Electronic Supplementary Information for

Synthesis and photochromism of a *turn-on* fluorescent diarylethene having benzo[*b*]selenophene groups as the aryl units

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Other Supplementary Files:

1) Supplementary Video S1. Fluorescence photoswitching of 1Ha in *n*-hexane.

Upon irradiation with 313 nm UV light, yellow-colored fluorescence immediately appeared under excitation with 365 nm light. Then, the fluorescence completely disappeared upon irradiation with >430 nm visible light.

2) CIF files for compounds 1F' and 1Ha.

1. General

General chemicals were purchased from Tokyo Chemical Industry (TCI), Wako Pure Chemicals, or Sigma Aldrich Chemical Co., and used without further purification. ^{1}H-NMR (400 MHz) spectra and ^{13}C-NMR (100 MHz) were recorded on JEOL JNMEX400 spectrometer with tetramethylsilane (TMS) as the internal standard. Mass spectra were measured with a mass spectrometer (Autoflex Speed, Bruker). High-resolution mass spectra (HRMS) were measured on a JEOL AccTOF LC mass spectrometer. UV-vis absorption spectra were recorded on a Hitachi U-3310 spectrophotometer. Fluorescence spectra were measured with a Hitachi F-7000 fluorescence spectrophotometer. The quantum yields of photocyclization and photocycloreversion reactions were determined by comparing the reaction rates of samples and **2F** with the standard procedure,[S1] where the quantum yields were measured at a small percentage of conversion by observing the initial rate of absorbance changes ($\Delta A/\Delta t$) at the absorption maxima of the closed-ring isomer. The fluorescence quantum yield of **1Hb** in *n*-hexane was determined using 4-[4-(diphenylamino)phenyl]-7-(4-tolyl)-2,1,3-benzothia-diazole (Φ_f = 0.86 in cyclohexane)[S2] as the reference. The fluorescence quantum yield of **1Hb** in the solid state was determined with an absolute photoluminescence quantum yield spectrometer (C9920-02, Hamamatsu). Irradiation experiments were carried out in a quartz cuvette using a Xe lamp (MAX-303, Asahi Spectra) equipped by narrow band interference filters (Semrock) or a monochromator (Horiba JobinYvon). The isolation of the photo-generated closed-ring isomer was performed with HPLC (ELITE LaChrom system, HITACHI) equipped with HITACHI L-2455 diode array detector, silica gel column (Wakosil-5SIL, Wako), using hexane as the eluent. UV and visible irradiations were carried out with a UV-LED irradiation system (LIGHTNINGCURE, LC-LIV3, Hamamatsu) and a 300 W xenon lamp (MAX-303, Asahi Spectra).

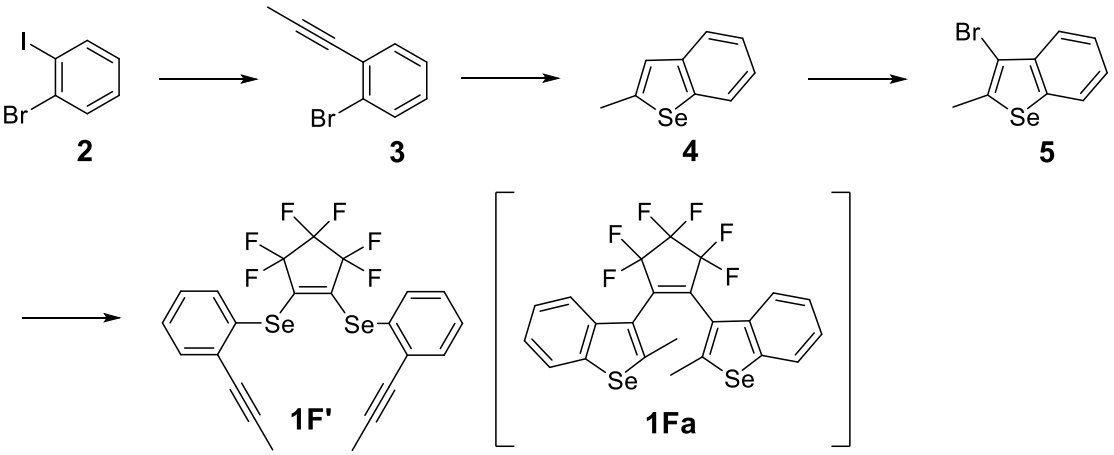
Single crystal X-ray crystallographic analysis was conducted using a Rigaku VariMax diffractometer with MoKα radiation (λ = 0.71073 Å) or a Rigaku XtaLAB Synergy-S diffractometer with CuKα radiation (λ =1.54184 Å). The crystal structures were solved by a direct method using SHELXS-97 and refined by the full-matrix least-squares method for F^2 with anisotropic displacement parameters for non-hydrogen atoms using SHELXL-2014.

The ps time-resolved emission measurements were performed by a 1 kHz Ti: Sapphire regenerative amplifier and a Time-correlated single photon counting (TCSPC) system. The sample was excited by the 430 nm pulse, generated by an optical parametric amplifier. Emission of the sample at the right angle to the excitation beam was detected by a single photon avalanche diode (MPD, PD-050-CTD) coupled with a spectrometer (Teledyne Princeton Instruments, SP2150). The detected photon signals were taken by the TCSPC module (Becker & Hickles, SPC130EM). The relative polarization between the excitation pulse and the detected emission was set to the magic angle of 54.7°, and the excitation intensity was set to 1 μW (1.0 nJ/pulse). The instrument response function of the system was approximately 20 ps. The measurements were performed at room temperature (296 K). The emission decay profile was fitted by a single exponential function convoluted with the IRF.

2. Synthesis

The synthetic route to **1Fa** and **1Ha** are illustrated in Scheme S1 and Scheme S2. Detailed synthetic procedures of these molecules are described below. The starting compound, 1-bromo-2-iodobenzene (**2**) was purchased from TCI. 1-Bromo-2-(prop-1-yn-1-yl)benzene (**3**) and 2-methylbenzo[*b*]selenophene (**4**) were prepared according to the procedures reported by Kashiki et al.[S3] and the NMR and MS data were identical with the literature[S4].

Scheme S1



Compound 5 (3-bromo-2-methylbenzo[*b*]selenophene)

To a solution of compound **4** (1.0 g, 5.1 mmol) in a mixture of chloroform (21 mL) and acetic acid (21 mL) was added NBS (1.0 g, 5.1 mmol) in several portion and stirred at room temperature for 12 h. The reaction was stopped by addition of water and the reaction mixture was extracted with chloroform. The organic layer was washed with saturated ammonium chloride aqueous solution, separated, dried over anhydrous Na_2SO_4 and filtrated. After that, the solvent was removed by evaporation and the residue was purified by silica gel column chromatography (hexane) to give 1.0 g (4.0 mmol) of **5** in 73% yield as a white powder.

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 2.62 (s, 3H), 7.26 (t, *J* = 7.7 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.77 (d, *J* = 8.2 Hz, 2H); Elemental analysis: Found: C, 39.47; H, 2.55 Anal. Calcd. for C_9H_7BrSe: C, 39.43; H, 2.57.

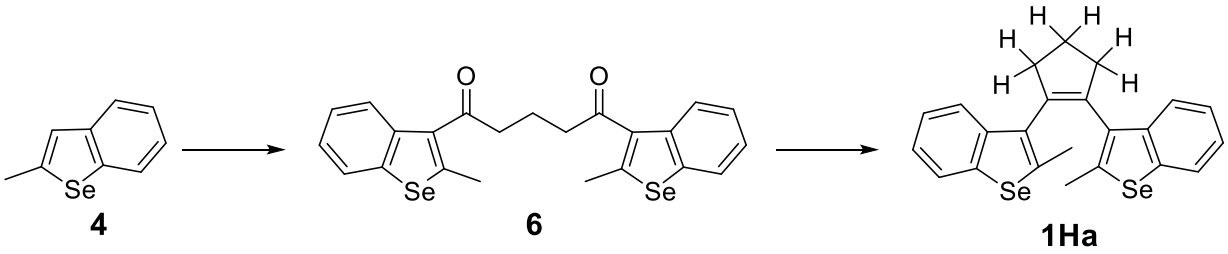
Synthesis of 1F'

1.6 M *n*-Butyllithium (*n*-BuLi) hexane solution (2.6 mL, 4.6 mmol) was slowly added to a solution of compound **5** (1.0 g, 4.0 mmol) in dry THF (37 mL) at −78 ºC under Ar atmosphere, and then stirred for 1 h at this temperature. Octafluorocyclopentene (243 μL, 4.0 mmol) was dissolved in dry THF (1 mL) and slowly added to the reaction mixture at −78 ºC, and the mixture was stirred for 2 h at this temperature. After warming to room temperature, the reaction was stopped by addition of water and the reaction mixture was extracted

with ethyl acetate. The organic layer was separated, washed with brine, dried over anhydrous Na_2SO_4, and filtrated. The solvent was removed by evaporation and the residue was purified by silica gel column chromatography (*n*-hexane) to give 400 mg (0.7 mmol) of **1F'** in 18% yield as a white powder.

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 2.08 (s, 6H), 7.20 (t, J = 7.8 Hz, 2H), 7.30 (d, J = 7.6 Hz, 2H), 7.45 (t, J = 6.9 Hz, 4H); HRMS (Positive ESI) Calcd for $C_{23}H_{15}F_6Se_2$ m/z = 564.94084; Found 564.94103. $[M+H]^+$; Elemental analysis: Found: C, 49.15; H, 2.52. Anal. Calcd. for $C_{23}H_{14}F_6Se_2$: C, 49.13; H, 2.51.

Scheme S2



Synthesis of compound 6

Aluminum chloride (650 mg, 4.9 mmol) was added to a mixture solution of compound **4** (950 mg, 4.9 mmol) and glutaryl chloride (300 μL, 2.5 mmol) in dry dichloromethane (12 ml) in several portions at ice bath. This mixture was stirred at room temperature. After 5 h, reaction solution was poured into ice water and neutralized with potassium carbonate aqueous solution. After extraction with dichloromethane, the organic layer was washed with brine, separated, dried over anhydrous Na_2SO_4 and then the solvent was removed in vacuo. The residue was used next reaction without further purification. (Yield: 950 mg, 80%)

Synthesis of 1Ha

THF (3 mL) and Zn dust (270 mg) were placed in a three-necked flask under nitrogen. $TiCl_4$ (330 μL, 0.3 mmol) was added very cautiously using a glass syringe. The solution turned yellow and was refluxed for 45 min. Next it was cooled in an ice bath and **6** (950 mg, 2.0 mmol) was added in portions. This mixture was refluxed for 3 h, subsequently quenched with 10% aq. K_2CO_3 and extracted with EtOAc. The combined organic layers were washed with water, dried over anhydrous Na_2SO_4 and the solvent was removed in vacuo. The compound was purified by column chromatography (hexane/EtOAc = 5/1) and recrystallized from *n*-hexane to yield (100 mg, 11%) of a white solid.

The antiparallel (ap) and parallel (p) conformations exist in a ratio of 2:1 as determined by the following ^{1}H-NMR. ^{1}H-NMR (400 MHz, $CDCl_3$) for ap-conformer, δ (ppm): 1.99 (s, 6H, -CH_3), 2.26 (quin, J = 6.9 Hz, 2H, -CH_2-), 2.68 (quin, J = 7.3 Hz, 2H, -CH_2-), 3.19 (quin, J = 7.1 Hz, 2H, -CH_2-), 7.18 (t, J = 7.3 Hz, 2H, Ar-H), 7.33 (t, J = 7.3 Hz, 2H, Ar-H), 7.64 (d, J = 7.8 Hz, 2H, Ar-H), 7.72 (d, J = 7.3 Hz, 2H, Ar-H); ^{1}H-NMR (400 MHz, $CDCl_3$) for p-conformer, δ (ppm): 2.26 (quin, J = 6.9 Hz, 1H, -CH_2-), 2.44 (s, 3H, -CH_3), 2.82-2.89 (m, 2H, -CH_2-), 2.97-3.00 (m, 1H, -CH_2-), 7.05 (br, 2H, Ar-H), 7.50 (br, 1H, Ar-H), 7.62 (br, 1H,

Ar-H): ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 17.41, 23.98 (p), 24.14 (ap), 37.66 (ap), 37.87 (p), 123.56 (ap), 123.77 (p), 124.03 (ap), 124.31(ap), 124.42 (p), 124.98 (p), 125.32 (ap), 133.06 (ap), 133.68 (p), 138.04 (p), 138.57 (ap), 139.15 (p), 139.43 (p), 139.57 (ap), 139.93 (ap), 141.61 (ap), 141.89 (ap); HRMS (Positive ESI) Calcd for $C_{23}H_{21}Se_2$ m/z = 456.99737; Found 456.99742. $[M+H]^+$; Elemental analysis: Found: C, 60.84; H, 4.46. Anal. Calcd. for $C_{23}H_{20}Se_2$: C, 60.80; H, 4.44.

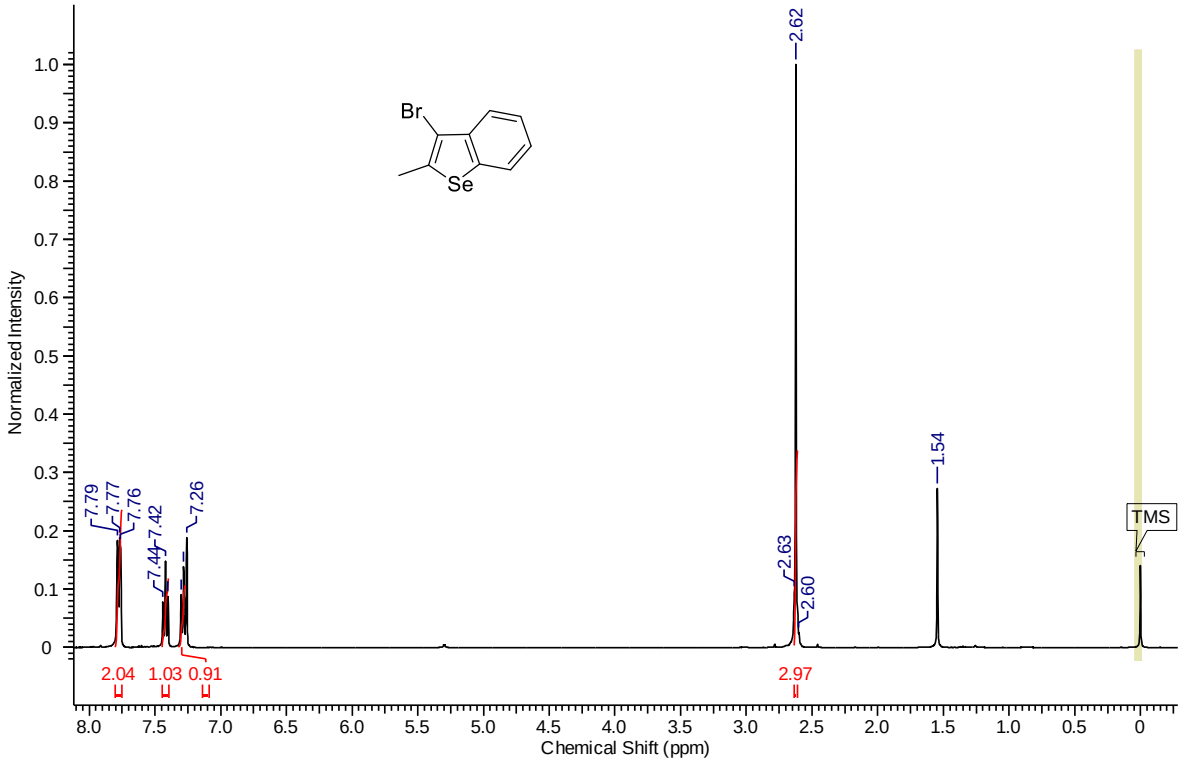
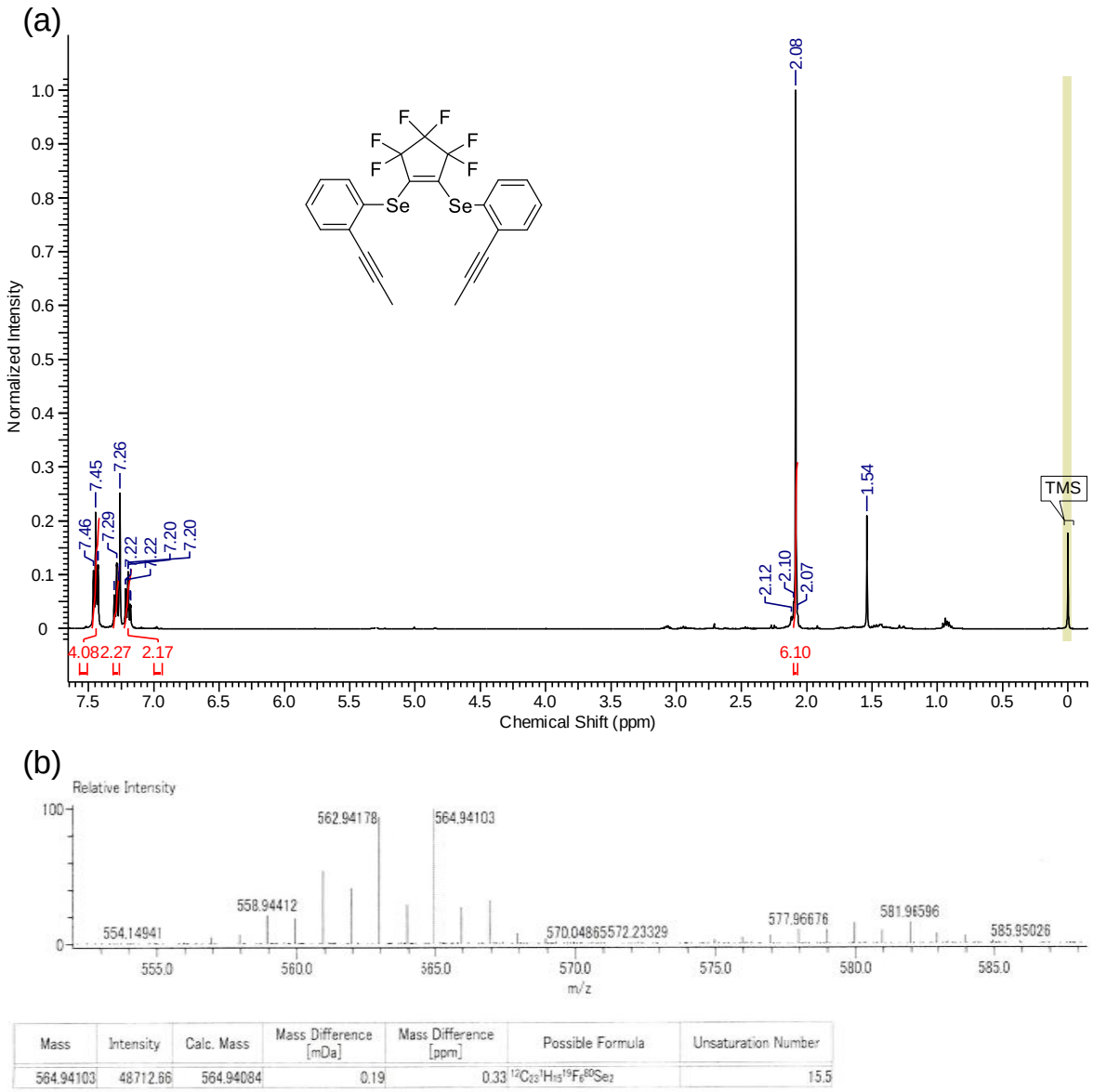


Figure S1 (a) ^{1}H-NMR spectrum of compound **5** (3-bromo-2-methylbenzo[*b*]selenophene).



Mass	Intensity	Calc. Mass	Mass Difference [mDa]	Mass Difference [ppm]	Possible Formula	Unsaturation Number
564.94103	48712.66	564.94084	0.19	0.33	$^{12}C_{23}{}^{1}H_{15}{}^{19}F_{6}{}^{80}Se_{2}$	15.5

Figure S2 (a) ^{1}H-NMR and (b) HRMS spectra of compound **1F'**.

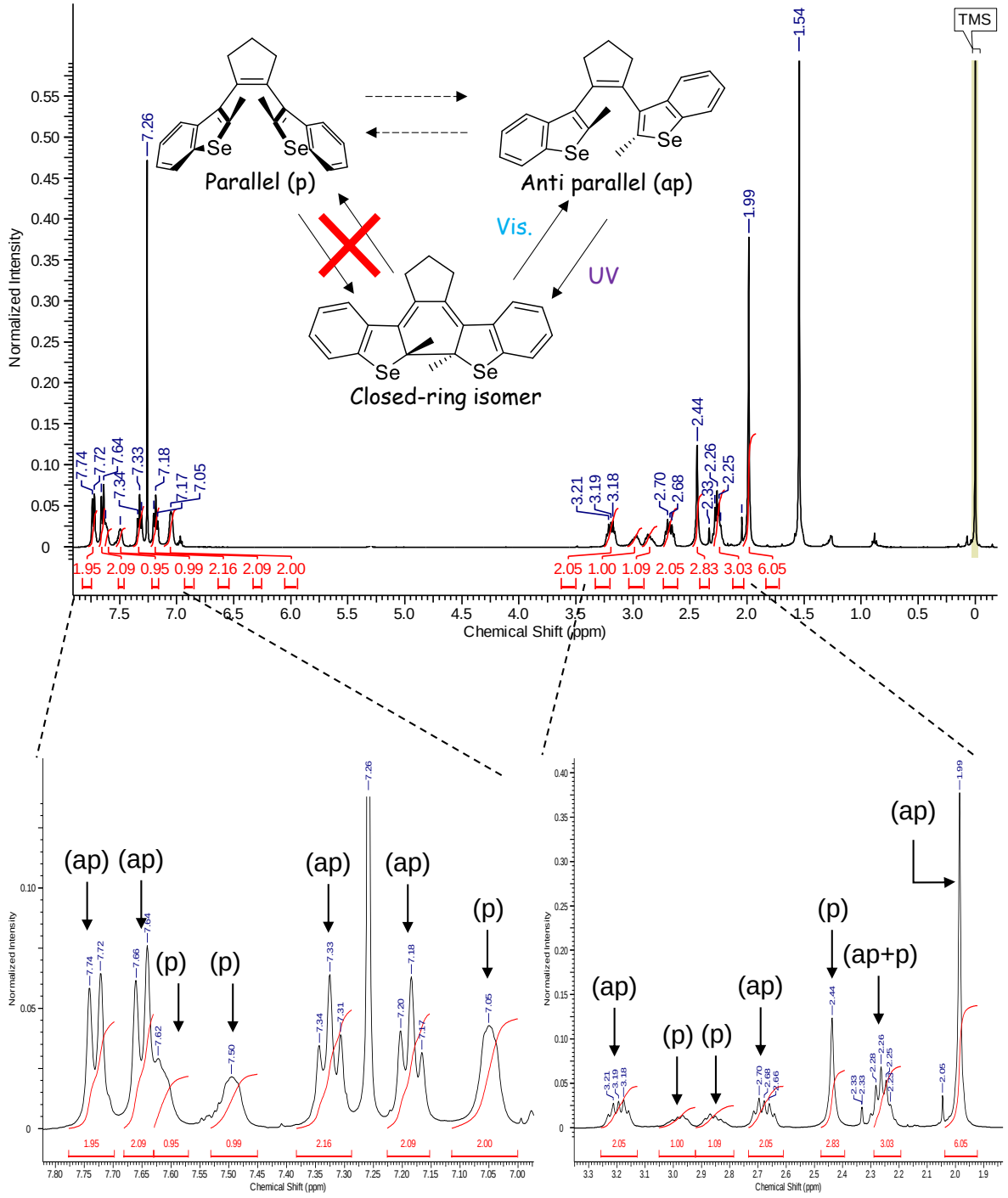
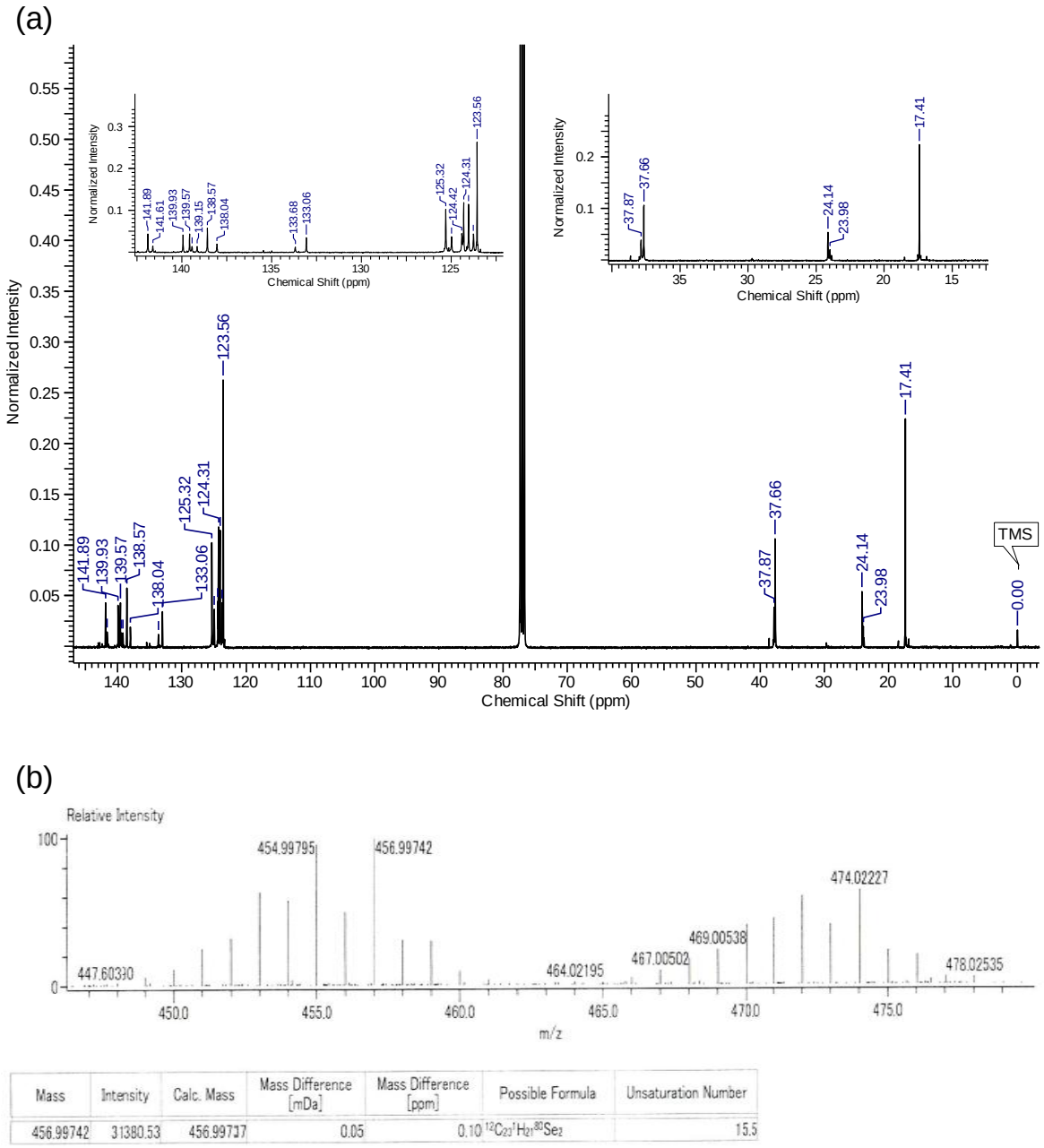


Figure S3 ^{1}H-NMR spectrum of compound **1Ha**.



Mass	Intensity	Calc. Mass	Mass Difference [mDa]	Mass Difference [ppm]	Possible Formula	Unsaturation Number
456.99742	31380.53	456.99737	0.05	0.10	$^{12}C_{23}{}^{1}H_{21}{}^{80}Se_2$	15.5

Figure S4 (a) ^{13}C-NMR and (b) HRMS spectra of compound **1Ha**.

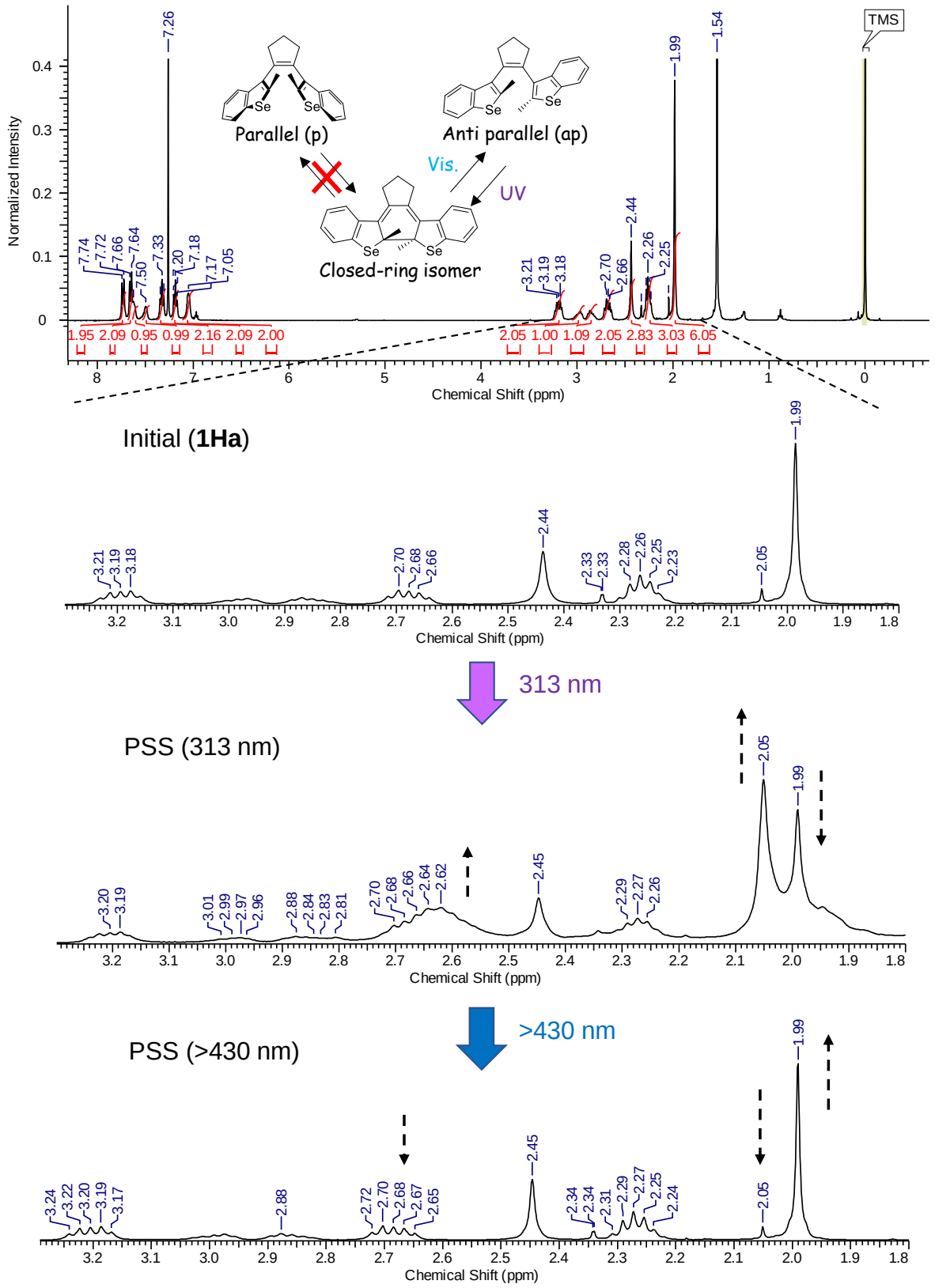


Figure S5 ^{1}H-NMR spectral changes of **1Ha** upon alternate irradiation with 313 nm and >430 nm light in $CDCl_3$.

3. X-ray crystallographic analysis

Table S1 Crystallographic data for **1F'** and **1Ha**

	1F'	**1Ha**
Formula	$C_{23}H_{14}F_6Se_2$	$C_{23}H_{20}Se_2$
Formula weight	562.30	454.36
T/K	100	100
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pbca*	$P2_12_12_1$
a/Å	13.7002(3)	9.0615(2)
b/Å	21.4550(5)	11.8873(3)
c/Å	27.9931(7)	17.2354(5)
α/°	90	90
β/°	90	90
γ/°	90	90
V/Å^3	8228.2(3)	1856.54(8)
Z	16	4
Density/g cm^{-3}	1.816	1.625
Goodness-of-fit on F^2	1.098	1.007
R_1 ($I > 2\sigma(I)$)	0.0355	0.0419
wR_2 ($I > 2\sigma(I)$)	0.0718	0.1087
R_1 (all data)	0.0494	0.0431
wR_2 (all data)	0.0768	0.1103
CCDC No.	2420104	2420105

4. Thermal stability and photoswitching cycle durability of 1H

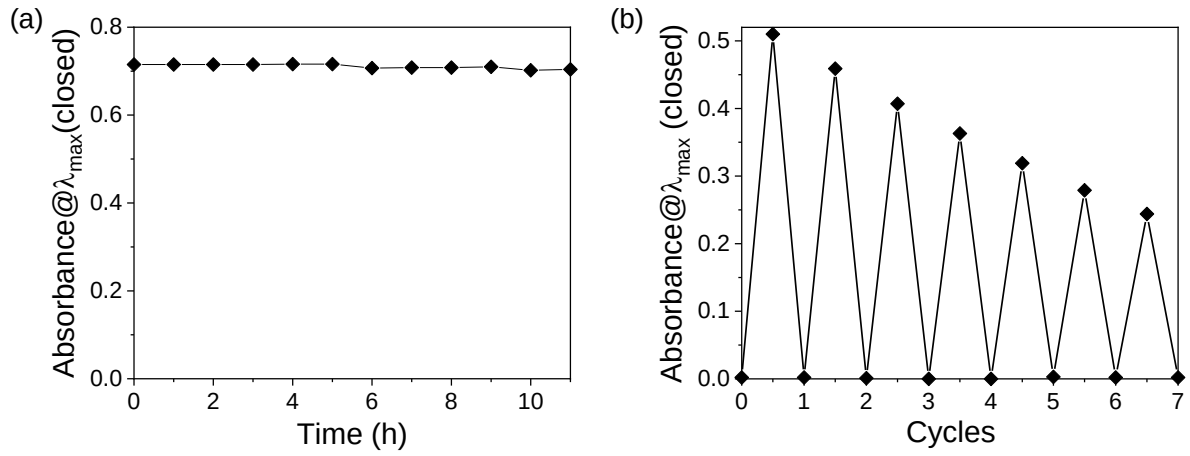


Figure S6 (a) Change in the absorbance at 448 nm corresponding to **1Hb** in toluene at 60 ºC under dark condition. (b) Change in the absorbance at 448 nm (corresponding to **1Hb**) in *n*-hexane upon alternate irradiation with 313 nm and >430 nm light.

5. Fluorescence spectra of 1H in *n*-hexane under excitation with 313 nm light

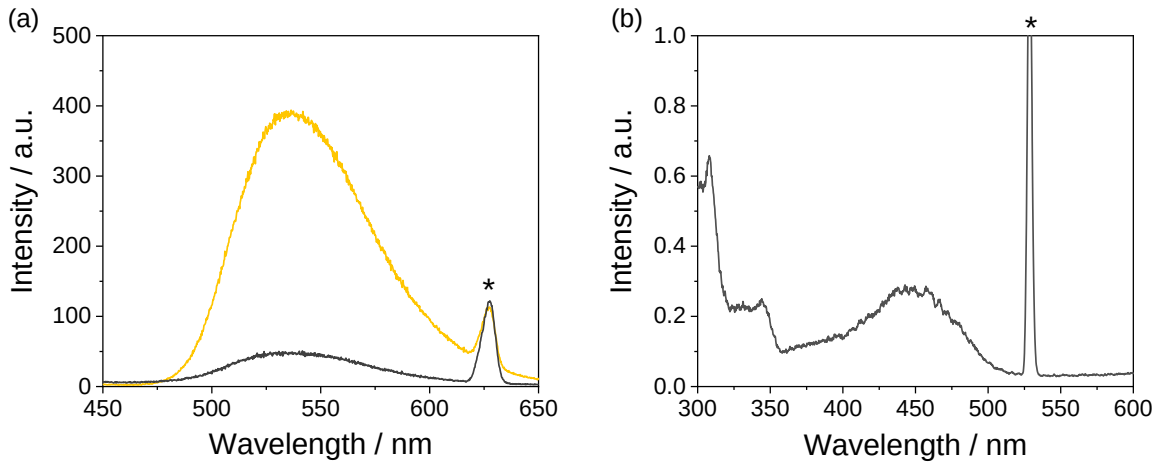


Figure S7 (a) Fluorescence spectra of **1H** in *n*-hexane under excitation with 313 nm light: open-ring isomer (black solid-line) and closed-ring isomer (yellow solid-line). "*" represents the second harmonic signal of the excitation light. (b) Excitation spectrum corresponding to the black-line in the fluorescence spectrum of Figure S7a. "*" represents the monitor wavelength.

6. Photochromism and fluorescence photoswitching of 2Ha in *n*-hexane

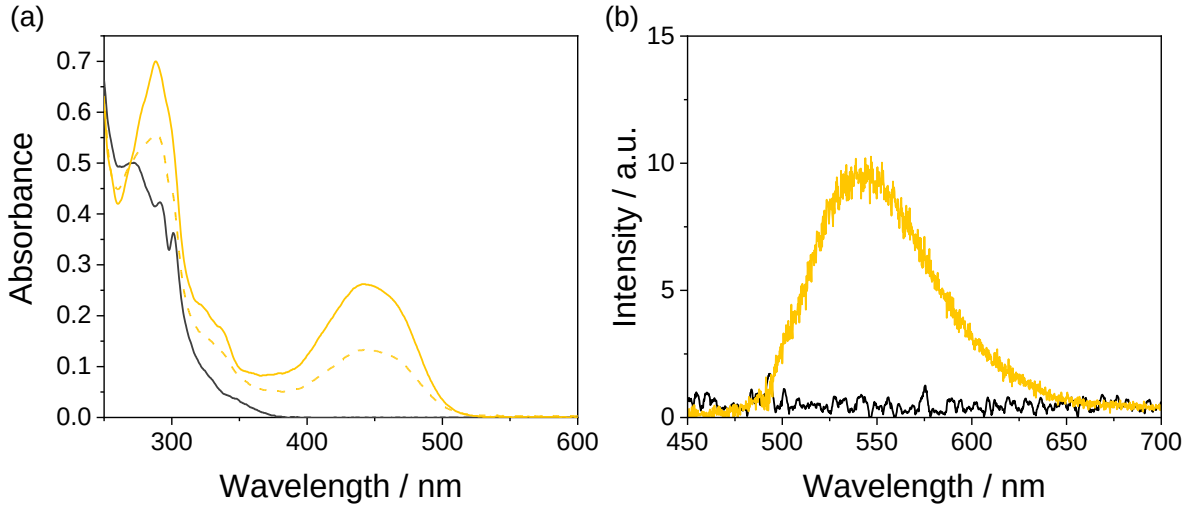


Figure S8 (a) Absorption spectra of **2H** in *n*-hexane: open-ring isomer (black solid-line), closed-ring isomer (yellow solid-line), and PSS under irradiation with 313 nm light (yellow dashed-line). (b) Fluorescence spectra of **2H** in hexane under excitation with 365 nm light: open-ring isomer (black solid-line) and closed-ring isomer (yellow solid-line).

7. Fluorescence lifetime of 1Hb in *n*-hexane

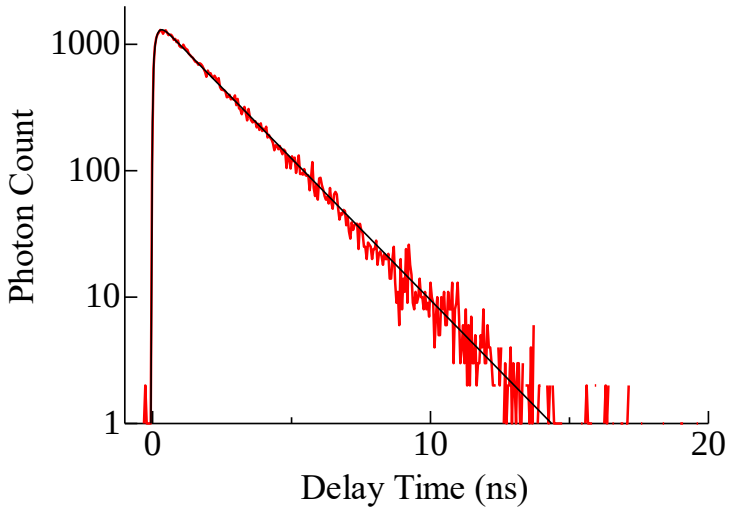


Figure S9 Emission decay profile detected at 530 nm for **1Hb** under excitation with 430 nm light (1 μW, 1 nJ/pulse) in *n*-hexane.

8. Fluorescence spectra of 1H in the solid powder state

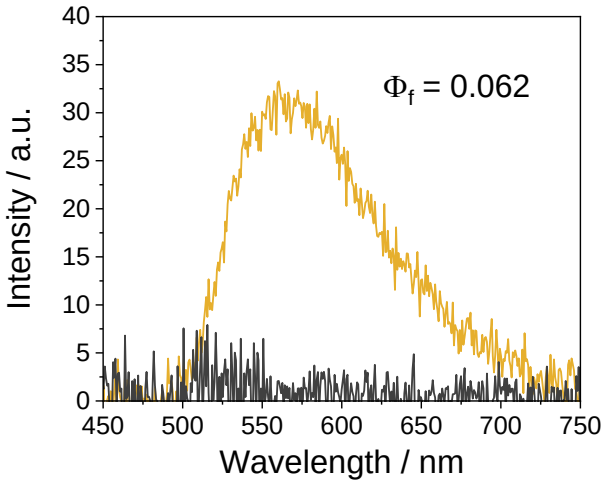


Figure S10 Fluorescence spectra of **1H** under excitation with 365 nm light in the solid powder: open-ring isomer (black solid-line) and PSS (yellow solid-line).

9. Summary of optical and photochromic properties of 1H

Table S2 Absorption, fluorescence and photochromic properties of **1H**, **2H**, and **2F** in *n*-hexane.

	Absorption		Fluorescence	Φ_{ab}[a]	Φ_{ba}[b]	Φ_f[c]
	Open-ring ε, $M^{-1}cm^{-1}$ (λ_{max})	Closed-ring ε, $M^{-1}cm^{-1}$ (λ_{max})	Closed-ring λ_{max}, nm			
1H	10700 (307 nm)	9800 (448 nm)	537	0.46	0.17	0.14
2H[d]	14600 (266 nm)	11400 (442 nm)	546	0.34	0.33	0.0049
2F[e]	15200 (258 nm)	10000 (516 nm)	n.d.	0.31	0.29	n.d.

a: Cyclization quantum yield, *b*: cycloreversion quantum yield, *c*: fluorescence quantum yield of the closed-ring isomer, *d*: data are extracted from ref. S5, *e*: data are extracted from ref. S1.

10. References

S1) T. Sumi, Y. Takagi, A. Yagi, M. Morimoto and M. Irie, *Chem. Commun.*, 2014, **50**, 3928.

S2) T. Ishi-i, K. Ikeda, M. Ogawa and Y. Kusakaki, *RSC Adv.*, 2015, **5**, 89171.

S3) T. Kashiki, S. Shinamura, M. Kohara, E. Miyazaki, K. Takimiya, M. Ikeda and H. Kuwabara, *Org. Lett.*, 2009, **11**, 2473.

S4) H. Sashida, K. Sadamori and T. Tsuchiya, *Synth. Commun.*, 1998, **28**, 713.

S5) T. Yamaguchi, M. Hosaka, K. Shinohara, T. Ozeki, M. Fukuda, S. Takami, Y. Ishibashi, T. Asahi and M. Morimoto, *J. Photochem. Photobiol. A*, 2014, **285**, 44.