Electronic Supplementary Information

A thermoresponsive fluorophore based on a photochromic diarylethene having donor-acceptor moieties

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1. Experimental details

General

^{1}H and ^{13}C NMR Spectrum was recorded in duteriochloroform ($CDCl_3$) on 500 MHz NMR spectrometers (DRX500, Bruker and ECA500, JEOL). *J* values are expressed in Hz and quoted chemical shifts are in ppm. Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet, m, multiplet. High-resolution mass spectrum was measured by an electrospray ionization mass spectroscopy (NanoFrontierLD, Hitachi High-Technology). Melting points were measured using a Yazawa BY-2 hot stage microscope, and those were uncorrected.

Optical Measurements

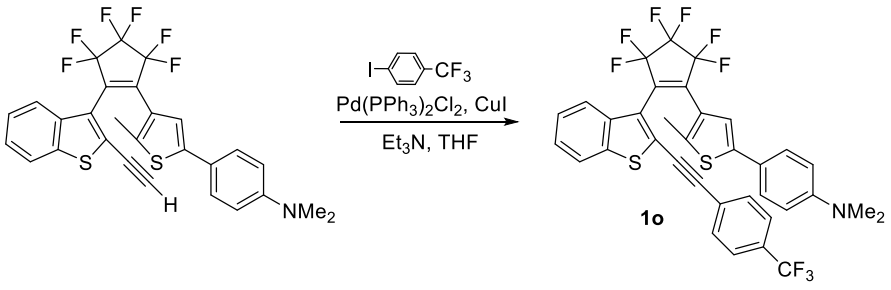
Absorption spectra of **1o** in toluene (2.07×10^{-5} mol dm^{-3}) were measured on a UV-visible spectrophotometer (V-550, JASCO). Fluorescence spectra of **1o** in toluene (2.05×10^{-5} mol dm^{-3}) were measured on a spectrofluorometer (FP-8300, JASCO). Photochemical reaction was carried out in a quartz cell with 10 nm optical path length. Photoirradiation with 366 nm light was carried out using a 500 W high-pressure mercury lamp (USHIO USH-500D), separated by filters (a 5 cm water filter, a 5 cm $CuSO_4$ aq filter, a UV-35 filter and a UV36A filter). Photoirradiation with 578 nm light was carried out using a 500 W xenon lamp (USHIO, UXL-500D), separated by filters (a 5 cm water filter, an O-57 glass filter and a KL-56 glass filter). High performance liquid chromatography equipped with a UV/Vis detector (X-LC 3070UV, JASCO) and a silica gel column (ZORBAX Rx-Sil RRHT, Agilent) was used to determine the concentration of isomers during photoirradiation. Photocyclization and photo cycloreversion quantum yields were determined with the procedures described eleswere.[1)]

Computational Details

DFT geometry optimization and the energy calculation of **1o** and **1o-H**$^{+}$ were carried out with the Spartan'18 (Wavefunction) employing the three-parameter hybrid functional of Becke based on the correlation functional of Lee, Yang and Parr (B3LYP). The 6-31G* basis sets were used for all atoms.

2. Synthesis details

2-1. Synthesis of **1o**



A solution of 4-(4-(2-(2-ethynylbenzo[b]thiophen-3-yl)-3,3,4,4,5,5-hexafluorocyclopent-1-en-1-yl)-5-methylthiophen-2-yl)-N,N-dimethylaniline[2)] (49.0 mg, 0.09 mmol, 1.0 eq), 1-iodo-4-(trifluoromethyl)benzene (0.02 mL, 0.14 mmol, 1.5 eq), $Pd(PPh_3)_2Cl_2$ (3.6 mg, 0.02 mmol, 0.2 eq) and CuI (7.9 mg, 0.01 mmol, 0.1 eq) in Et_3N (1 mL) and THF (1 mL) was stirred for overnight at room temperature. The reaction was quenched by adding 3 mol dm^{-3} aq.HCl, and the resultant mixture was extracted with ethyl acetate. The combined organic layer was dried over anhydrous Na_2SO_4, the drying agent filtered off, and evaporated. The residue was purified by column chromatography on silica gel using ethyl acetate/ hexane (3 %) as the eluent, to give 38.8 mg (0.056 mmol) of **1o** as a pale yellow solid in 63% yield.

^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ/ppm: 1.85 (3H, s) 2.95 (6H, s) 6.55 (2H, d, J=8.83 Hz) 6.90 (1H, s) 7.00 (2H, d, J=6.74 Hz) 7.46 (2H, m) 7.52 (2H, d, J=8.50 Hz) 7.57 (2H, d, J=8.20 Hz) 7.74 (1H, d, J=7.57 Hz) 7.81 (1H, m).
^{13}C NMR (125 MHz, $CDCl_3$, TMS) δ/ppm: 14.76, 40.41, 83.48, 98.01, 112.31, 120.36, 121.56, 122.42, 122.85, 123.37, 123.42, 124.69, 125.02, 125.09, 125.55, 125.57, 125.60, 125.63, 125.87, 126.36, 126.62, 128.65, 130.71 (q), 131.98, 136.65, 139.57, 142.47, 150.14.
ESI-MS $[M]^+$: calcd. for $C_{35}H_{23}NF_9S_2$: 692.1123; found: 692.1203.
IR (neat) ν/ cm^{-1}: 513, 537, 584, 729, 753, 809, 843, 892, 954, 975, 1016, 1064, 1075, 1101, 1127, 1167 1190, 1258, 1276, 1320, 1340, 1485, 1523, 1609, 2319, 2352, 2370, 2801, 2855, 2894, 2925, 2958.
M.p. = 161.1-162.2 ºC.

3. Experimental data

3-1 ^{1}H NMR spectrum of **1o**

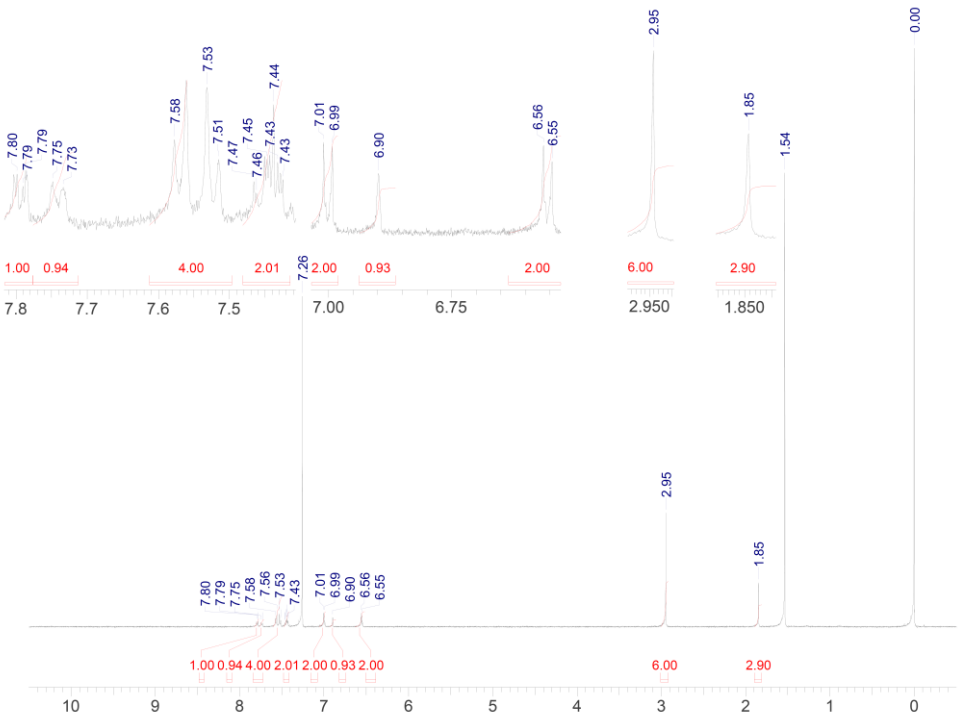


Fig. S1 ^{1}H NMR spectrum of **1o**.

3-2 ^{13}C NMR spectrum of **1o**

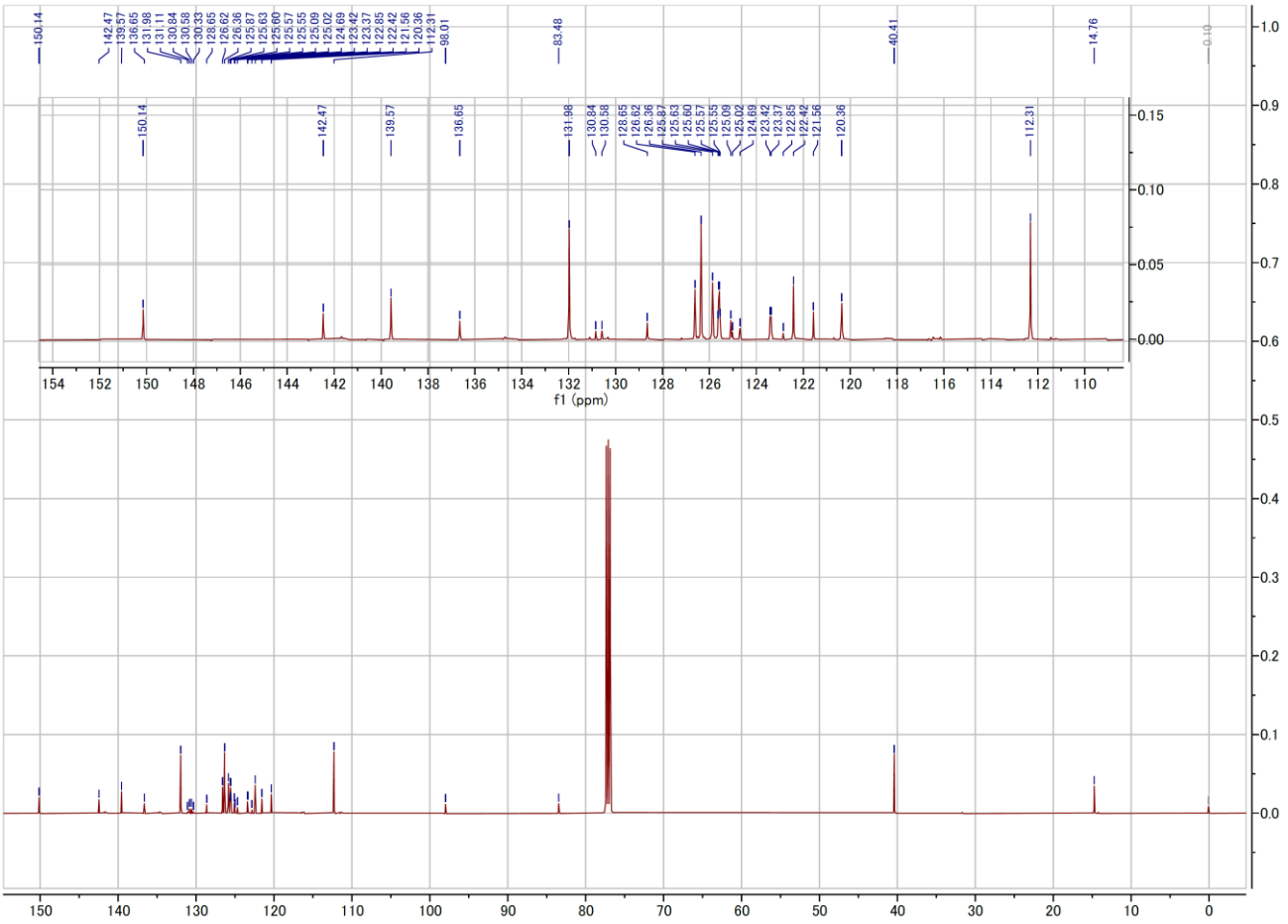


Fig. S2 ^{13}C NMR spectrum of **1o**.

3-3 ESI-Mass spectrum of **1o**

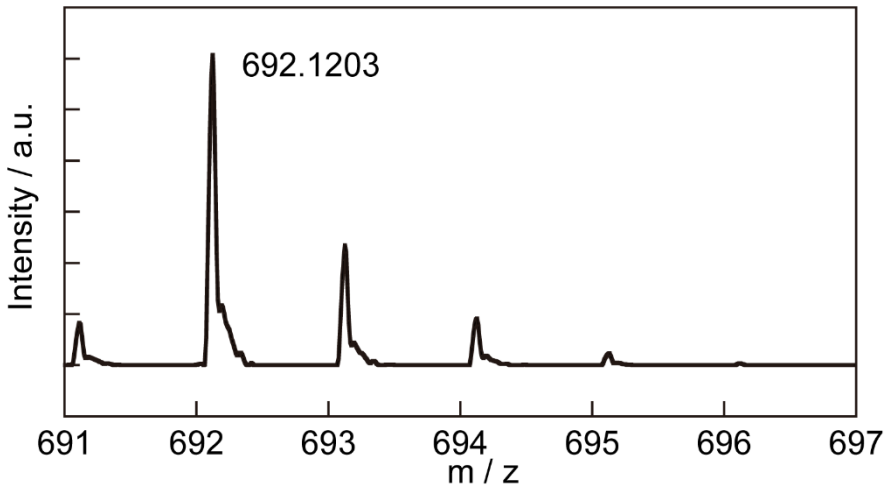


Fig. S3 ESI-Mass spectrum of **1o**.

3-4 Fluorescence spectral change of **1o**

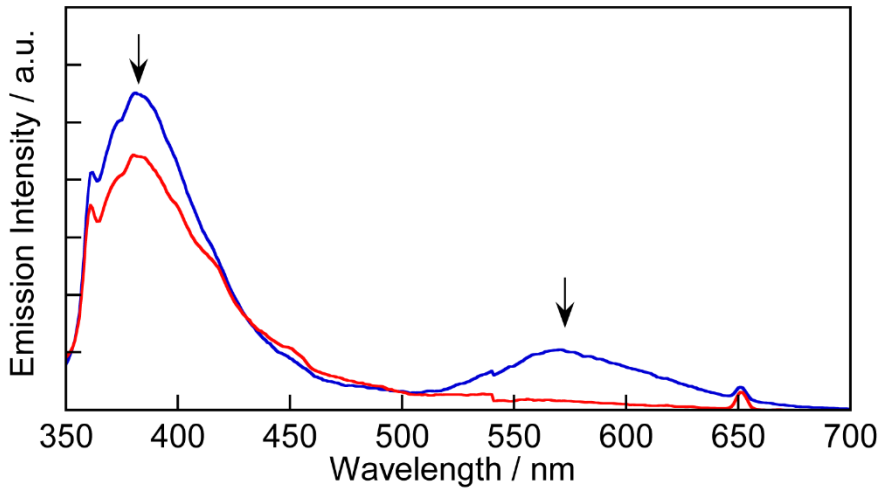


Fig. S4 Fluorescence spectral change of **1o** (blue line) and **1** in **pss** (red line) in toluene (2.05×10^{-5} mol dm^{-3}) upon irradiation with a 366 nm light. Excitation wavelength: 326 nm.

3-5 DFT calculation results of **1o** and **1o-H**$^+$

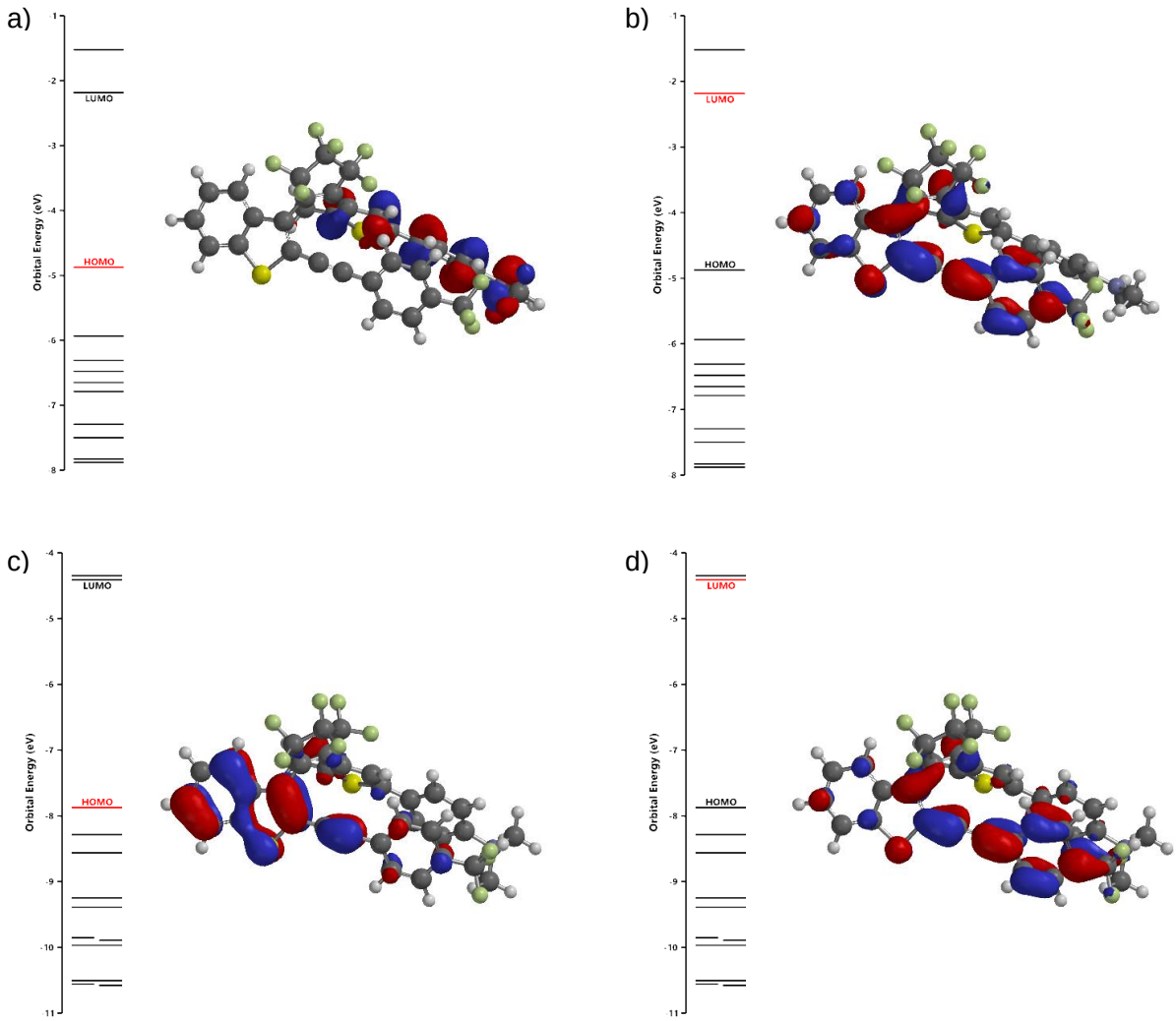


Fig. S5 HOMO and LUMO of **1o** and **1o-H**$^+$ calculated at B3LYP/6-31G* level.

a) HOMO of **1o**. b) LUMO of **1o**. c) HOMO of **1o-H**$^+$. d) LUMO of **1o-H**$^+$.

3-6 Fluorescence spectrum of **1o-H**$^+$

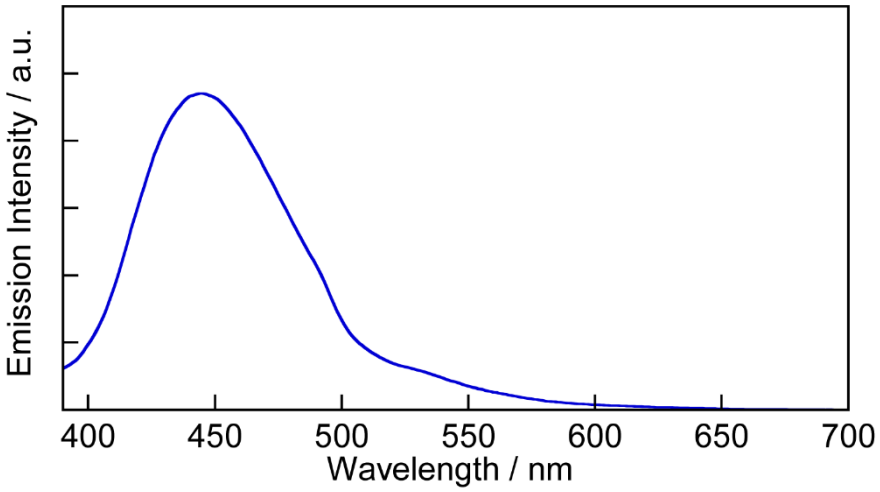


Fig. S6 Fluorescence spectrum of **1o-H**$^+$ in toluene (2.07×10^{-5} mol dm^{-3}).

Excitation wavelength: 326 nm.

4. References

1) Y. Yokoyama, T. Inoue, M. Yokoyama, T. Goto, T. Iwai, N. Kera, I. Hitomi, Y. Kurita, *Bull. Chem. Soc. Jpn.*, 1994, **67**, 3297.

2) S. Mahvidi, S. Takeuchi, S. Kusumoto, H. Sato, T. Nakagawa and Y. Yokoyama, *Org. Lett.*, 2016, **18**, 5042.