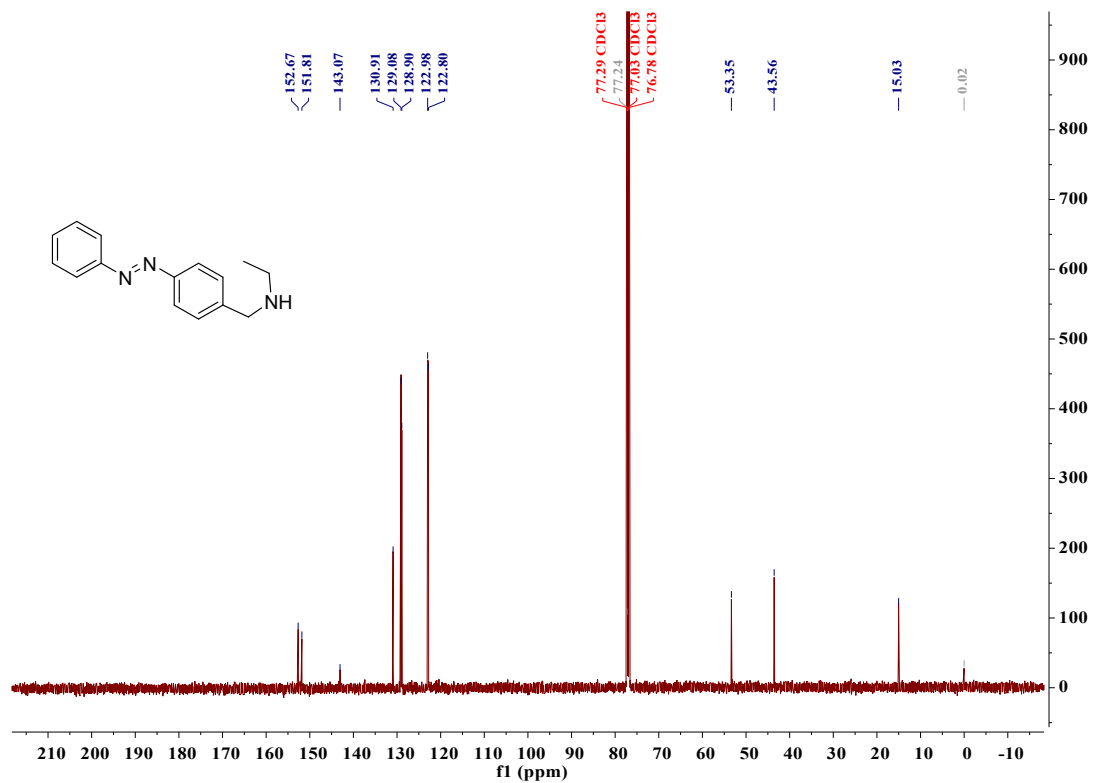


Fig. S21. ¹³C NMR spectra of compound 3.

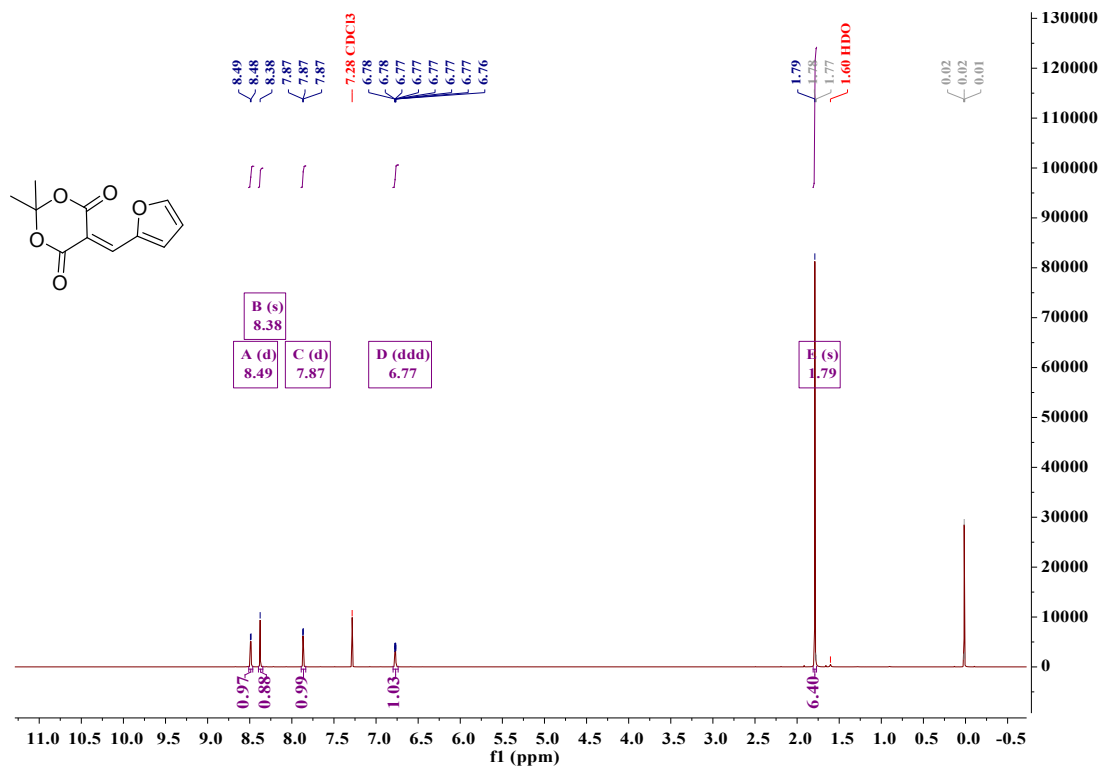


Fig. S22. ¹H NMR spectra of compound 5.

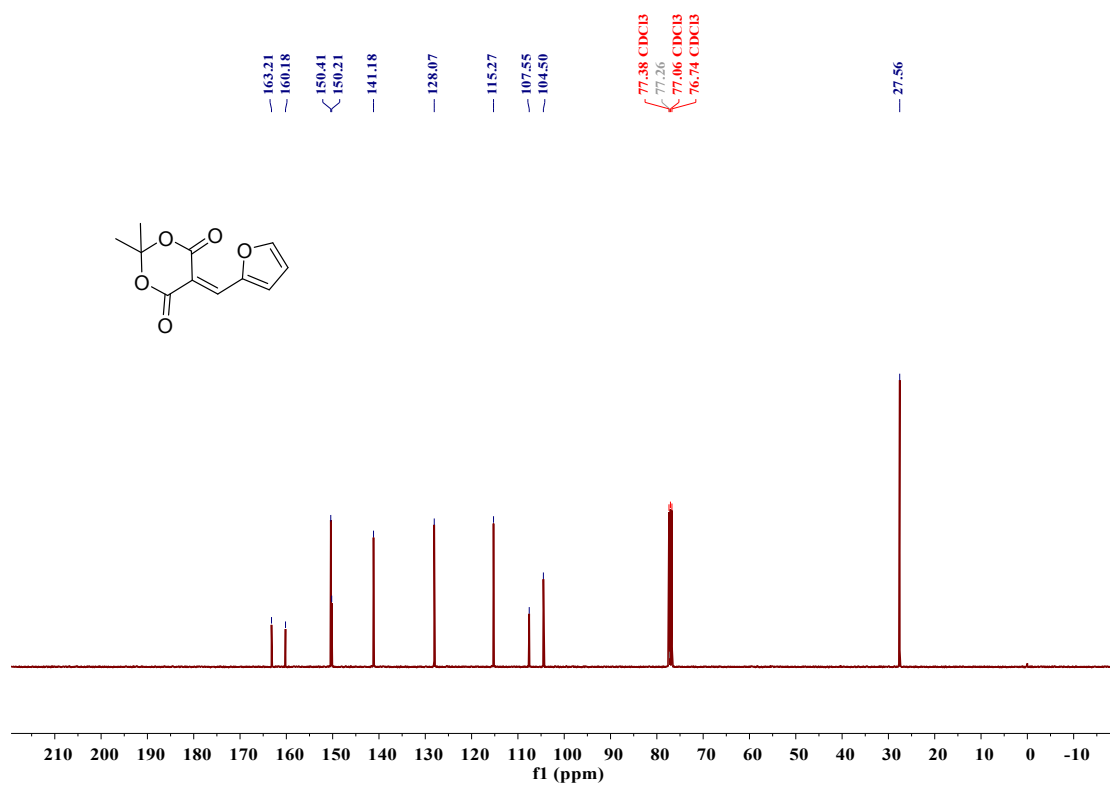


Fig. S23. ¹³C NMR spectra of compound 5.

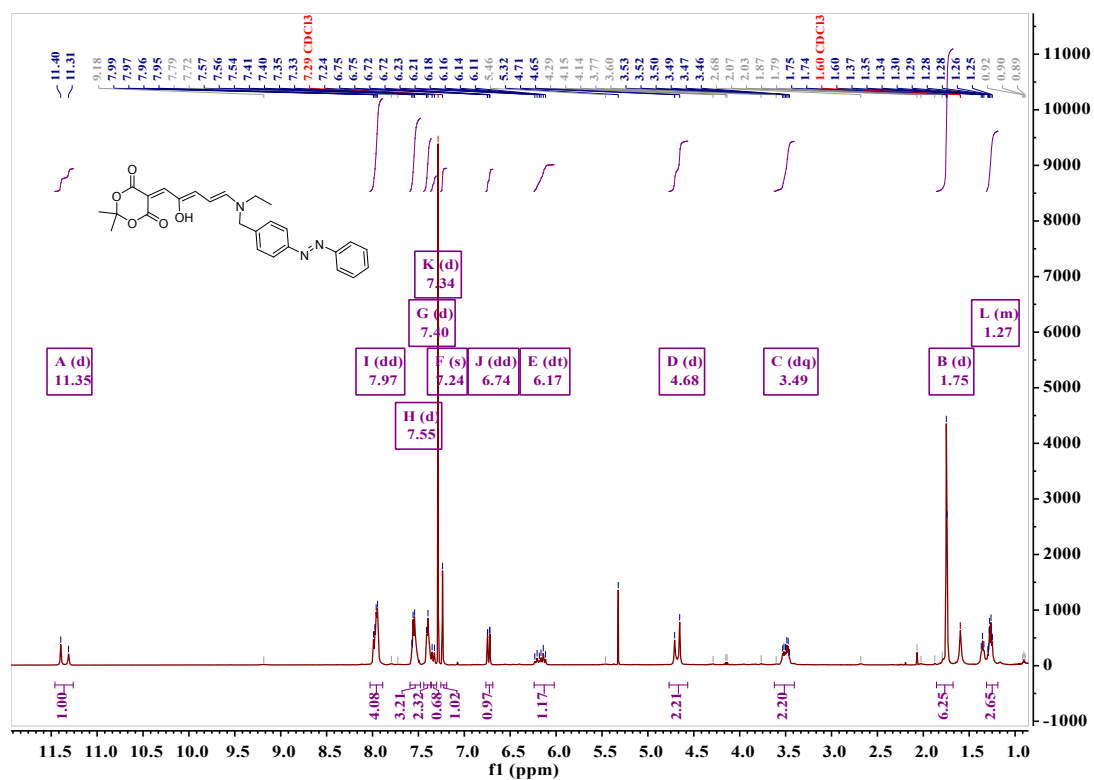


Fig. S24. ^1H NMR spectra of compound *DASA-azo*.

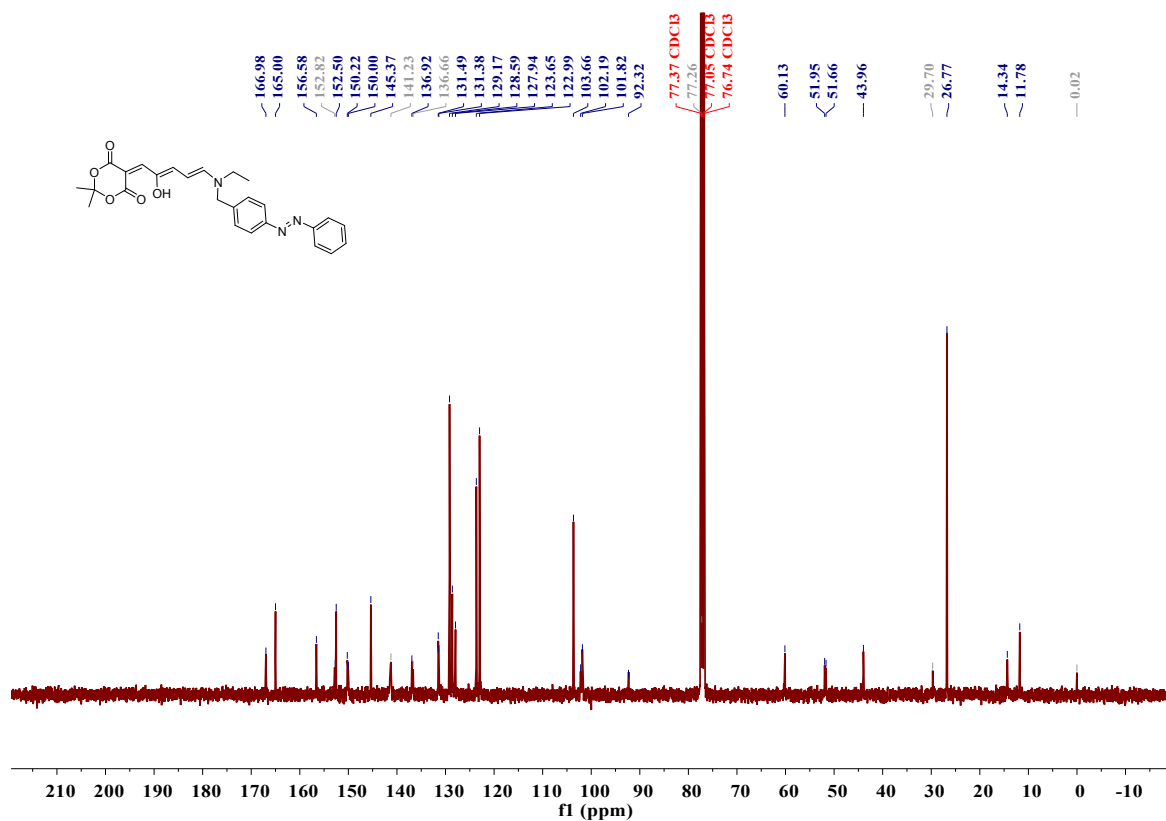


Fig. S25. ^{13}C NMR spectra of compound *DASA-azo*.