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Supporting Information

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Efficient Photoswitching of the Nonlinear Optical Properties of Dipolar Photochromic Zinc(II) Complexes

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Experimental

General Procedure. All manipulations were performed using Schlenk techniques under an Ar atmosphere. All solvents were dried and purified by standard procedures. NMR spectra were recorded on Bruker DPX-200, AV 300 or AV 500 MHz spectrometers. ^{1}H and ^{13}C chemical shifts are given versus $SiMe_4$ and were determined by reference to residual ^{1}H and ^{13}C solvent signals. Assigments of carbon atoms were based on HMBC, HMQC and COSY experiments. High resolution mass spectra (HRMS) were performed on a MS/MS ZABSpec TOF at the CRMPO (Centre de Mesures Physiques de l'Ouest) in Rennes. Elemental analyses were performed by Muriel Escadeillas at the CRMPO. UV/vis absorption spectra were recorded using a UVIKON 9413 or Biotek Instruments XS spectrophotometer using quartz cuvettes of 1 cm pathlength. Compound **3** was prepared according to a reported procedure, namely by bromination of 5-methyl-thiophene-2-carboxaldehyde, and was subsequently converted into its dimethyl acetal **3-(OMe)$_2$** for further use.[1] Compounds **5a,b** [2] were prepared by a Suzuki coupling reaction between the appropriate arylboronic acid and 2,4-dibromo-5-methylthiophene[1] (Scheme S1). 4,4'-bis(diethylphosphonomethyl)-[2,2']-bipyridine [4] was synthesized using published procedure. Zinc acetate dihydrate was obtained from Acros Organics and used as received.

Spectroscopic grade chloroform and dichloromethane were used for all optical measurements. Photoisomerization experiments and kinetics were performed by using a Hamamatsu UV Spot Light Source (Xe-Hg lamp) as an excitation light source equipped with bandpass filters (0.63 mW.cm^{-2} at 365 nm; 18.6 mW. cm^{-2} at 588 nm) and an optical fiber while simultaneous probing was performed with a continuous Xe lamp (450 W) and a CCD camera coupled with a spectrometer (Princeton Instruments).

EFISH experiment

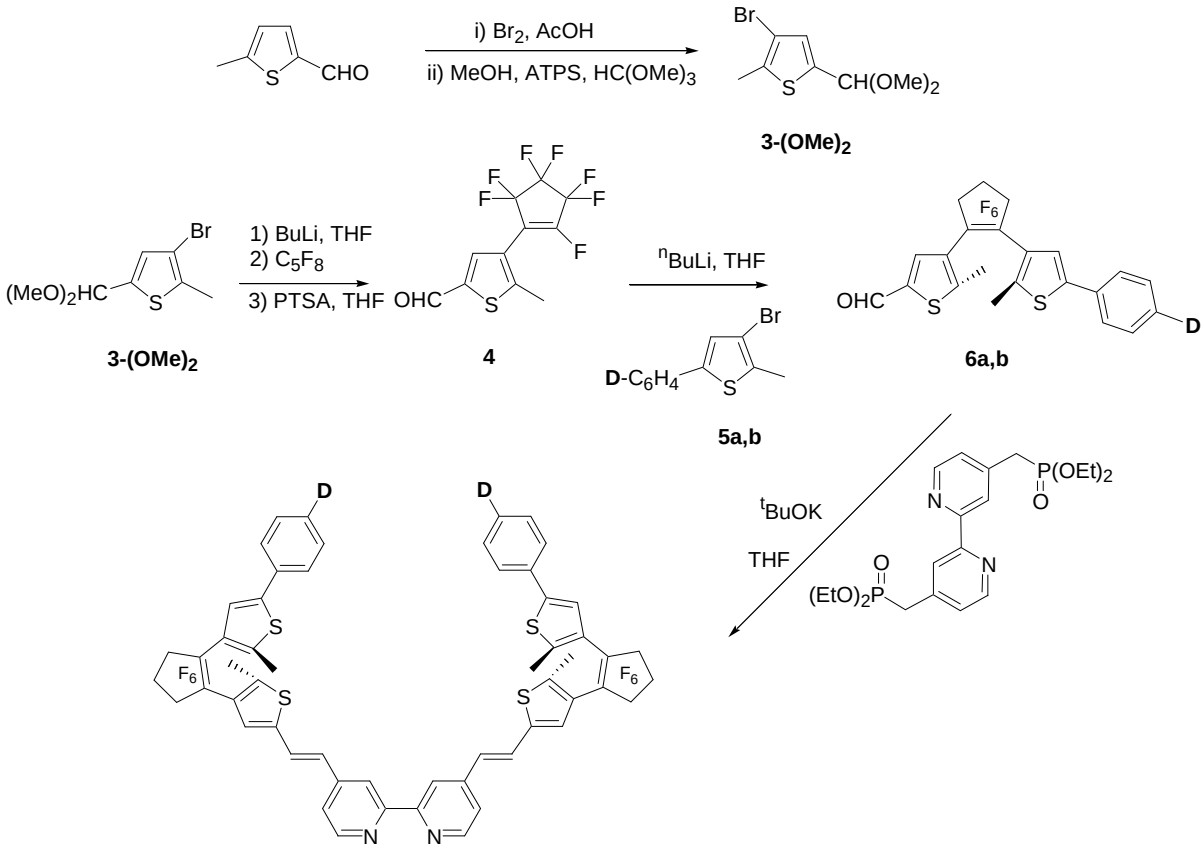
The values of μβ for the chromophores are measured using the electric-field induced second harmonic generation (EFISH) technique. The amplified nanosecond Nd^{3+}:YAG laser at 1.06 μm and 10 Hz repetition rate pumps a hydrogen Raman cell so as to obtain a larger wavelength (1.907 μm) for which both the fundamental and harmonic frequencies are far away from the resonance of the investigated molecule. A Schott RG 1000 filter is used to filter out any remaining visible light from the laser flash lamp. Suitable neutral density filters are used to control the power of the incident beam and a half wave plate and polarizer are used to set the incident polarisation along the direction of the applied electric field. In addition, a band pass filter is mounted on the front of the detection PMT along with a filter to remove any remaining radiation at the fundamental wavelength. A high voltage (5 kV), synchronized with the 1.907 μm laser pulse, is applied across the EFISH cell containing the solution. The EFISH cell consists of a stainless steel container with two quartz optical windows, which are fixed to form a wedge shaped cavity within the cell. The interelectrode distance is 2 mm, giving a static electric field around 25 kVcm^{-1}. The cell is mounted on an electrically isolated translation stage. The whole cell is then translated horizontally relative to the

incident beam to produce Maker fringes. Every measurement is referenced separately to the Maker fringes of the pure reference solvent used to dissolve the chromophores. A home-made computer program is used to calculate the interfringe distance and the fringe amplitude. These data are then used to calculate the μβ value of the chromophore.

The zero-frequency hyperpolarisability (μβ(0)) value is inferred from the experimental μ.β(λtwo level dispersion model:) value using a

$$\beta(0) = \left(1 - \left(\frac{\lambda_0}{\lambda}\right)^2\right)\left(1 - \left(\frac{2\lambda_0}{\lambda}\right)^2\right)\beta(\lambda)$$

where λ_0 is the maximum absorption wavelength of the molecule in solution, and λ the fundamental laser wavelength (here 1.9 μm).



Scheme S1

5-methyl-4-(perfluorocyclopent-1-enyl)thiophene-2-carbaldehyde, 4[3]**:** *n*-Butyllithium (2.4 M in hexane, 15.6 mmol, 6.5 mL) was added dropwise to a stirred solution of **3-OMe$_2$** (3.00 g, 12 mmol) in 100 mL of THF at -78°C under a nitrogen atmosphere. After 60 min, the reaction mixture was transferred in a Schlenk tube containing a solution of perfluorocyclopentene (4.8 mL, 36 mmol) in 20 mL of THF. The reaction mixture was stirred for 1 hour at -78°C, then allowed to warm up to room temperature, and stirred for additional 16 h. After addition of 200 mL of water, THF was removed under reduced pressure, and the residue was extracted with CH_2Cl_2 (3 x 30 mL). The combined organic phases were dried over $MgSO_4$, filtered and evaporated in vacuo. The residue was extracted with 50 mL of THF. p-toluene sulfonic acid (PTSA) (1.2 mmol, 228 mg) and a few drops of water were added. The reaction mixture was stirred for 16 h at 40°C. After addition of water (100 mL), THF was removed under reduced pressure, and the residue was extracted with CH_2Cl_2 (3 x 30 mL). The

combined organic phases were dried over $MgSO_4$, filtered and evaporated in vacuo and chromatographed with silica gel. Elution with a 2:3 dichloromethane/pentane mixture afforded **4** as orange crystals (1.9 g, 50%). ^{1}H NMR (200 MHz, $CDCl_3$): 9.87 (s, 1H, CHO), 7.76 (s, 1H, thio), 2.58 (d, $^6J_{H\text{-}F}$= 3 Hz, 3H, CH_3). HRMS: *m/z* 317.9924 $[M]^+$ calcd for $C_{11}H_5F_7O_5$ 317.9949.

4-(3,3,4,4,5,5-hexafluoro-2-(2-methyl-5phenylthiophenyl-3)cyclopent-1-enyl)-5-methyl-thiophene-2-carbaldehyde, 6a. To a solution of 3-bromo-2-methyl-5-phenylthiophene **5a** (1.09 g, 4.43 mmol) in 50 mL of THF, which was cooled to -78°C, was added dropwise *n*BuLi (0.92 M in hexane, 5.1 mL, 4.65 mmol). After stirring at -78°C for 1 h, a solution of **4-(OMe)$_2$** (1.61 g, 4.42 mmol) in 50 mL of THF was added to the reaction mixture. After stirring at -78°C for 1 h and at room temperature for 16 h, the reaction mixture was hydrolyzed with water, and the solvent was removed in vacuo. The residue was extracted with CH_2Cl_2 (2 x 30 mL) and then dried over $MgSO_4$. After evaporation of the solvent, the residual orange oil was dissolved in 20 mL of THF, then PTSA (85 mg, 0.44 mmol) and a few drops of water were added. After stirring at 40°C for 16 h, the solvent was removed and the oil was purified by column chromatography (SiO_2, pentane-ethyl acetate 95 : 5) to give an yellow oil (1.1 g, 55%). ^{1}H NMR (300 MHz, $CDCl_3$): 9.88 (s, 1H, CHO), 7.80 (s, 1H, thio), 7.55 (d, ^3J = 7.7 Hz, 2H, Ph*ortho*), 7.46 (m, 3H, Ph), 7.28 (s, 1H, thio), 2.05 (s, 3H, CH_3), 1.95 (s, 3H, CH_3). HRMS: *m/z* 472.0387 $[M]^+$ calcd for $C_{22}H_{14}F_6OS_2$ 472.0390.

4-(3,3,4,4,5,5-hexafluoro-2-(2-méthyl-5-*N*,*N*-dimethylaminophenylthiophenyl-3) cyclopent-1-enyl)-5-methylthiophene-2-carbaldehyde, 6b. Compound **6b** was prepared according to the above procedure, from **5b** (2.10 g, 7.12 mmol) and **4-(OMe)2** (2.6 g, 7.12 mmol). Work-up as above gave green microcrystals (1.80 g, 50%). ^{1}H NMR (200 MHz, CD_2Cl_2): 9.88 (s, 1H, CHO), 7.80 (s, 1H, thio), 7.75 (d, ^3J = 8.8 Hz, 2H, C_6H_4), 7.05 (s, 1H, thio), 7.40 (d, ^3J = 8.8 Hz, 2H, C_6H_4), 3.00 (s, 6H, NMe_2), 2.05 (s, 3H, Me), 1.95 (s, 3H, Me). HRMS: *m/z* 515.0813 $[M]^+$ calcd for $C_{24}H_{19}NF_6OS_2$ 515.0812.

4,4'-bis((*E*)-2-(4-(3,3,4,4,5,5-hexafluoro-2-(2-methyl-5-phenylthiophen-3-yl)cyclopent-1-enyl)-5-methylthiophen-2-yl)vinyl)-2,2'-bipyridine, 1a*(o)*. To a CH_2Cl_2 solution (40 mL) of **6a** (0.72 g, 1.53 mmol) and 4,4'-bis(diethylphosphonomethyl)-2,2'-bipyridine (0.33 g, 0.73 mmol) was added a THF solution (10 ml) of ^{t}BuOK (0.3 g, 2.6 mmol). The reaction mixture was stirred for 3 h. After addition of water, the organic layer was washed with brine and water, dried over magnesium sulfate, filtered and concentrated. Crystallization in a CH_2Cl_2-pentane mixture afforded **1a** as a white powder. (0.48 g, 60%). ^{1}H NMR (300 MHz, CD_2Cl_2): 8.66 (d, ^3J = 4 Hz, 2H, Py^6), 8.56 (s, 2H, Py^3), 7.60 (d, ^3J = 7 Hz, 4H, Ph *ortho*), 7.55 (d, ^3J = 16 Hz, 2H, =CH), 7.43 (t, ^3J = 7.4 Hz, 4H, Ph *meta*), 7.40 (d, ^3J = 3.7 Hz, 2H, Py^5), 7.36 (m, 2H, Ph *para*), 7.34 (s, 2H, thio), 7.22 (s, 2H, thio), 6.92 (d, ^3J = 16 Hz, 2H, =CH), 2.04 (s, 6H, CH_3), 2.03 (s, 6H, CH_3). ^{13}C [^{1}H] NMR (75 MHz, CD_2Cl_2): 156.4 (Py^2), 149.6 (Py^6), 144.9 (Py^4), 142.9 (C_{12}-thio), 142.4 (C_{23}-thio), 141.6 (C_{21}-thio), 139.9 (C_9-thio), 133.2 (Ph*ipso*), 129.0 (Ph*meta*), 125.3 (=CH), 127.9 (Ph*para*), 127.5 (CH-thio), 126.2 (=CH), 125.5 (Ph*ortho*), 122.3 (C_{24}-thio), 120.6 (Py^5), 117.8 (Py^3), 14.6 (CH_3), 14.4 (CH_3). HRMS: *m/z* 1115.14670 $[M+Na]^+$ calcd for $C_{56}H_{36}F_{12}N_2S_4Na$ 1115.1475. Anal. Calcd. for $C_{56}H_{36}F_{12}N_2S_4,H_2O$: C, 60.53; H, 3.45; N, 2.52. Found: C, 60.79; H, 3.68; N, 2.53.

Spectroscopic data of the photocyclized 1a(*c*). A solution of **1a(*o*)** (150 mg, 0.137 mmol) in 100 mL of CH_2Cl_2 was irradiated (λ = 350 nm) for 12 h. Evaporation of the solvent gave **1a(*c*)** as a blue powder in a quantitative yield. ^{1}H NMR (200 MHz, CD_2Cl_2): 8.70 (d, ^3J = 4.8 Hz, 2H, Py^6), 8.56 (s, 2H, Py^3), 7.60 (d, ^3J = 7 Hz, 4H, Ph *ortho*), 7.55 (d, ^3J = 16 Hz, 2H, =CH), 7.43 (t, ^3J = 7.4 Hz, 4H, Ph *meta*), 7.40 (d, ^3J = 3.7 Hz, 2H, Py^5), 7.36 (m, 2H, Ph *para*), 6.88 (d, ^3J = 16 Hz, 2H, =CH), 6.82 (s, 2H, thio), 6.55 (s, 2H, thio), 2.24 (s, 6H, CH_3), 2.23 (s, 6H, CH_3).

4,4'-bis((*E*)-2-(4-(3,3,4,4,5,5-hexafluoro-2-(2-methyl-5-*p*-*N*,*N*-dimethylaminophenyl- thiophen-3-yl)cyclopent-1-nyl)-5-methylthiophen-2-yl)vinyl)-2,2'-bipyridine, 1b*(o)*.

Compound **1b** was prepared according to the above procedure described for **1a**, from **6b** (0.78 g, 1.53 mmol) and 4,4'-bis(diethylphosphonomethyl)-2,2'-bipyridine (0.33 g, 0.73 mmol). Work-up gave **1b** as a brown powder (0.47 g, 55 %).

^{1}H NMR (200 MHz, CD_2Cl_2): 8.66 (d, ^3J = 5 Hz, 2H, Py^6), 8.50 (s, 2H, Py^3), 7.55 (d, ^3J = 16 Hz, 2H, =CH), 7.40 (d, ^3J = 8.6 Hz, 4H, C_6H_4), 7.35 (d, ^3J = 3.7 Hz, 2H, Py^5), 7.20 (s, 2H, thio), 7.10 (s, 2H, thio), 6.82 (d, ^3J = 16 Hz, 2H, =CH), 6.70 (d, ^3J = 8.6 Hz, 4H, C_6H_4), 3.00 (s, 12H, NMe_2), 2.04 (s, 6H, CH_3), 2.03 (s, 6H, CH_3). HRMS: *m/z* 1179.24920 $[M+H]^+$ calcd for $C_{60}H_{47}N_4F_{12}S_4$ 1179.2492. Anal. Calcd. for $C_{60}H_{46}F_{12}N_4S_4$: C, 61.11; H, 3.93; N, 4.75. Found: C, 60.91; H, 4.15; N, 4.56.

Spectroscopic data of the photocyclized 1b(*c*). 1b(*c*) (150 mg, 0.127 mmol) was obtained as a green powder upon irradiation (λ = 350 nm) of a CH_2Cl_2 solution of **1b(*o*)** for 12 h.

^{1}H NMR (300 MHz, CD_2Cl_2): 8.69 (d, ^3J = 5 Hz, 2H, Py^6), 8.57 (s, 2H, Py^3), 7.54 (d, ^3J = 16 Hz, 2H, =CH), 7.52 (d, ^3J = 8.6 Hz, 4H, C_6H_4), 7.40 (d, ^3J = 3.7 Hz, 2H, Py^5), 6.82 (d, ^3J = 16 Hz, 2H, =CH), 6.73 (d, ^3J = 8.6 Hz, 4H, C_6H_4), 6.62 (s, 2H, thio), 6.53 (s, 2H, thio), 3.10 (s, 12H, NMe_2), 2.18 (s, 6H, CH_3), 2.16 (s, 6H, CH_3).

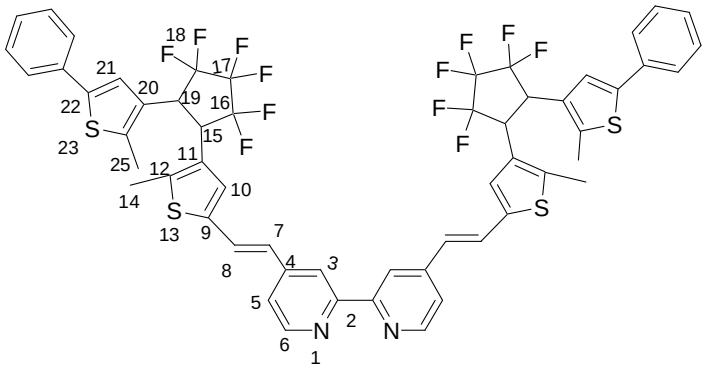
Preparation of 2a*(o)*. To a CH_2Cl_2 solution (40 mL) of **1a** (471 mg, 0.43 mmol) was added $Zn(OAc)_2.2\ H_2O$ (95 mg, 0.43 mmol). The reaction mixture was stirred for 16 h at room temperature. The solvent was then evaporated and crystallization of the residue in a CH_2Cl_2/pentane mixture afforded a black powder (0.515 mg, 95%).

^{1}H NMR (500 MHz, $CDCl_3$): 8.80 (br. d, 2H, Py^6), 8.24 (s, 2H, Py^3), 7.62 (m, 8H, =CH, Ph *ortho* and Py^5), 7.43 (t, ^3J = 7.4 Hz, 4H, Ph *meta*), 7.34 (s, 6H, Ph *para*, thioH^{21}, thioH^{10}), 6.90 (d, ^3J = 16 Hz, 2H, =CH), 2.07 (s, 6H, CH_3), 2.05 (s, 6H, CH_3), 2.03 (s, 6H, OAc). ^{13}C [^{1}H] NMR (75 MHz, CD_2Cl_2): 180.1 (CO), 149.35 (C^2-Py, C^6-Py), 148.9 (C^4-Py), 144.5 (C_{12}-thio), 142.5 (C_{22}-thio), 141.7 (C_{24}-thio), 139.1 (C_9-thio), 133.2 (Ph*ipso*), 129.3 (C_{10}-thio), 129.0 (Ph*meta*), 128.9 (=CH^8), 128.0 (Ph*para*), 126.0 (C_{11}-thio), 125.5 (Ph*ortho* , C_{20}-thio), 123.9 (=CH^7), 122.9 (C^5-Py), 122.3 (C_{21}-thio), 118.0 (C^3-Py), 22.0 (OAc), 14.8 (CH_3), 14.4 (CH_3). HRMS: *m/z* 1215.0988 [M-.OAc]$^+$calcd for $C_{58}H_{39}N_2O_2F_{12}S_4Zn$ 1215.09943. Anal. Calcd. for $C_{60}H_{50}F_{12}N_2O_8S_4Zn$, 4 H_2O: C, 53.43; H, 3.74; N, 2.08. Found C, 53.55; H, 3.27; N, 1.98.

Preparation of 2b*(o)*. Compound **2** was prepared as above from **1b** (322 mg, 0.27 mmol) and $Zn(OAc)_2.2\ H_2O$ (60 mg, 0.27 mmol) and isolated after crystallization in a CH_2Cl_2/pentane mixture as a brown powder (250 mg, 95 %).

^{1}H NMR (300 MHz, $CDCl_3$): 8.75 (br. d, 2H, Py^6), 8.24 (s, 2H, Py^3), 7.62 (d, ^3J = 16 Hz, 2H, =CH), 7.52 (s, 2H, Py^5), 7.46 (d, ^3J = 8 Hz, 4H, C_6H_4), 7.35 (s, 2H, thio), 7.15 (s, 2H, thio), 6.84 (d, ^3J = 16 Hz, 2H, =CH), 6.73 (d, ^3J = 8 Hz, 4H, C_6H_4), 3.00 (s, 12H, NMe_2), 2.07 (s, 6H, CH_3), 2.05 (s, 6H, CH_3), 2.03 (s, 6H, OAc). ^{13}C [^{1}H] NMR (75 MHz, CD_2Cl_2): 180.0 (CO), 150.4, 149.6, 144.6, 143.5, 139.3, 138.9, 129.4, 128.7, 126.4, 126.1, 125.3, 123.8, 122.8, 121.1, 119.5, 117.9, 112.3, 40.11 (NMe_2), 21.8 (OAc), 14.8 (CH_3), 14.3 (CH_3). Anal. Calcd. for $C_{64}H_{52}F_{12}N_4O_4S_4Zn$, H_2O: C, 55.67; H, 3.94; N, 4.06. Found C, 55.47; H, 3.87; N, 3.85.

Numbering



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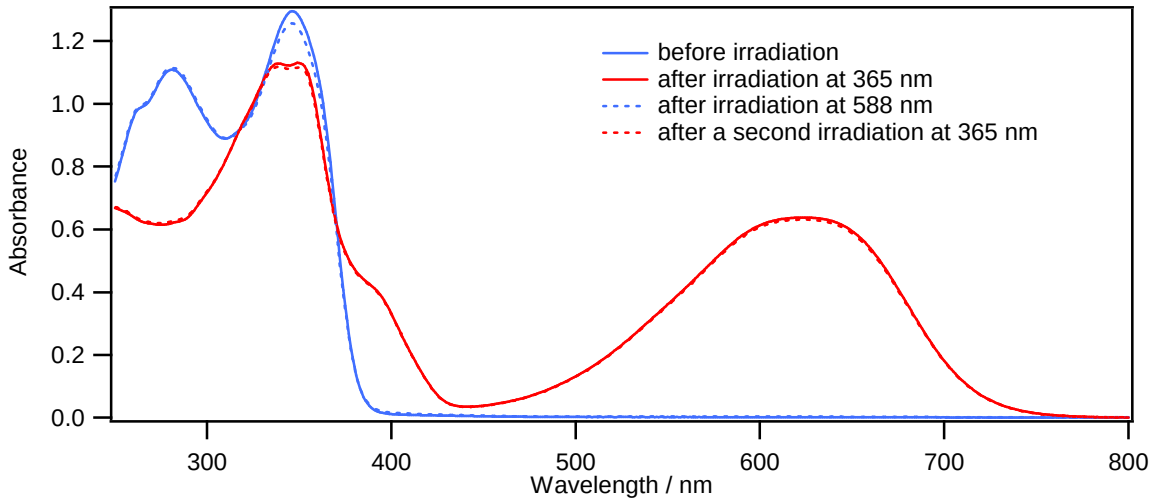

Figure S1. UV-vis absorption spectral change of **1a** in CH_2Cl_2 upon irradiation

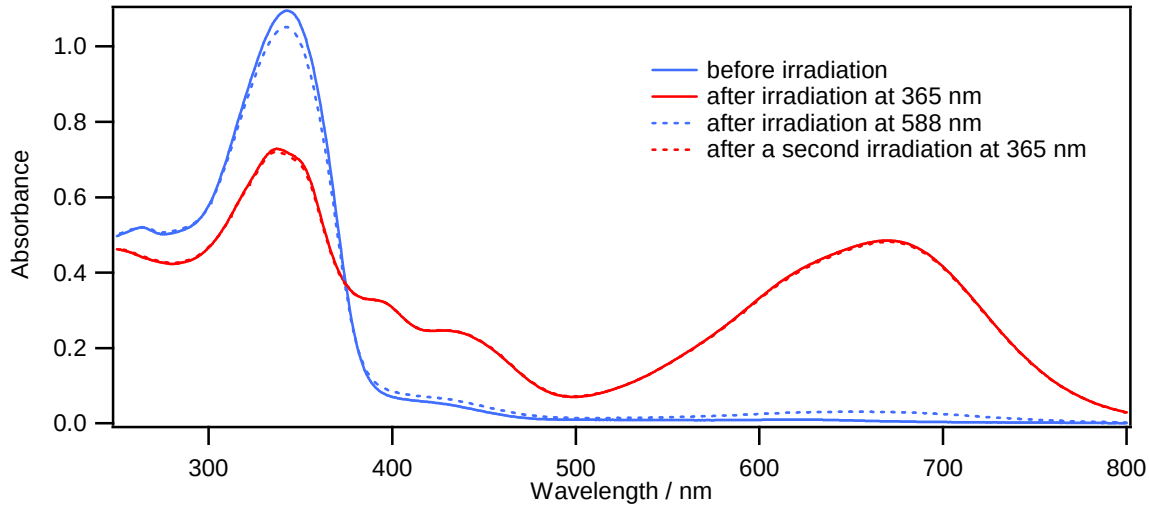

Figure S2 UV-vis absorption spectral change of **1b** in CH_2Cl_2 upon irradiation.