Electronic Supplementary Information

DNA gated photochromism and fluorescent switch in a thiazole orange modified diarylethene

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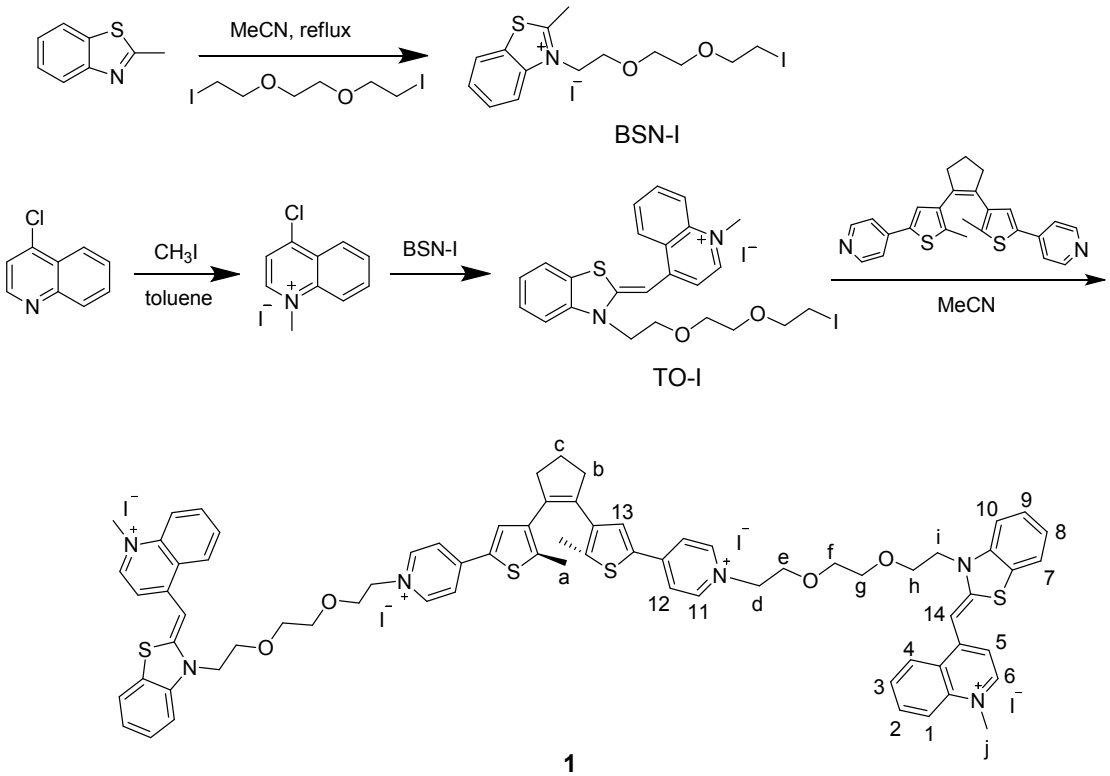
Contents

1. Materials and general procedures

All starting materials were obtained from commercial suppliers and were used as received. Solvents were dried and distilled under nitrogen before used. Glutaric acid, anhydrous aluminium chloride, titanium tetrachloride, 2-methyl thiophene and methyl iodide were supplied from Sinopharm Chemical Reagent Co. Ltd., Shanghai. Tetrakis(triphenylphosphine) palladium, *n*-butyl lithium, 4-bromopyridine hydrochloride were purchased from Sigma-Aldrich. 2-Methyl benzothiazole and 4-cholorquinoline were obtained from TCI. Oligo-DNA with 10 basepairs per chain, in 5-20 OD package was obtained from Sangon Biotech (Shanghai) Co. Ltd.

NMR spectra were recorded with Bruker DRX 500 spectrometer at room temperature. ^{1}H NMR was recorded at 400 and 500 MHz, and ^{13}C NMR was recorded at 100 MHz. Proton chemical shifts are reported in parts per million downfield from tetramethylsilane (TMS). All HRMS (high resolution mass spectrometry) data were performed on a Micro TOF II 10257 instrument (Bruker Daltonics Inc., Germany).

2. Synthesis details



Scheme S1. Synthesis of 1

2.1 Synthesis of BSN-I

2-Methylbenzo[d]thiazole (1.0 g, 6.71 mmol), 1,2-bis(2-iodoethoxy)ethane (10.0 g, 27.03 mmol) and acetonitrile (50 mL) were added in a 100 mL round flask. The mixture was heated at 110°C for 4 days under argon and cooled to room temperature. The solvent was removed under reduced pressure and the solid was washed by petroleum ether and further purified by silica gel column. BSN-1 was finally obtained

as a colorless solid (0.65 g, 1.25 mmol), yield: 18.66%. ^{1}H NMR, ($CDCl_3$, 400 MHz): δ (ppm), 3.15 (t, J = 6.4 Hz, 2H, CH_2), 3.48 (s, 3H, CH_3), 3.50- 3.52 (m, 2H, CH_2), 3.57- 3.61 (m, 4H, CH_2), 4.12 (t, J = 4.8 Hz, 2H, CH_2), 5.26 (t, J = 4.8 Hz, 2H, CH_2), 7.74 (t, J = 7.6 Hz, 1H, *ArH*), 7.84 (t, J = 7.6 Hz, 1H, *ArH*), 8.23 (d, J = 8.0 Hz, 1H, *ArH*), 8.36 (d, J = 8.0 Hz, 1H, *ArH*). ^{13}C NMR (DMSO-d6, 100 MHz): δ (ppm), 12.19, 44.19, 62.13, 63.65, 64.46, 65.28, 111.69, 119.22, 122.66, 123.34, 123.85, 135.52, 172.84. HRMS (ESI, m/z): calcd for $C_{14}H_{19}INO_2S^+$ $[M\text{-}I^-]^+$, 392.0176; found, 392.0147.

2.1 Synthesis of 4-chloro-1-methylquinolin-1-ium iodide

4-Chloroquinoline (0.5 g, 3.05 mmol), CH_3I (0.56 g, 3.94 mmol) and 50 mL toluene were added in a 100 mL round bottom flask. The mixture was heated to 80^{o}C overnight under argon protection. The slurry was filtered and the yellow solid was washed twice with 2 × 10 mL toluene to give pure product (0.75 g, 2.45 mmol), yield: 80.33%. ^{1}H NMR, (DMSO, 400 MHz): δ (ppm), 3.01 (s, 3H, CH_3), 4.59 (s, 3H, CH_3), 8.07 (m, 2H, *ArH*), 8.28 (t, J = 8.0 Hz, 1H, *ArH*), 8.50 (d, J = 8.8 Hz, 1H, *ArH*), 8.55 (d, J = 8.8 Hz, 1H, *ArH*), 9.38 (d, J = 6.0 Hz, 1H, *ArH*).

2.3 Synthesis of TO-I

To a 50 mL round bottom flask containing BSN-I (50.3 mg, 0.97 mmol) and 4-chloro-1-methylquinolin-1-ium iodide (33.5 mg, 0.97 mmol), 1,2-dichloroethane (1 mL), methanol (1 mL) and tri-ethyl amine (68 μL) were added. [1, 2] The mixture was stirred under argon for 3 hours at room temperature. The red solution was concentrated in vacuum and the residue was further purified by silica gel column ($MeOH/CH_2Cl_2$ = 2: 98, v/v). TO-I was obtained as a red solid (50.0 mg, 0.76 mmol), yield: 78.35%. ^{1}H NMR (DMSO-d6, 400 MHz): δ (ppm), 3.04 (t, J = 6.4, 2H, CH_2), 3.37- 3.42 (m, 5H, CH_2), 3.54 (t, J = 4.8 Hz, 2H, CH_2), 3.96 (t, J = 4.8 Hz, 2H, CH_2), 4.19 (s, 3H, CH_3), 4.85 (t, J = 4.8 Hz, 2H, CH_2), 7.11 (d, J = 13.2 Hz, 1H, *CH*), 7.42 (t, J = 7.2 Hz, 2H, *ArH*), 7.60 (d, J = 8.4 Hz, 1H, *ArH*), 7.77 (t, J = 8.4 Hz, 1H, *ArH*), 7.81 (t, J = 8.4 Hz, 1H, *ArH*), 8.03- 8.09 (m, 3H, *ArH*), 8.62 (d, J = 7.2 Hz, 1H, *ArH*), 8.71 (d, J = 8.4 Hz, 1H, *ArH*). ^{13}C NMR (DMSO-d6, 100 MHz): δ (ppm), 42.89, 43.83, 46.97, 68.56, 69.79, 70.12, 70.71, 70.90, 71.30, 88.96, 108.41, 113.90, 118.76, 123.22, 124.13, 124.59, 124.89, 125.89, 127.42, 128.45, 133.68, 138.53, 140.93, 145.51, 149.10, 160.37. HRMS (ESI, *m/z*): calcd for $C_{24}H_{26}IN_2O_2S^+$ $[M\text{-}I^-]^+$, 533.0760; found: 533.0717.

2.4 Synthesis of 1

To a round bottom flask containing 1,2-bis(2-methyl-5-(pyridin-4-yl)thiophen-3-yl) cyclopent-1-ene (50 mg, 0.12 mmol) [3, 4] and TO-I (175.4 mg, 0.266 mmol), acetonitrile 30 mL was added. The mixture was heated at 110^{o}C under argon for 7 days. The solvent was removed in vacuum and the residue was further purified by silica gel column, eluted with methanol/dichloromethane from 1: 100 to 1: 10. **1** was obtained as a red solid (100 mg, 0.0576 mmol), yield: 48%. ^{1}H NMR, (CD_3OD, 400 MHz): δ (ppm), 2.16 (s, 6H, CH_3), 2.18 (m, 2H, CH_2), 2.94 (t, J = 7.6 Hz, 4H, CH_2),

3.56- 3.61 (m, 8H, CH_2), 3.74 (t, J = 4.4 Hz, 4H, CH_2), 4.00 (t, J = 4.8 Hz, 4H, CH_2), 4.07 (s, 6H, CH_3), 4.44 (t, J = 4.8 Hz, 4H, CH_2), 4.67 (t, J = 4.8 Hz, 4H, CH_2), 6.94 (s, 2H, *ArH*), 7.27- 7.30 (m, 4H), 7.45- 7.54 (m, 4H, *ArH*), 7.66- 7.70 (m, 2H, *ArH*), 7.77 (t, J = 7.6 Hz, 2H, *ArH*), 7.87- 7.96 (m, 10H, *ArH*), 8.30 (d, J = 7.2 Hz, 2H, *ArH*), 8.48 (d, J = 8.4 Hz, 2H, *ArH*), 8.53 (d, J = 8.4 Hz, 4H, *ArH*). ^{13}C NMR (DMSO-d6, 100 MHz): δ (ppm), 15.19, 22.75, 42.96, 47.13, 59.38, 68.56, 69.11, 70.09, 70.56, 88.73, 108.38, 113.76, 118.69, 121.67, 123.21, 124.03, 124.42, 124.83, 125.84, 127.44, 128.38, 133.48, 133.66, 133.86, 135.08, 138.37, 139.00, 140.84, 143.97, 145.24, 145.45, 148.00, 149.00, 160.18. HRMS (ESI, *m/z*): calcd for $C_{73}H_{74}I_3N_6O_4S_4^+$ $[M\text{-}I^-]^+$, 1607.1783; found: 1607.1776.

3. Techniques

Fluorescent spectra were tested on Edinburgh Instruments FLS 920 (or FLS 900). Absorption spectra were recorded on a Shimadzu UV-vis 2550 spectroscope. Fluorescent quantum yield in aqueous solution was measured using Rh-B in ethanol solution as a standard. CD (circular dichroism) spectra were performed on an MOS-450 spectropolarimeter. 1D and 2D ^{1}H NMR were performed on a Bruker DRX 500 spectrometer at room temperature. The photo cyclization process of **1** was performed by UV light, generated by a low pressure mercury lamp with 360 nm long wavelength pass filter. In the visible light induced ring open process, a 670 nm laser (I = 0.8 A) was used as light source.

4. DNA titration

Two kinds of DNA with 10 basepairs per chain was used, namely Poly(dA-dT)10 (AT10): ATATATATATATATATATAT, and Poly(dC-dG)10 (CG10): CGCGCGCGCGCGCGCGCGCG. The stock solution of **1** (5.0×10^{-4} M) was made in pure water with 2.5% DMSO. The stock solution was diluted in Tris buffer for DNA titration experiments. In the process of titration, aliquot of oligo DNA stock solution in 100 μM chain concentration (1 mM in basepair concentration) was added to a buffer solution (pH = 7.2) containing 5 mM Tris-HCl, 5 mM NaCl and 5 μM **1**. The mixture was stirred for 10 min before spectral testing.[5] The process was traced with absorption and fluorescence spectra at intervals.

5. Cell culture and confocal laser scanning microscopy

Hela cells were planted on glass dishes and allowed to adhere for 12 h. The cells were then washed and incubated with **1** in nutrient solution or physiological saline (0.9% NaCl, pH = 7.0) for 15 to 60 min in 37^{o}C incubator. Cell imaging was performed after washing the cells with physiological saline or nutrient solution on Confocal Laser Scanning Microscope (CLSM).

Fix cell co-localization with Hoechst33258. The cells were fixed with paraformaldehyde at 4^{o}C for 30 min, washed thoroughly with nutrient solution or physiological saline. The fixed cells were then incubated with **1** (5 μM) for 30 min at 37^{o}C incubator, washed with saline buffer and incubated in Hoechst33258 (10 μM)

for another 30 min, washed with saline and watched on CLSM.

Luminescence imaging on CLSM (*xy*-scan, *xz*-scan and *λ*-scan) was performed with an Olympus confocal fluorescence microscope and a 60 × oil immersion objective lens. Cell incubated with **1** were excited at 488 nm with a semiconductor laser, the emission band was collected at 520- 620 nm. Hoechst33258 was excited by 405 nm laser and collected at 420-480 nm. Quantization by line plots was accomplished with the software package provided by Olympus instruments. For the photochromism of **1** in cell imaging, a 405 nm laser was used as light source to induce photocyclization and the reverse process was irradiated with a 633 nm laser installed in the instrument.

6. Cytotoxicity experiments

MTT assay. The cytotoxicity was performed by 3-(4,5-dimethylthiazol-2-yl) -2,5-diphenyltetrazolium bromide (MTT) assay with Hela cell lines. Cells growing in log phase were planted into a 96-well cell culture plate at 1×10^5/ well. The cells were incubated for 12 h at 37 ^oC under 5% CO_2 in an incubator. A solution of **1** (100.0 μL/ well) at concentrations of 5.0, 10.0, 20.0, 40.0, 60.0 μM in nutrient with 1‰ DMSO was added to the wells of the treatment group, respectively. In control group, 100 μL of nutrient with 1‰ DMSO was used. The cells were incubated at 37^{o}C under 5% CO_2 for 6 h. The solvent was removed from 96 well plate, then washed with nutrient solution. A combined solution of 5 mg/mL MTT in PBS was diluted to 10 times with nutrient solution and added to each well of the 96 well plate assay in 100.0 μL/well. The cells were incubated for an additional 4 hours. The solvent was removed and Formazan extraction was performed with DMSO, the quantity was determined colorimetrically using a Mutil reader (TECAN, Infinite M200). The absorbance values at wavelengths of 570 and 690 nm were collected, the absorption at 690 nm was used as correction of interference. The following formula was used to calculate the viability of cell growth: Viability (%) = (mean of absorbance value of treatment group/mean absorbance value of control) × 100.[2]

7. Photophysical and photochemical properties of 1

Table S1 Photophysical and photochemical properties of **1** in different conditions

Medium, [a]	state	Absorption	Emission		Photochromism	
		λ/nm (ε/dm^{3}mol^{-1}cm^{-1} × 10^{-3}) [b]	λ_{em}/nm	Φ_{FL} [c]	Conversion at PSS [d]	$\Phi_{o\to c}$ [e]
acetonitrile	open	292 (30), 328 (29), 383 (31), 475^{sh} (64), 504 (115)	570	< 0.01%	86%	46.9%
	close	286 (50), 504 (115), 680 (20)	-	-		
H_2O	open	292 (31), 382 (29), 475 (100), 504^{sh} (48)	620	0.25%	-	
With AT10 (*R*= 1.3: 1) Binding I	open	340 (25), 406 (26), 492 (78), 514^{sh} (42)	590	2.4%	90%	49.3%
	close	339 (14), 492^{sh} (38), 514 (41), 700 (11)	-	-		
With AT10 (*R* = 10: 1) Binding II	open	337 (21), 398 (22), 492^{sh} (52), 514 (74)	550	3.4%	-[f]	52.0%
	close	335 (18), 492^{sh} (53), 514 (80), 710 (15)	-	-		
With CG10 (*R* = 3: 1)	open	337 (21), 398 (22), 482^{sh} (52), 510 (74)	540	8.3%	-[f]	47.3%
	close	335 (18), 482^{sh} (53), 510 (80), 710 (15)	-	-		

a: The initial concentration of **1** is 5.0 × 10^{-6} M, *R*: molar ratio of basepair to **1**. The absorption and emission spectra were collected after 10 min stirring in the presence of DNA. All the data were collected at 25^{o}C. b: sh, shoulder peak. c: Fluorescent quantum yield was measured using Rhodamine-B in absolute ethanol solution as a standard. d: Photochromic transformation yield in PSS (the photo stationary state) was measured by signal of ^{1}H NMR at 25^{o}C. e: Photochromic quantum yields were calculated according to method reported by literature. [6] f: The ^{1}H NMR change before and after UV light irradiation is unconspicuous due to the dominant signals of DNA.

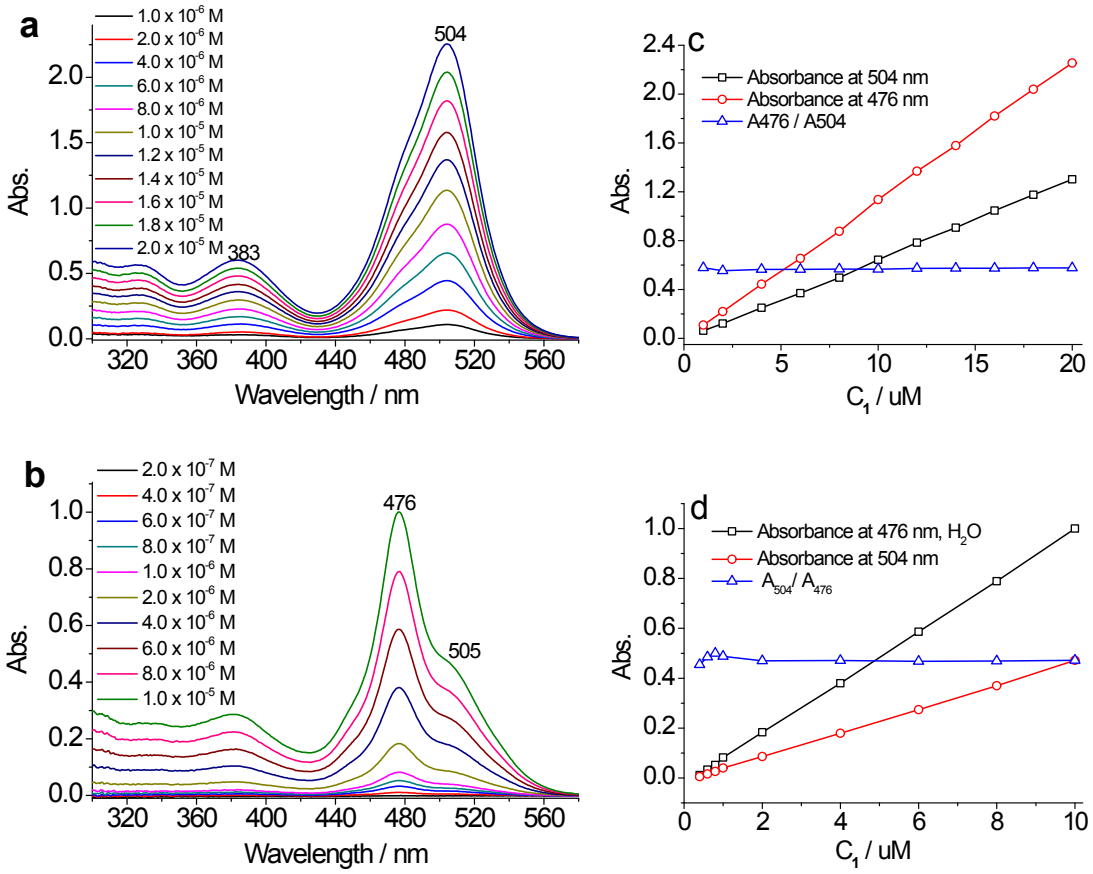


Fig. S1 The absorption spectra of **1** in (a) acetonitrile from 1.0×10^{-6} to 2.0×10^{-5} M and (b) water from 2.0×10^{-7} M to 1.0×10^{-5} M, 1 cm cell, room temperature. (c) and (d) show the linear relationship between absorbance of the maximum absorption and the shoulder ones with the concentration of **1** in acetonitrile and water, respectively.

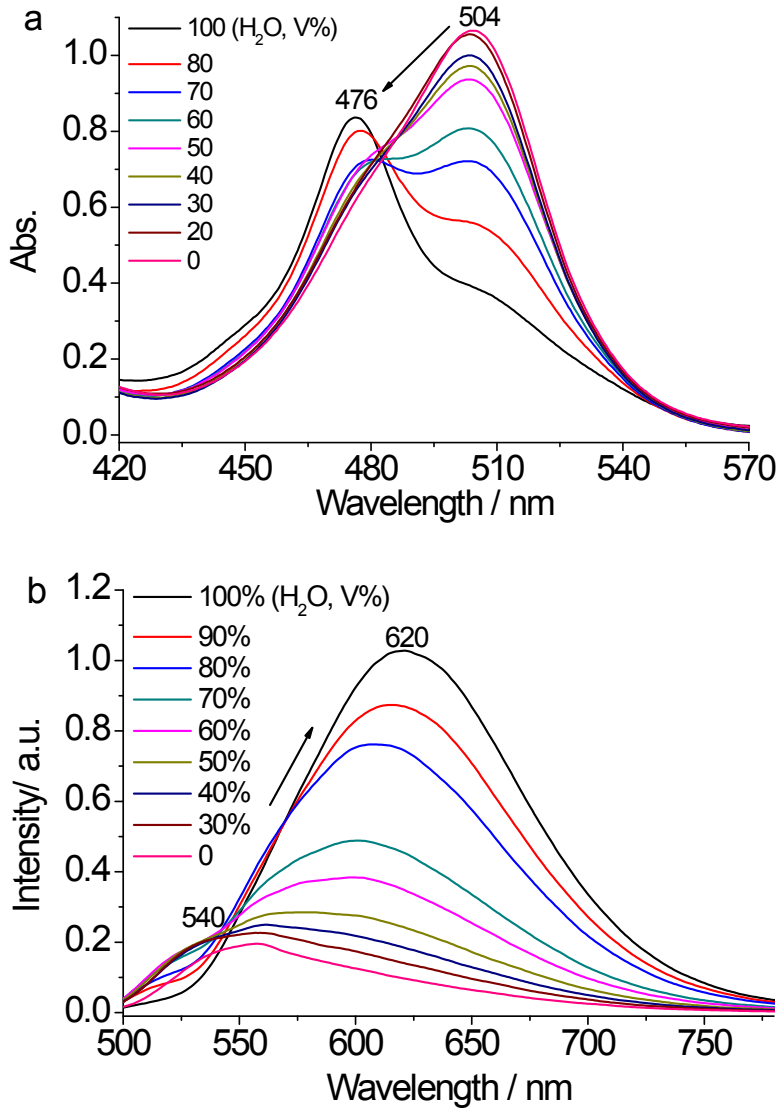


Fig. S2 The absorption (a) and emission (b) spectra of **1** (1.0×10^{-5} M) in a mixed solvents of acetonitrile and water with different volume ratio, 1 cm cell, room temperature, λ_{ex} = 480 nm.

8. Photochromic process and ^{1}H NMR NOESY spectra of 1

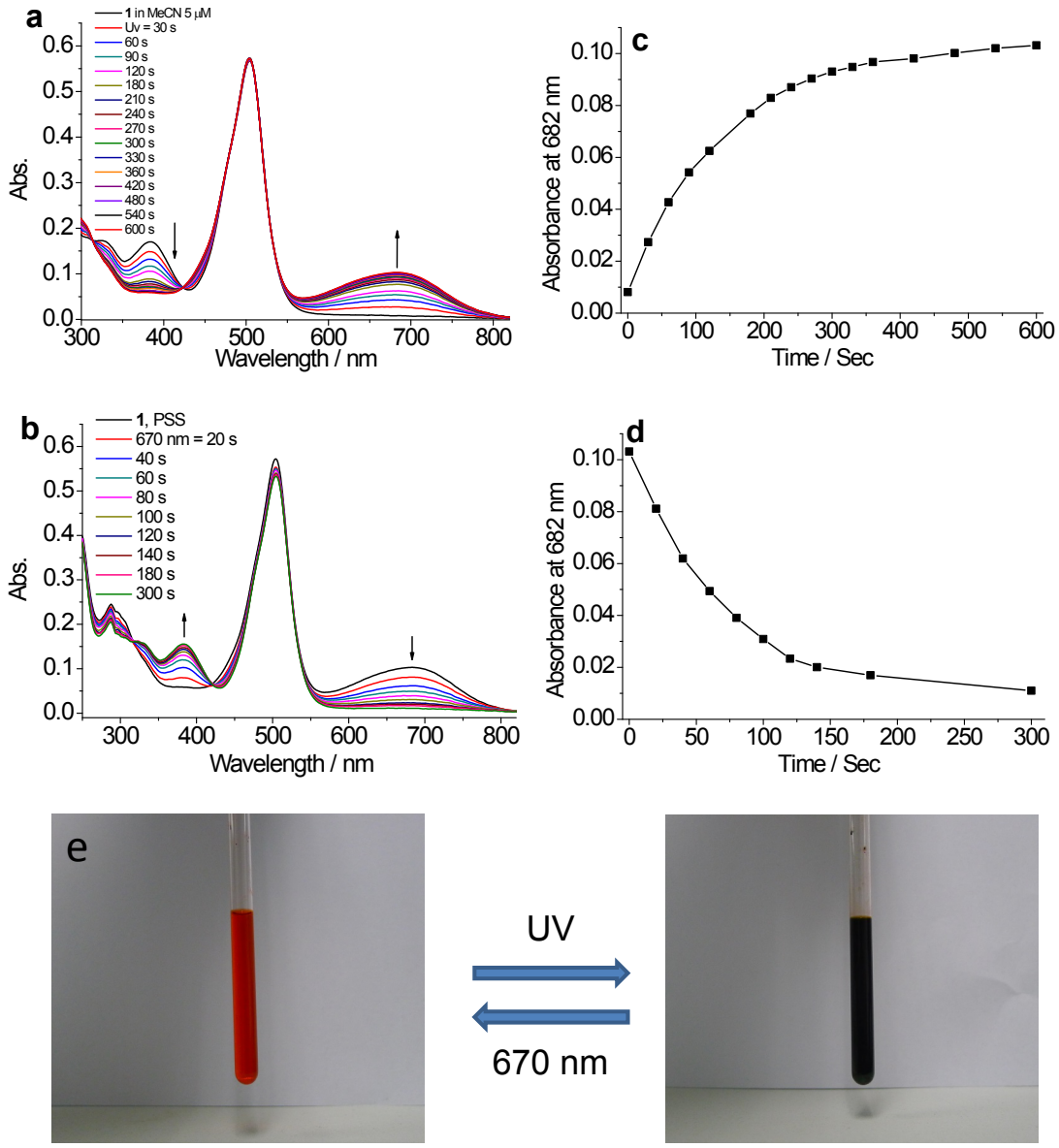


Fig. S3 The absorption spectral change of **1** (5.0×10^{-6} M in acetonitrile) with alternate (a) UV and (b) 670 nm light irradiation; the absorption change at 670 nm with the irradiation time of UV (c) and 670 nm (d) light, 1 cm cell, at room temperature; (e) images of the open and closed form of **1** in acetonitrile-d_3 solution (1.2×10^{-3} M) before and after UV light irradiation.

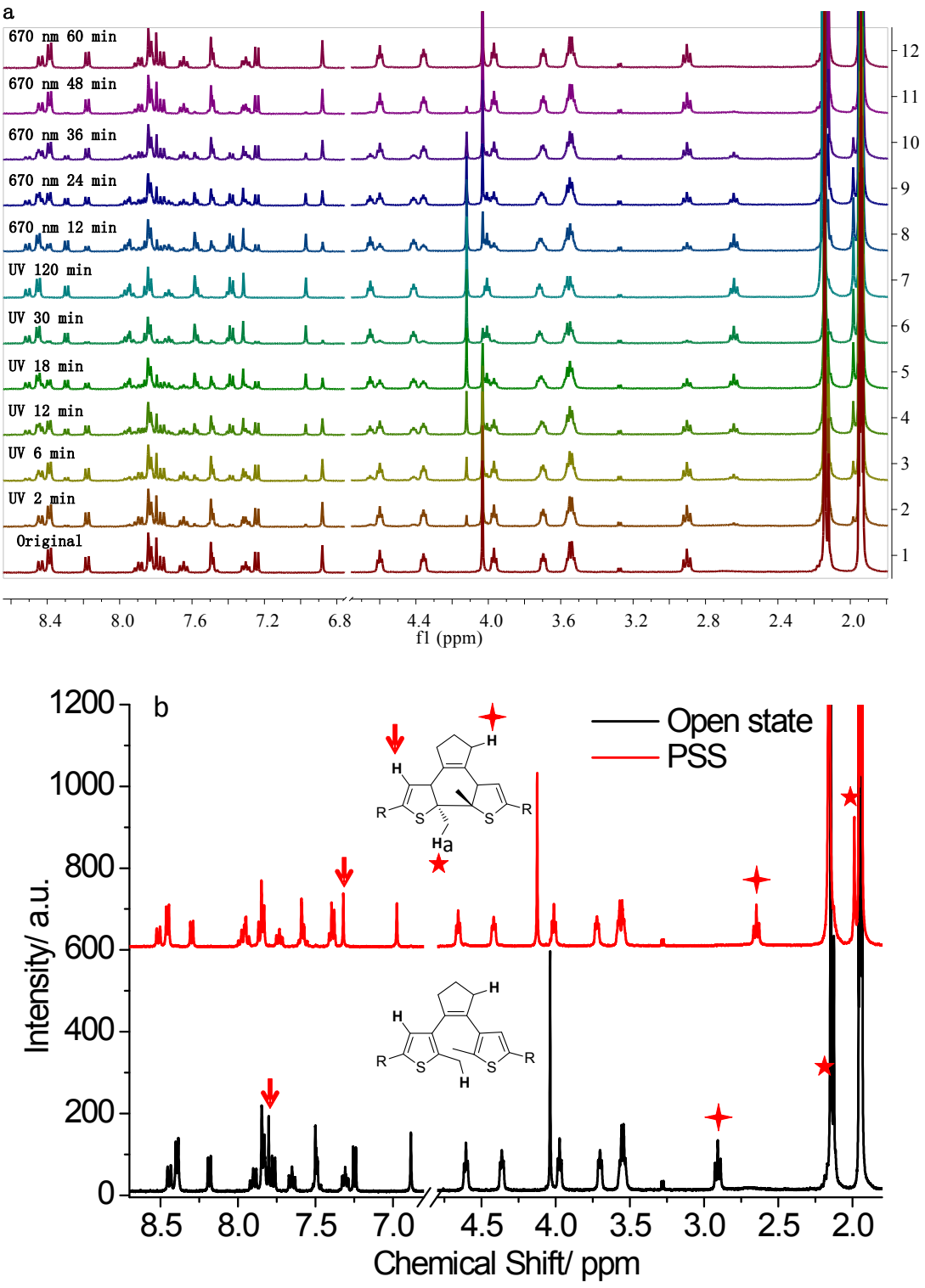


Fig. S4 ^{1}H NMR spectra of **1** (a) alternately irradiated with UV and 670 nm laser light for different period of time in acetonitrile-d_3 solution (1.2×10^{-3} M) and (b) the open and PPS state of **1** in acetonitrile-d_3 at room temperature.

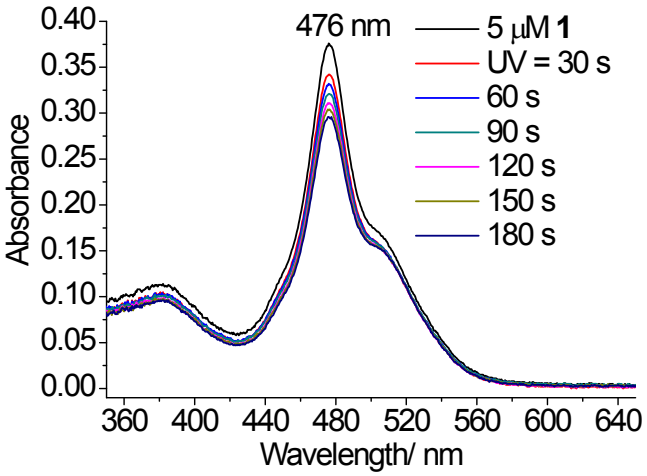


Fig. S5 The absorption spectra of **1** (5.0×10^{-6} M) in water with irradiation of UV light.

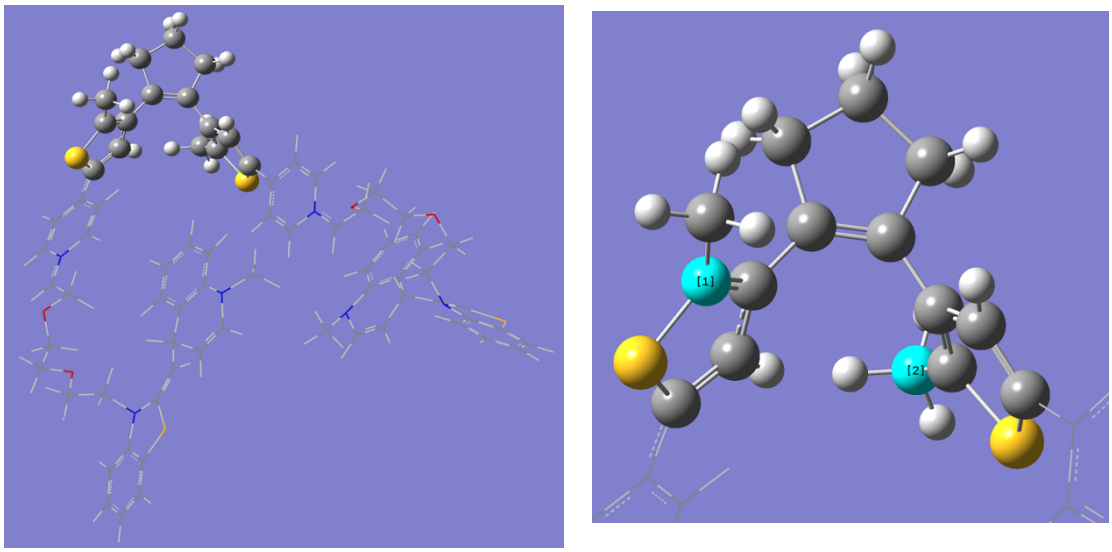
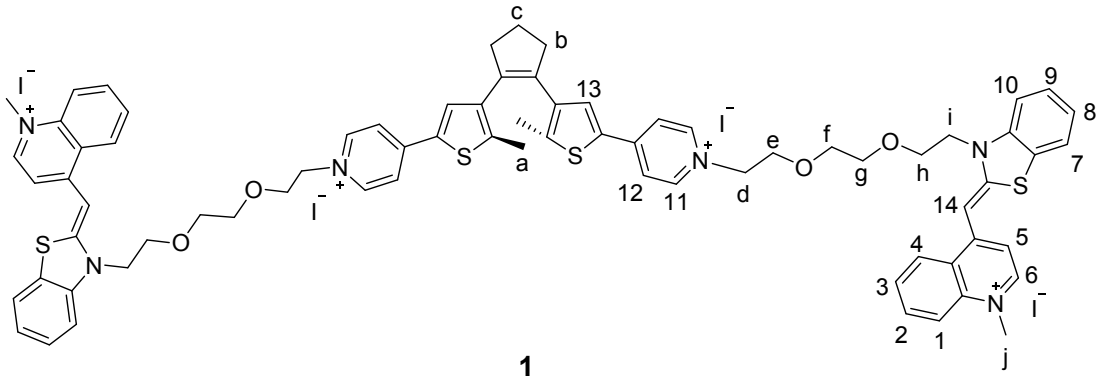


Fig. S6 (a) The possibly optimized conformation of **1** in water from PM3 calculation; (b) the amplified structure in diarylethene part.

^{1}H NOESY (nuclear Overhauser effect spectroscopy) spectra of 1: 1.0 mg of **1** was dissolved in 0.5 mL MeCN-d_3 or D_2O/DMSO-d_6 (96: 4, v/v), the solution was degassed for 30 min in a NMR tube before performing 2D NMR experiment at room temperature.



1

In NOESY spectrum of **1** in D_2O/DMSO-d_6 (96: 4, v/v), nuclear Overhauser effects (NOEs) were observed between $\mathbf{H_j}$ and $\mathbf{H_7}$ (or $\mathbf{H_3}$), which might be an evidence of intramolecular π-π stacking between TOs[7] (Fig. S7). The proton on benzylidene ($\mathbf{H_{14}}$) has two NOEs, namely, $\mathbf{H_{14}}$-$\mathbf{H_i}$ and $\mathbf{H_{14}}$-$\mathbf{H_4}$, which indicates a *cis* relationship between the methine bridged thiazole and quinoline ring in TO.[8] NOEs observed in protons between **Hg** (or **Hf**) and **H11**, **H12**, **H3**, respectively, and the correlation signals between $\mathbf{H_a}$ and $\mathbf{H_{12}}$, $\mathbf{H_{13}}$, respectively, strongly suggest a parallel conformation of diarylethene group. However, all those NOEs don't exist in the NOESY spectrum of **1** in CD_3CN, indicating an extended antiparallel conformation of **1** in CD_3CN (Fig. S8).

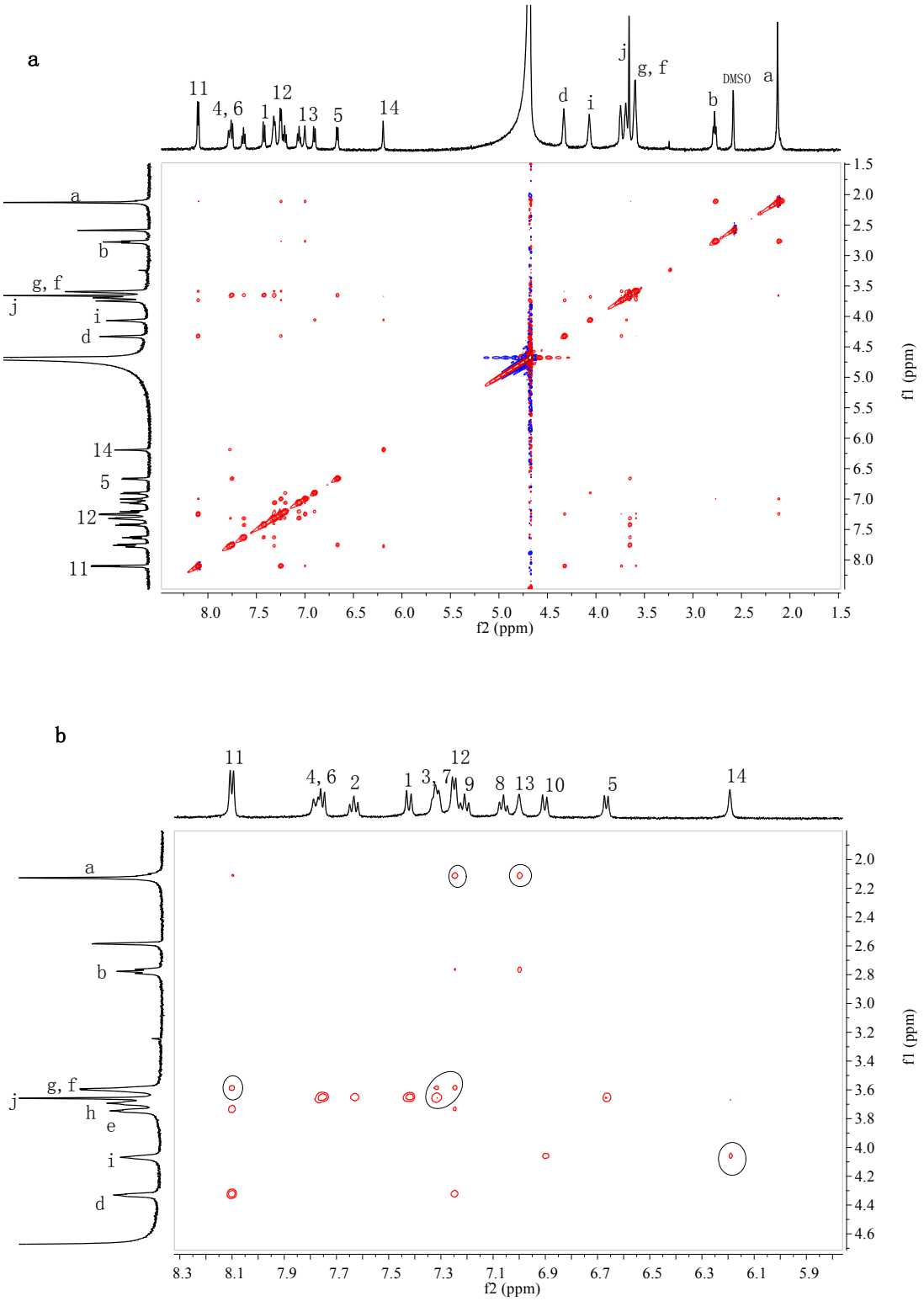


Fig. S7 NOESY spectrum (a) and expanded partial spectrum (b) of **1** (1.2×10^{-3} M) in D_2O/DMSO-d_6 (96: 4, v/v) at room temperature (the black circles show the correlation signals of related protons).

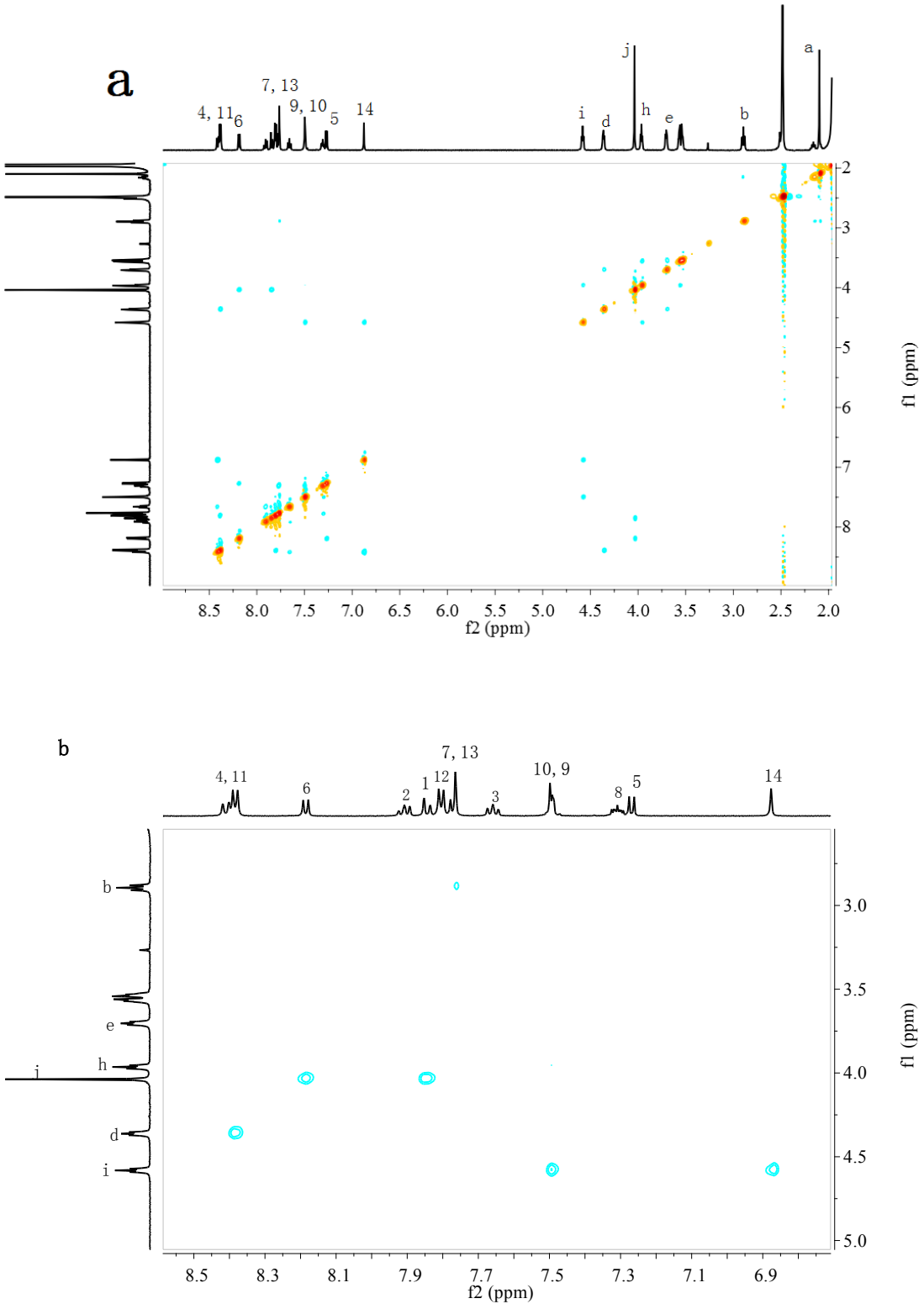


Fig. S8 NOESY spectrum (a) and expanded partial spectrum (b) of **1** (1.2×10^{-3} M) in acetonitrile-d_3 at room temperature.

9. Photophysical properties of 1 with DNA

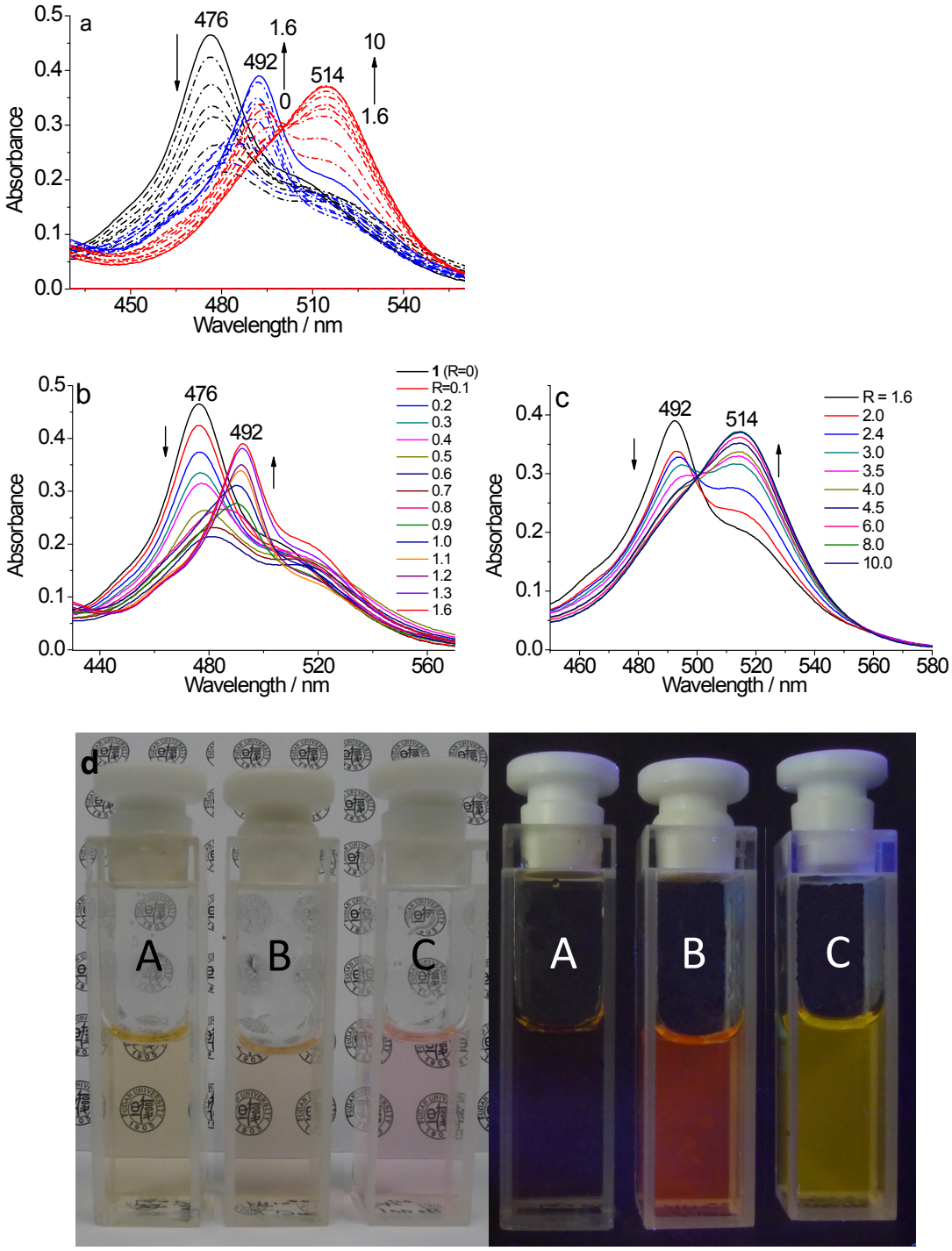


Fig. S9 (a) The absorption spectral change of AT10/**1** (5.0×10^{-6} M in aqueous buffer solution pH = 7.2) with increasing concentration of AT10; (b) and (c), the separated spectral change with (b) R = 0-1.6 and (c) R = 1.6-10.0. (d) Images of **1** (A), AT10/**1** with R = 1.6 (B) and 10.0 (C) under day light (left) and in the dark with excitation of 365 nm UV light (right). Condition: 1 cm cell, room temperature.

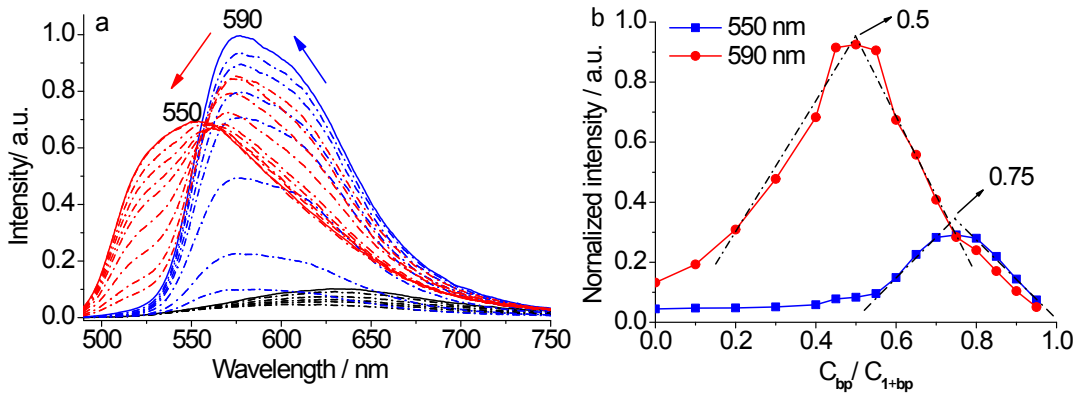


Fig. S10 (a) The emission spectral change of AT10/**1** with increasing concentration of AT10 (R = **0**-10) (solid black line: sole 1, solid blue line: binding I (R=1.6), solid red line: bonding II (R = 10); (b) the Job's plot of AT10/**1** by florescent intensity change at 590 (red) and 550 (blue) nm, the black dot dash line is the linear fitting of the curve.

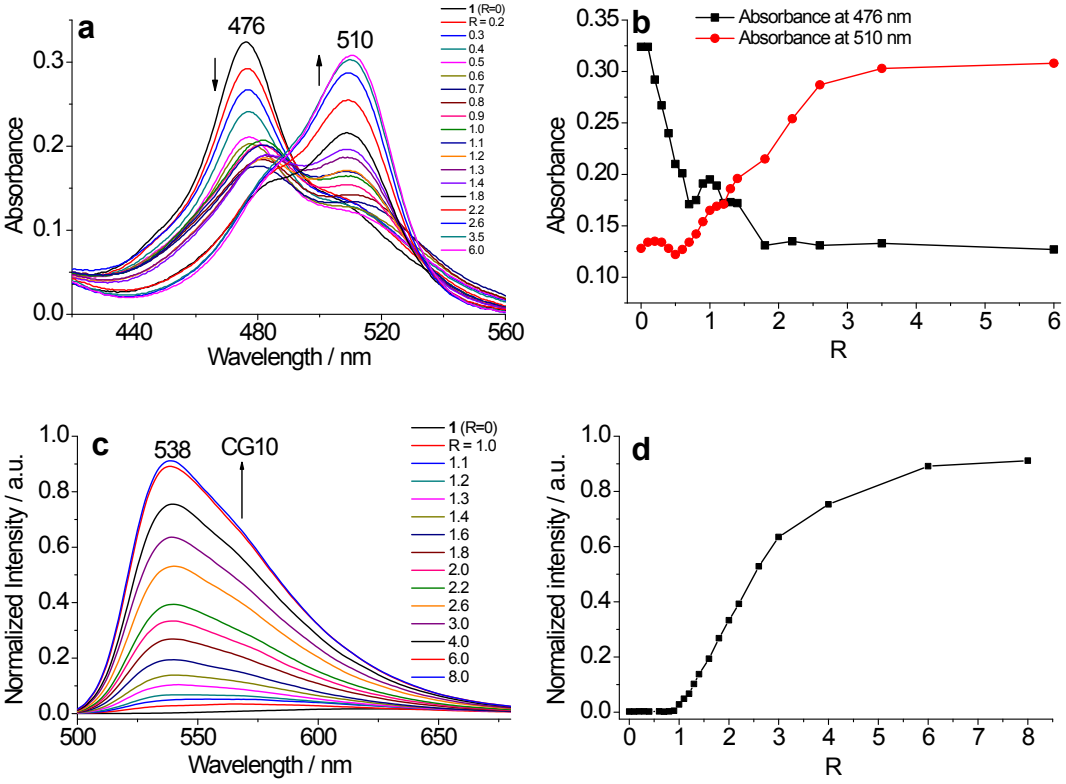


Fig. S11 (a) The absorption spectra of CG10/**1** (5.0×10^{-6} M in aqueous buffer solution, pH = 7.2) with increasing concentration of CG10 (R = 0 - 6.0) and (b) the absorption change at 476 and 510 nm with different R value. (c) The fluorescent spectra of **1** (5.0×10^{-6} M) with increasing concentration of CG10 (R = 0-8.0) and (d) the change of fluorescent intensity at the wavelength of 538 nm with different R value.

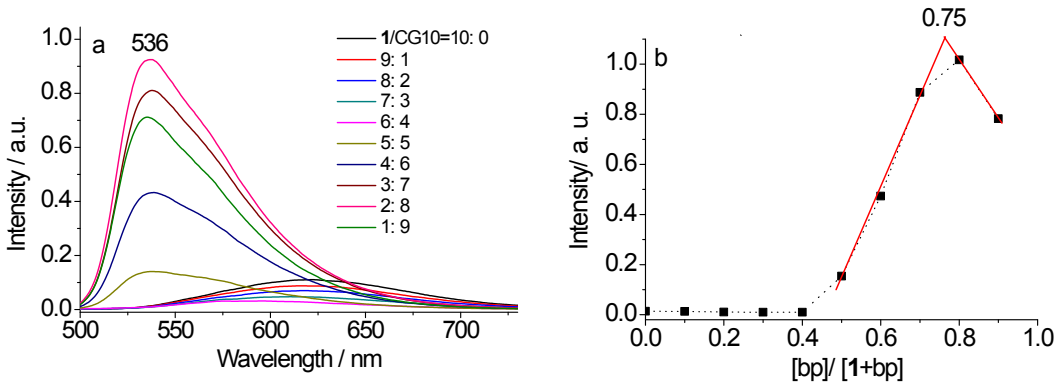


Fig. S12 (a) The emission spectral change of CG10/**1** with change of [**bp**]/ [**bp**+**1**], the total amount of **1** and CG basepair was 10 uM; (b) the Job's plot of CG10/**1** by florescent intensity change at 536 nm.

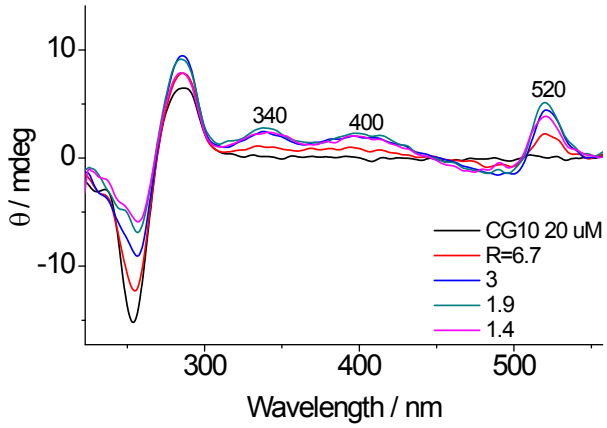


Fig. S13 CD titration of CG10 (2.0×10^{-5} M) with increasing amount of **1** from 0 to 1.4×10^{-5} M.

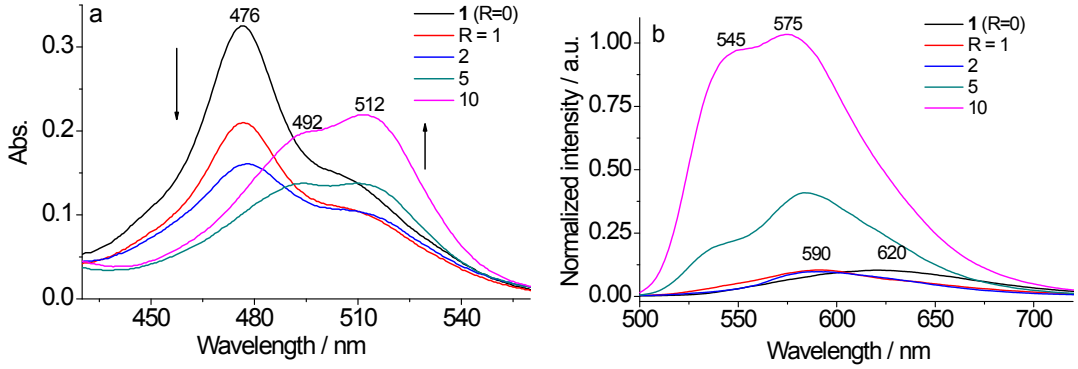


Fig. S14 (a) The absorption and (b) emission spectral change of **1** (5 μM in aqueous buffer solution, pH = 7.2) with increasing amount of CtDNA (*R*=0-10), λ_{ex} = 480 nm, 1 cm cell, room temperature.

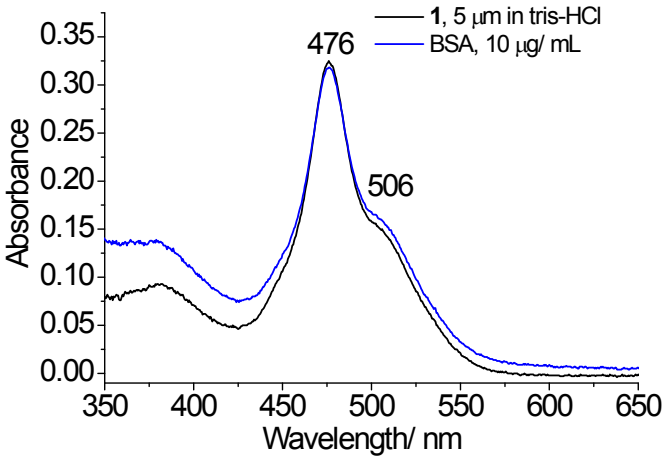


Fig. S15 The absorption spectra of **1** (5.0×10^{-6} M) in water in the presence of 10 μg/mL BSA (Bovine serum albumin) with irradiation of UV light.

10. Photochromic process of 1 with AT10

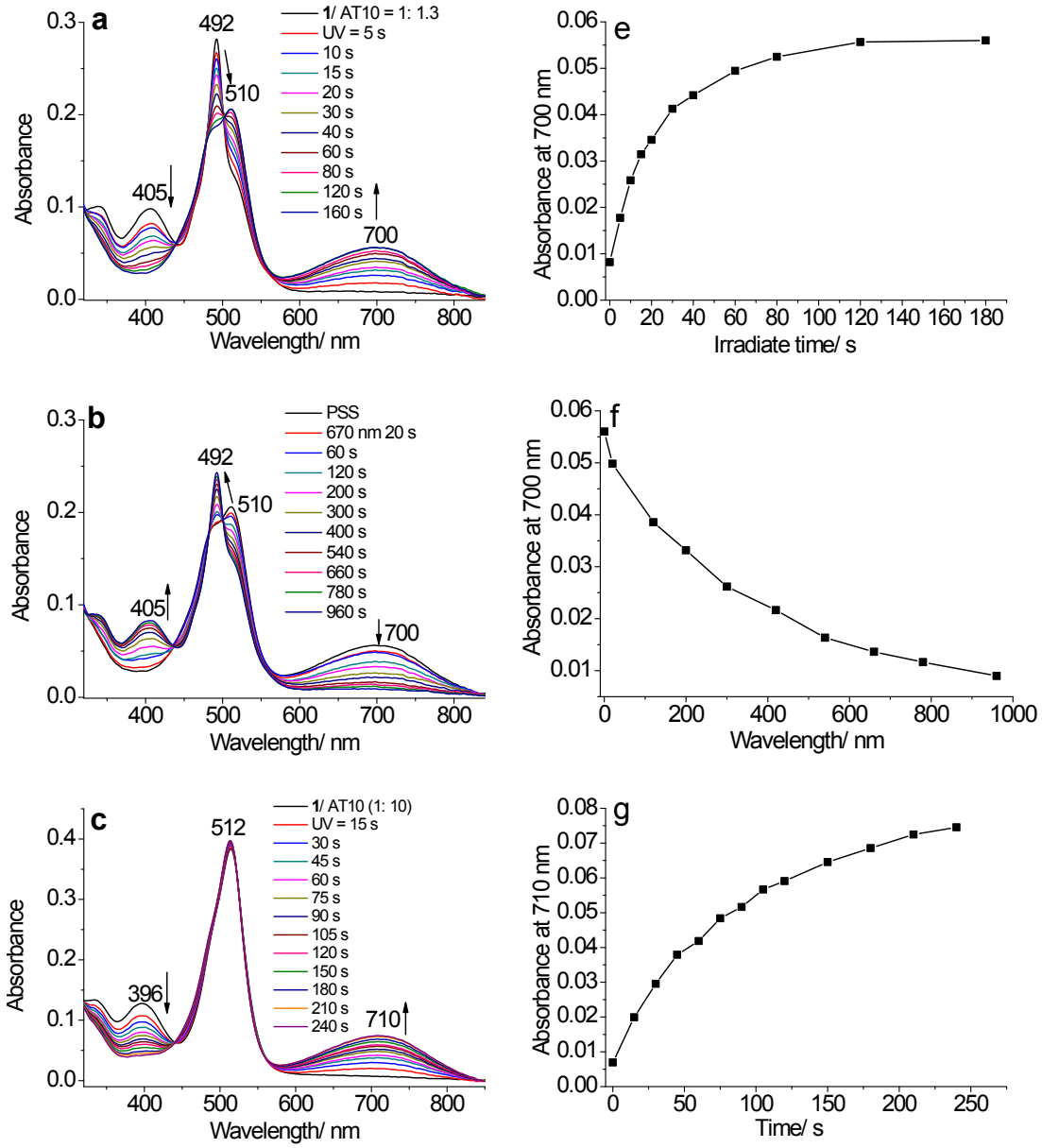


Fig. S16 The absorption spectral change of **1** (5.0×10^{-6} M) in the presence of DNA with a molar ratio of R = 1.3 with alternate irradiation of (a) UV and (b) visible light; and a molar ratio of R = 10.0 with irradiation of (c) UV light; the related absorbance change at 700 nm (710 nm for (g)) *vs* irradiation time for (a), (b) and (c) are shown in (e), (f) and (g), respectively.

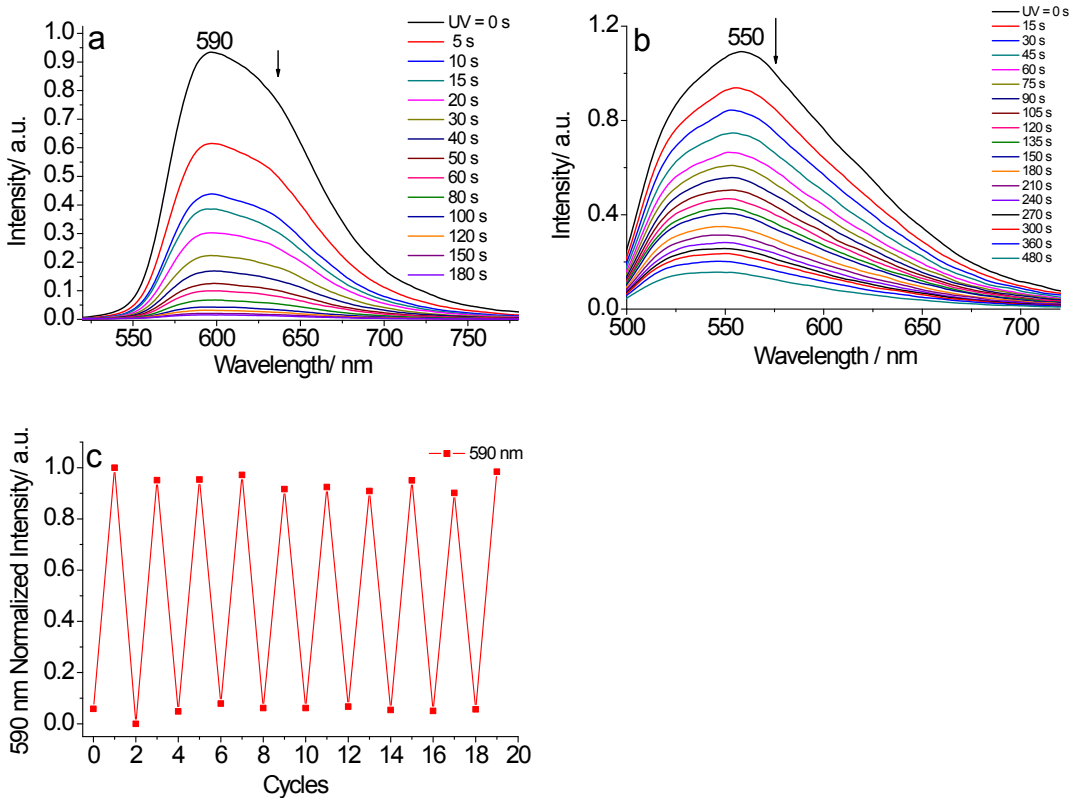


Fig. S17 The emission spectral change of AT10/**1** (C_1 = 5.0 × 10^{-6} M) with (a) R = 1.3 and (b) 10.0 with UV light irradiation. (c) The change of emission intensity at 590 nm at intervals of UV and 670 nm light irradiation under the condition of R = 1.3.

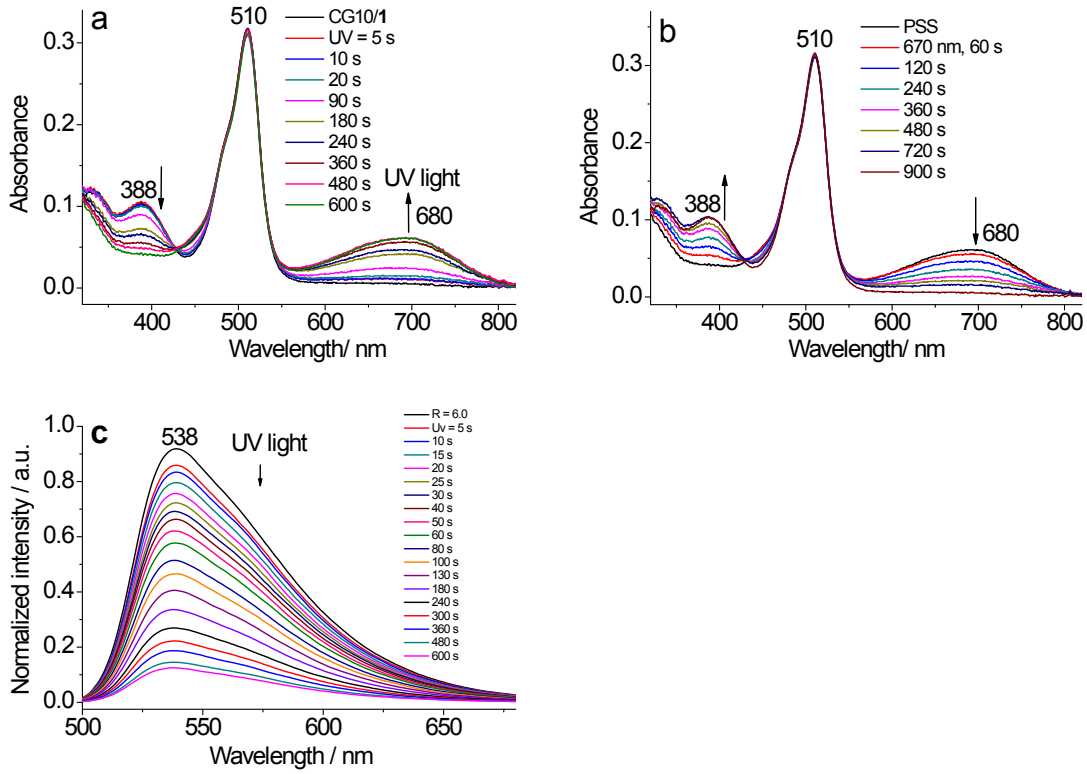


Fig. S18 The absorption change of CG10/**1** (R = 3.0) with (a) UV light irradiation and (b) the PSS state with 670 nm light irradiation. (c) The fluorescence change of R = 6.0 with UV light irradiation. λ_{ex} = 480 nm, λ_{em} = 540 nm.

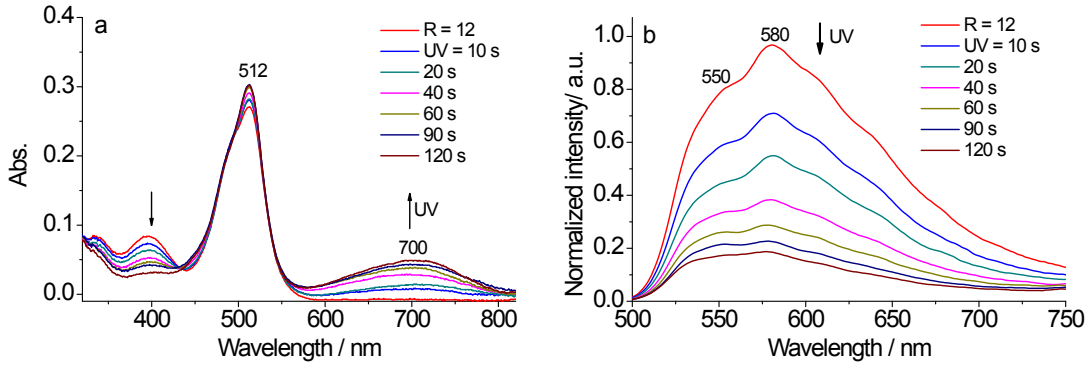


Fig. S19 The absorption and emission (λ_{ex} = 480 nm) change of CtDNA/**1** (R=12) with UV irradiation.

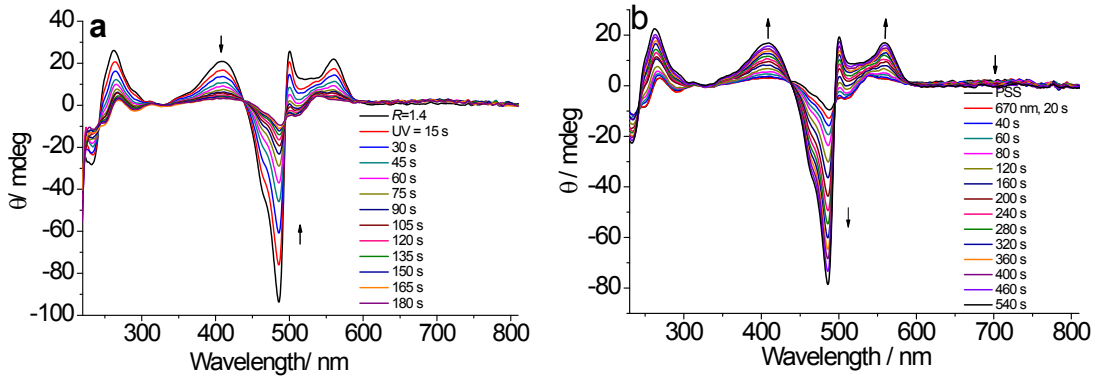


Fig. S20 CD spectral change of **1**/AT10 in binding mode I (C_1 = 1.4 × 10^{-5} M, R = 1.4) with successive irradiation of (a) UV and (b) 670 nm light at room temperature.

11. CLSM images for living and fixed Hela cells incubated with 1

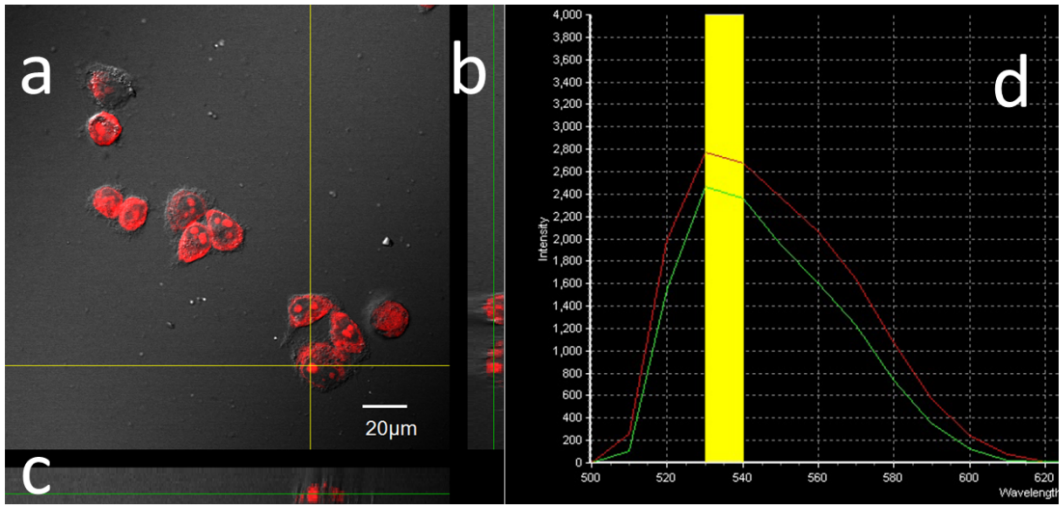


Fig. S21 Three-dimensional fluorescent images of fixed Hela cell incubated with 5 μM of **1** in physiological saline buffer for 10 min at 37°C. (a) *xy* image, (b) and (c), *yz* and *xz* cross sections, respectively, taken at the lines shown in (a); (d) the *λ*-scan of a cell at steps of 10 nm.

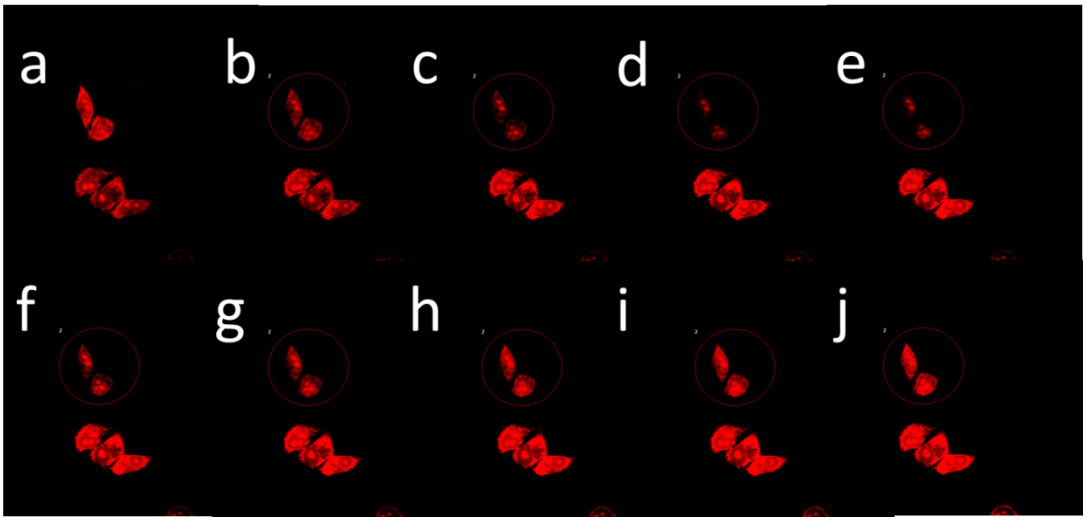


Fig. S22 Images of fixed Hela cell incubated with **1** for 10 min at 37°C, followed by irradiation of different light source. (a-e) selected cells in red circle irradiated with 405 nm laser for 0, 5, 10, 15 and 20 min, respectively; (f-j) followed by irradiation of 633 nm laser for 0.5, 1, 2, 3 and 5 min, respectively.

12. Characteristics of 1 and the intermediate products

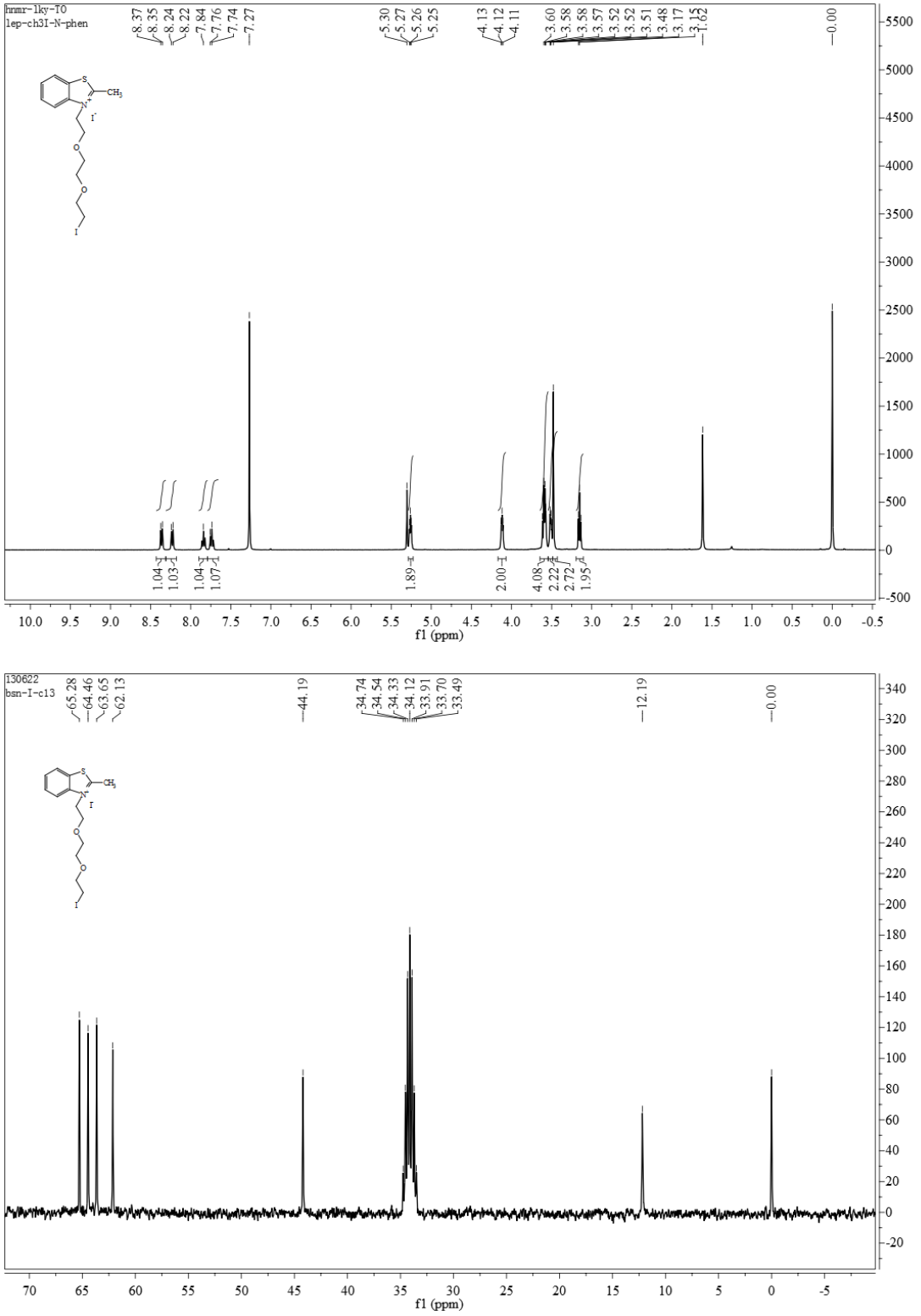


Fig. S23 ^{1}H and ^{13}C NMR spectrum of BSN-1 in $CDCl_3$ and DMSO-d6, respectively.

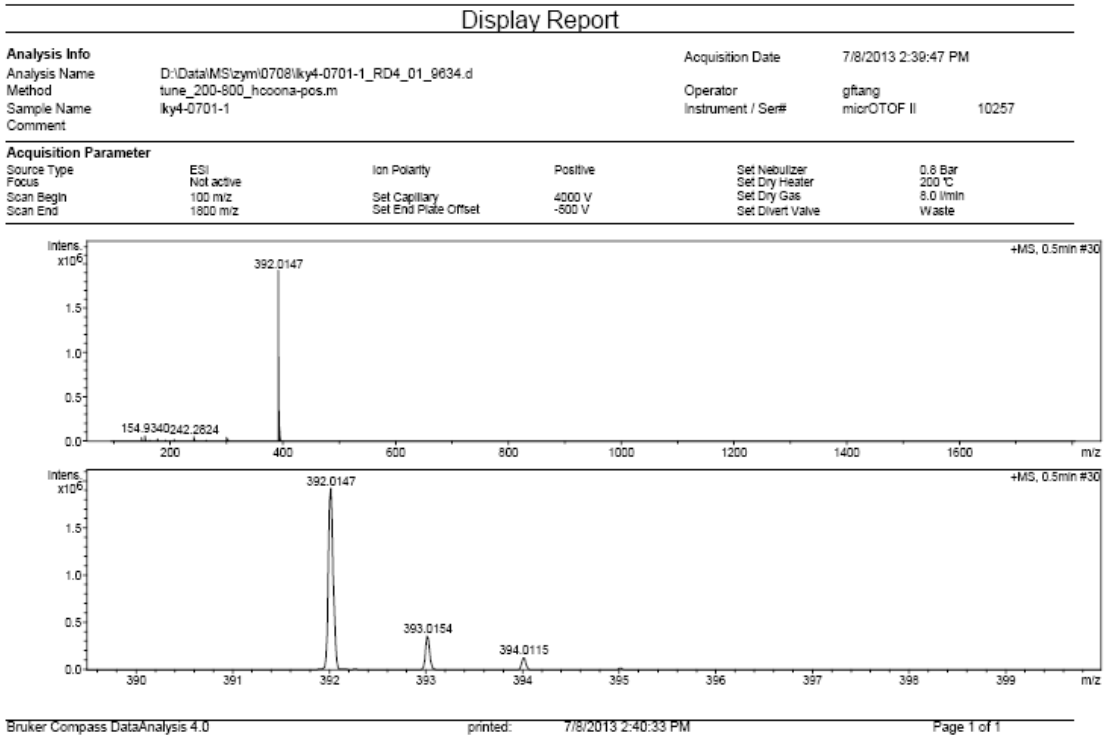


Fig. S24 HRMS of BSN-1

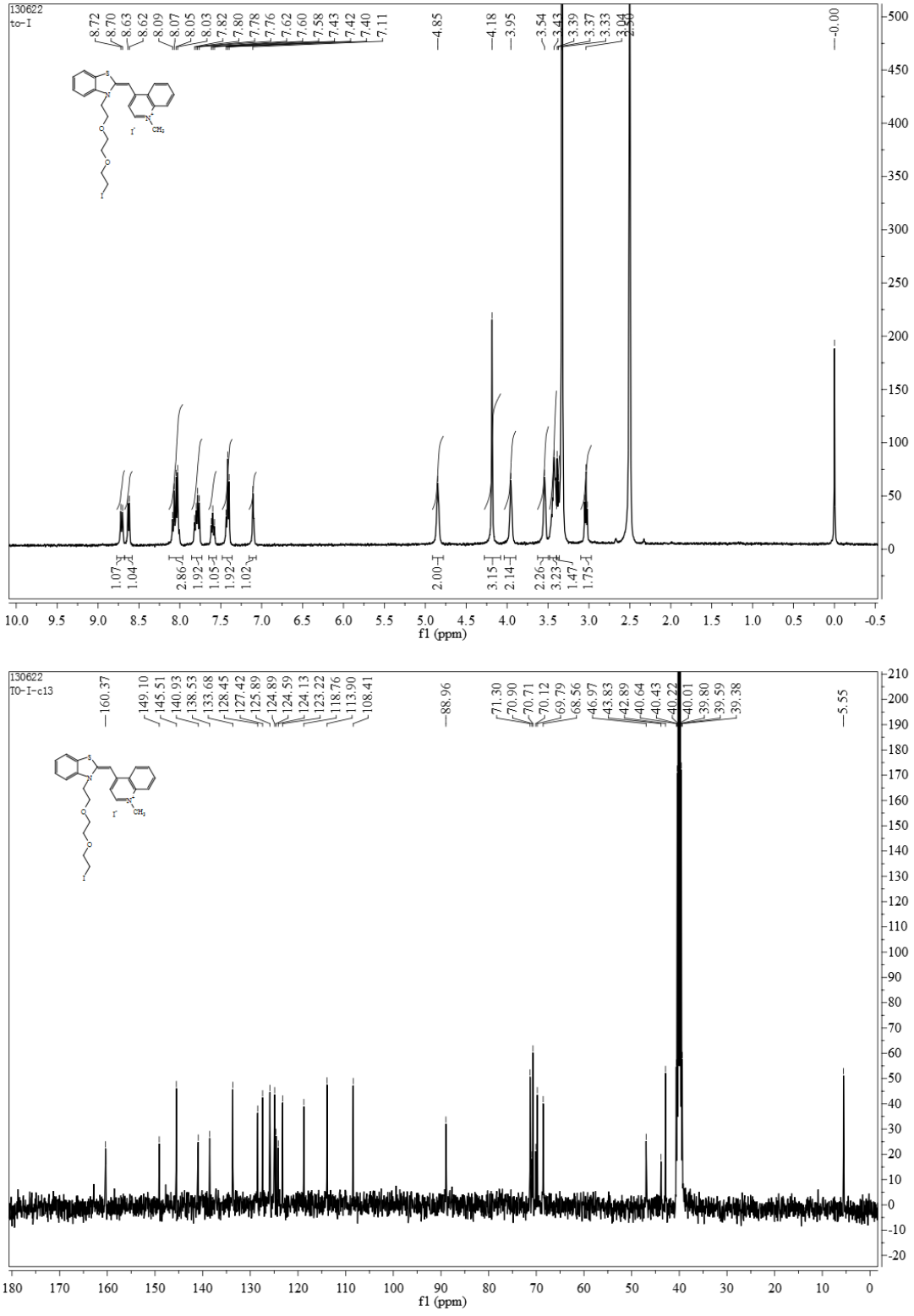


Fig. S25 ^{1}H NMR and ^{13}C NMR spectra of TO in DMSO-d6

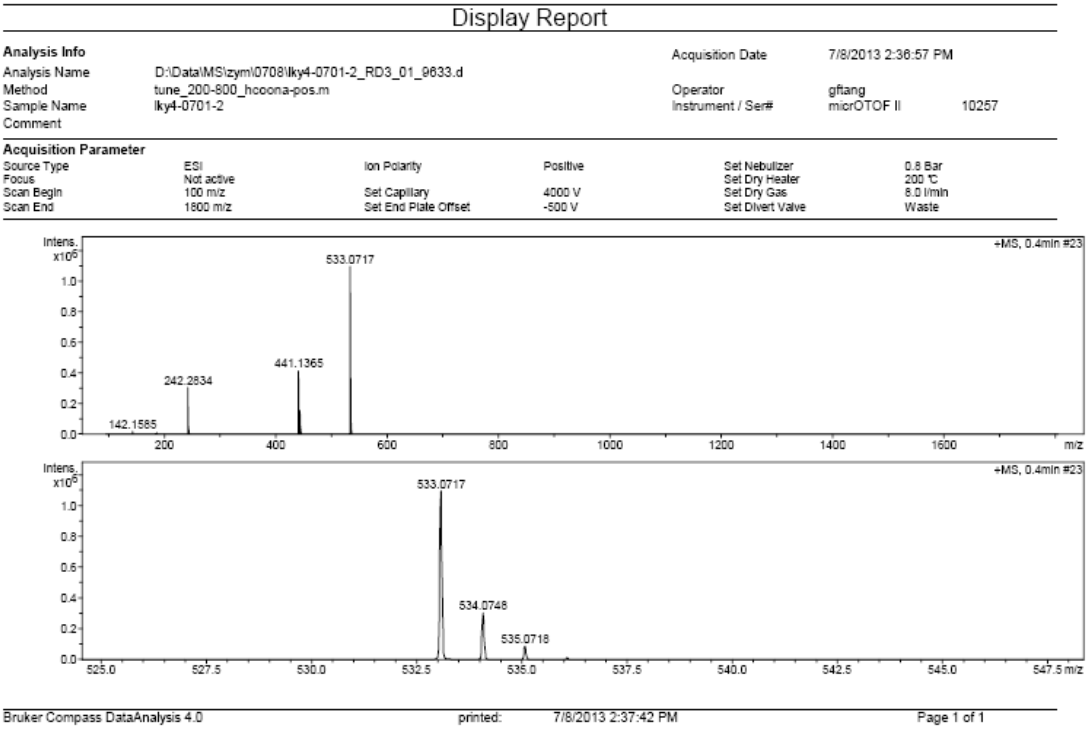


Fig. S26 HRMS of TO

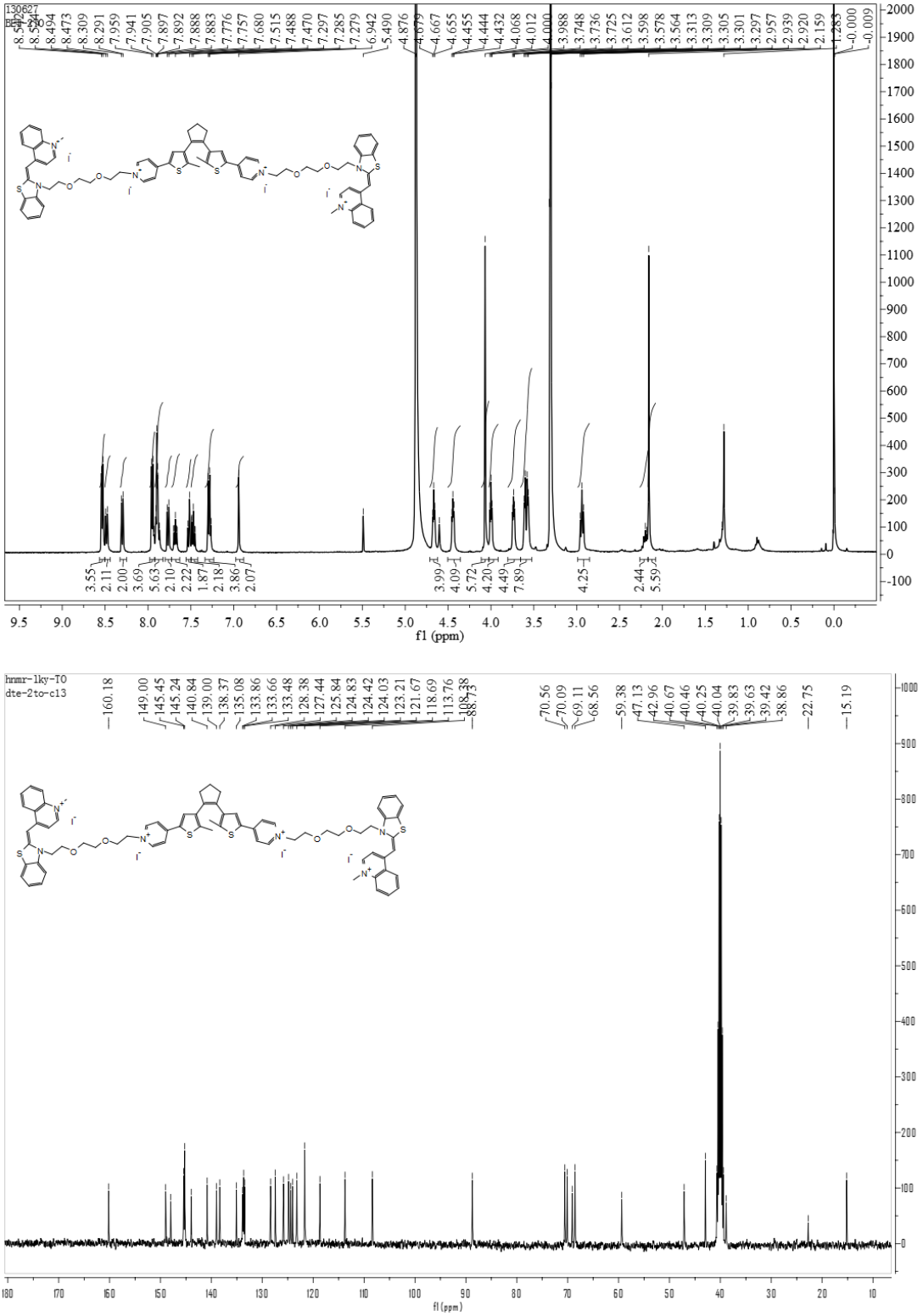


Fig. S27 ^{1}H NMR (CD_3OD) and ^{13}C NMR spectra of **1** (DMSO-d6)

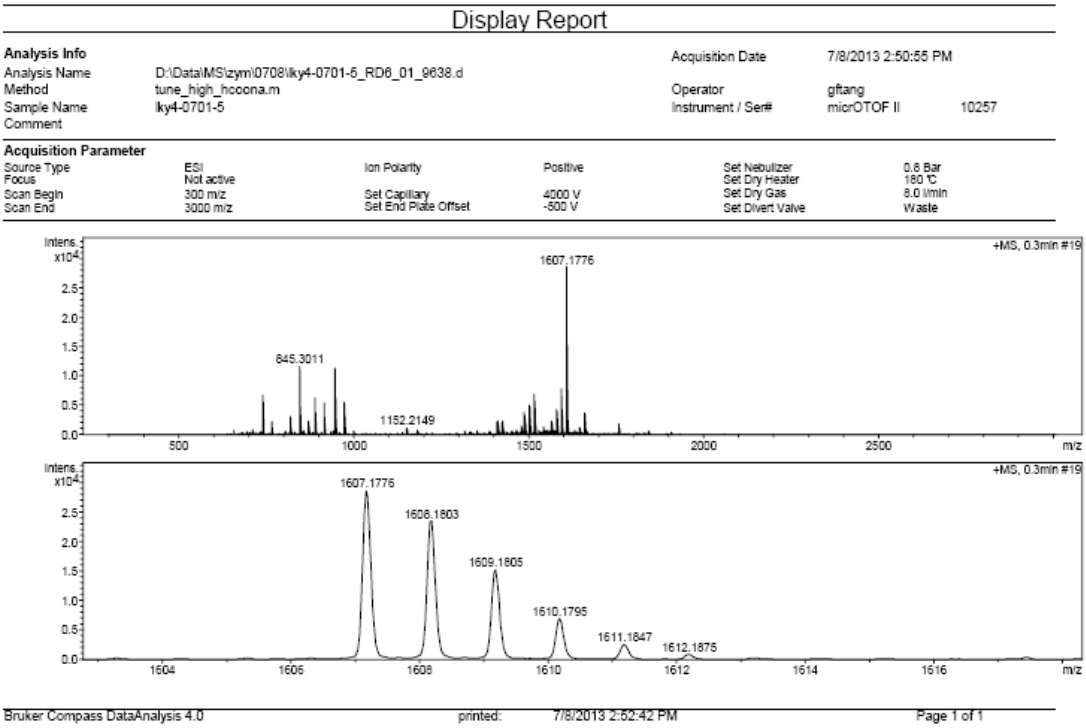


Fig. S28 HRMS of **1**

13. References

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